

7TH EDITION

Industrial Minerals & Rocks



**Commodities,
Markets,
and Uses**

Edited by

Jessica Elzea Kogel

Nikhil C. Trivedi

James M. Barker

Stanley T. Krukowski

SME

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Dedication

*With deep admiration for his countless contributions to the field of industrial minerals,
we dedicate this 7th edition of Industrial Minerals and Rocks to the memory of
our friend and colleague, Albert Francis Alsobrook, 1942–2004.*

*Frank was an industrial minerals geologist who was widely respected by his peers
and admired by his colleagues throughout an illustrious career that spanned 35 years.
He was a Distinguished Member of SME and received the Hal Williams Hardinge Award
in 2003. He served with us as a senior editor in the early stages of the
multiyear effort to publish this 7th edition.*

*As the inspirational force behind this endeavor,
Frank is truly most deserving
of this dedication.*



Preface

The vision for the 7th edition of *Industrial Minerals and Rocks* is to build on the strengths of the previous editions while adding significant new content to ensure utility and relevance to readers for years to come. The success of previous editions made this book a widely read global reference that serves as one of the most authoritative single sources for timely information on industrial minerals, their uses, and the markets where they find myriad applications.

We recognize that since the publication of the 6th edition in 1994, changes in the global economy have had a significant impact on mining, processing, and marketing industrial minerals. The challenge for this edition, then, was to capture the substantial and wide-ranging changes and their complex ramifications for the industry. For example, numerous mergers and acquisitions within the minerals and mining industries, consolidations among consuming industries, and the emergence of China and India as major players in industrial minerals markets have altered the landscape in which the industry operates. At the same time, development of new technologies and globalization of the customer base have driven fast-paced innovation in processing, packaging, transportation, and end use.

Growing emphasis on sustainable development and increasing concerns for the environment and health and safety have also affected the industry in many ways. In one positive example, we now have a common platform for advancing environmental stewardship and a universal goal to use mineral resources wisely. Rapidly rising energy costs will also shape the future of industrial minerals. Higher fuel prices affect mining, processing, and transportation, and push the industry to discover innovative ways to reduce energy consumption and to process minerals more efficiently. Increasingly, industrial minerals are an integral part of the solution to rising energy costs because they serve as raw materials for products such as solar panels designed to conserve or generate energy.

As in previous editions, we divided the book into three parts. The first part contains standalone introductory chapters focusing on topics relevant to the industry as a whole: industrial minerals transportation, marketing, sustainable development, health and safety, and mining and environmental law. Chapters covering more than 60 individual industrial minerals, rocks, and materials make up the second part. Where appropriate, a few chapters in this part include updated statistics, but otherwise retain most of the content from the previous edition. In the third part, readers can find information organized by market or end use. Here, information is presented on industrial minerals used in various applications such as construction and metallurgy, among many others. The 7th edition also offers appendixes containing frequently referenced information as well as a comprehensive index.

To ensure the publication of a complete and accurate reference that readers can depend on for many years, an international group of volunteer authors, coauthors, and associate editors—all recognized experts and leaders in their fields—was assembled. Drawing on experts from around the world has given the 7th edition a more global perspective than previous editions. Next, an exhaustive review process was implemented that included five stages of content and technical editing and at least one peer review. Finally, an outstanding group of professional copy editors, proofreaders, graphic designers, and indexers worked to bring clarity, readability, and visual appeal to *Industrial Minerals and Rocks*.

In Appreciation


The authors, editors, and publisher of *Industrial Minerals and Rocks: Commodities, Markets, and Uses* express appreciation to the Robert M. Dreyer Fund and AIME's Seeley W. Mudd Memorial Fund for support in the publication of this 7th edition.

Robert M. Dreyer Fund

Proceeds from the trust established by the late Robert M. Dreyer are used to fund the Dreyer Award, to recognize outstanding achievement in applied economic geology, and to support the professional development of geologists in the field of nonmetalliferous geology. Robert Dreyer received his BS degree from Northwestern University, and an MS and Ph.D. in geology and geophysics from the California Institute of Technology. Dreyer's professional career was extensive in scope: he was employed as minerals manager for Associated Oil and Gas Co., served as assistant chief geologist for Reynolds Metals Co., and was employed as chief geologist for Kerr-McGee Oil Corp. and for Kaiser Aluminum Co. Additionally, Dr. Dreyer was a professor and department chair for the University of Kansas and served as president of Western Mineral Associates. Dreyer retired in 1984. Dr. Dreyer was a former chair of the SME Industrial Minerals Division and an SME board member.

Seeley W. Mudd Memorial Fund

The Seeley W. Mudd Memorial Fund was entrusted to AIME by his family in 1929. Proceeds from the fund are intended to perpetuate Mudd's lifelong interest in the mining industry. Mudd graduated from Washington University in St. Louis, Missouri, in 1883, and served as a colonel during World War I. Seeley W. Mudd gained lasting recognition in the mining profession for the discovery and development of extensive mineral deposits. He is still widely known for his contributions to the growth of mining enterprises such as Ray Consolidated Copper Co., Texas Gulf Sulphur Co., and Cyprus Mining Corp. Colonel Mudd was a member of AIME for 43 years and during that time served as vice president and director.



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PART ONE



Introduction and Overview



Characteristics of the Industrial Minerals Sector

Kip Jeffrey

INTRODUCTION

If DNA is the building block of life, then industrial minerals and rocks are literally the building blocks of our way of life. Industrial minerals and rocks are an exceptionally diverse and vital group of raw materials that underpin almost all aspects of human activity, infrastructure, and standard of living. More than 60 commodities are commonly considered industrial minerals and rocks, and they provide myriad products used by every conceivable industry. Although industrial minerals permeate every aspect of daily life, their presence and their role are often invisible.

In certain respects, the production of industrial minerals and rocks constitutes one of the most intimate and familiar of industries because few domestic or industrial products do not contain industrial minerals and rocks or require them at some point in their manufacture. To use a popular slogan, “If it’s not grown, it’s mined.” This applies to all mining but particularly to the larger and more diverse industrial minerals and rocks sector. Add to this that most crops could not be grown, harvested, or transported to market without industrial minerals-based fertilizers, equipment, and infrastructure, and the all-pervading presence of industrial minerals and rocks comes into sharper focus.

DEFINITION

The precise definition of industrial minerals and rocks is far from straightforward. However, a widely used definition is “any rock, mineral, or other naturally occurring substance of economic value, exclusive of metal ores, mineral fuels, and gemstones: one of the non-metallics” (Bates 1975, p. 3).

This definition includes the hugely important construction materials sector as well as specialized industrial minerals, but complex interactions between consuming industries produce a number of apparent anomalies (and, as such, would not be regarded as falling under this definition). Bauxite, for example, is the main ore of aluminum, but it is also used to manufacture alumina and other aluminum compounds that have applications in the refractories, abrasives, and fillers markets. Titanium metal is produced from the mineral rutile, but the bulk of this mineral is mined to produce titanium dioxide (TiO_2), one of the most important white pigments. Similarly, sulfur is still widely produced from the metallic mineral pyrite (iron disulfide) produced as the by-product of copper-lead-zinc mining in volcanic massive sulfide deposits. Such deposits containing metallic minerals are therefore also important nonmetallic industrial minerals sources.

The position of gemstones is much debated, but they are included in this book because of their importance as high-value minerals. Diamonds and garnets, for example, are not just gems but also important industrial abrasives, and beryl can be both an ore of beryllium and the gemstone emerald or aquamarine. In many respects, gemstones are the ultimate industrial minerals, exhibiting the highest quality, perfect crystal form, and which, with minimal processing, can command the extremes of value. Most fall firmly in the nonmetallics camp.

Waste products of several bulk industrial processes are also included, because they are important industrial raw materials in their own right. Pulverized fuel ash from power stations may not be a natural raw material, but it is an important pozzolan used in the cement or construction industry. Sulfur is now dominantly extracted as a by-product of cleaning natural gas, one of the world’s major mineral fuels. On reflection, perhaps oils used for lubricants or petrochemicals should be considered industrial minerals and rocks under the preceding definition.

Industrial minerals and rocks are used in the manufacture of many products, from ceramics to plastics and refractories to paper. This book could never encompass all the downstream industries. The mining and extraction of ceramic clays, for example, is sensibly within this edition of *Industrial Minerals and Rocks*, whereas the firing of ceramics is not (Bates 1994). Even this has its exceptions, because the manufacture of cement is typically included. Equally, at a brine chlorine or rare earth processing plant, it is difficult to define when the raw materials cease to be an industrial mineral or rock and become an industrial chemical.

Clearly defining the exact extent of this industrial sector is difficult, and it is frequently easier to highlight the differences among the commodities than what they have in common. Lines must be drawn, and the contents of this book represent a consensus of many professionals in the field as to what defines the scope of industrial minerals and rocks. Nevertheless, the debate will continue, particularly as new applications and markets develop. An account of the attempts to produce classification systems for industrial minerals and rocks is given in the chapter on the classification of industrial minerals and rocks.

HISTORY

The history of industrial minerals and rocks can quite literally be traced back to the Stone Age; indeed, it defines the development of humankind through time (Kuzvart 1984). Perhaps the scale of use

was preindustrial, but the materials and technical requirements at that time were not dissimilar to some present-day natural stone and abrasives industries. The total amount and diversity of industrial minerals and construction materials used by a society are always closely linked to, and a measure of, its overall economic strength (Noetstaller 1988). Some minerals are used more as an industrial society develops, whereas others are more characteristic of postindustrial, service-dominated economies. As a country develops, however, the per capita use of minerals inevitably increases. Dominance of industrial minerals and rocks production over metal minerals production has been a measurement of economic development and a defining characteristic of a developed country (Bristow 1987). Given a still-rising world population, dominantly with in developing countries, which have a justified aspiration to higher standards of living, the future demand for industrial minerals is certain to increase.

SCOPE

The industrial minerals and rocks sector operates worldwide, and no nation on earth does not in some way use the natural raw materials at its disposal. The motivation for and magnitude of this resource utilization, however, varies widely from local subsistence activity to global-scale trade. Unlike other types of manufacturing, minerals can be worked only where they are found. Mineral resources are also a “wasting asset,” so eventually an individual deposit becomes depleted and new ones must be found or the business will close. Mines and quarries will therefore always open and close, and new deposits will constantly be sought.

Natural geological endowment dictates that some countries or regions have certain minerals they need but not others, and linked to the varying requirements for industrial raw materials, this sets up a driver for both interregional flow and international trade in industrial minerals. On a more local scale, villages, towns, and cities all need these important products, so an infrastructure of companies develops to work, distribute, and upgrade the mined materials to products that are in demand. Industrial minerals key in to the manufacturing base of each area, promoting the development of downstream industries where commodities are abundant. They drive development of road, rail, and other infrastructure to allow their extraction and transport to market, and to facilitate their import if there are not indigenous supplies. Industrial growth is almost impossible without them (Noetstaller 1988). As new uses for minerals develop or markets disappear, the demand for specific minerals fluctuates.

The range and diversity of materials are enormous, and this can be illustrated by describing two end members. Aggregates are the classic low-value, high-bulk material and are the largest sector by volume produced. Strength and other physical properties are important, but their value is largely in the inability to reduce the need for expensive components such as cement or bitumen in construction materials. The main asset is that they occupy space. They have significant “place value”; that is, the location of the deposit is vitally important because the cost of transportation is a large proportion of the delivered price (Bates 1969). Deposits near markets have major cost advantages, and most extraction sites are close to the urban centers they supply. Although often assumed to be common to the point of ubiquity, industrial minerals and rocks still need to meet strict standards or specifications, and the amount of unsuitable material always massively outweighs those deposits that can be used. For higher quality products, the specifications become tighter and the proportion of available material that can be used rapidly decreases.

At the other end of the spectrum are the high-value, low-bulk materials such as gemstones, iodine, bromine, and rare-earth elements. In a large diamond mine, for example, 50 percent of the annual revenue could be generated from only half a dozen individual large stones easily held in one hand. Deposit location is less critical and product quality will often be significantly improved by complex processing. Low-cost rocks such as aggregates and brick clays may be economically sold over only a 30- to 60-km radius, whereas borates and phosphates, for example, are truly globally traded. Between these two extremes are the majority of industrial minerals and rocks commodities such as kaolin and salt that service local, national, and international industries.

The industrial minerals and rocks sector embraces scales of activity from artisanal mining of gems through family-operated gravel or building stone quarries (so-called Ma and Pa operations) and limestone quarries supplying construction materials to a large region, and ultimately to some of the world's largest mining and processing plants. Most industrial minerals operations, however, are small- to medium-sized and play a major role in local economic development.

Because good transport infrastructure is required, and transshipment of minerals is costly, deposits located near existing ports, railways, waterways, and major roads are the most important. In many larger, low-population countries, plans showing the distribution of industrial minerals deposits often mirror the road and rail networks. In other words, only deposits that have the potential to be easily accessed have been identified; the rest of the deposits await expansion of transport networks before they are sought in earnest. Even more than metal resources, a new road or railway can transform the economics of an industrial minerals deposit, making it feasible.

PRODUCTS AND SPECIFICATIONS

Many industrial minerals are used in an essentially raw form whereby much of their intrinsic characteristics remain. Specific companies, deposits, and even sections of a deposit therefore supply materials of varying qualities, and these may also change over time. Quality and competitive advantage are therefore crucial issues imbued by the deposit itself. This is again completely unlike the metals industry, where copper metal from Chile is little different from copper from Zambia or the United States.

Industries using industrial minerals and rocks generally demand tight specifications based on a wide range of physical and chemical criteria, often unique to particular applications or products (Harben and Bates 1984); the clump factor for bentonite used in pet litters is one that immediately comes to mind. These specifications have tended to become more stringent over time as more advanced manufacturing methods have lower tolerance of raw material variation.

As a consequence, mineral processing has increased considerably to meet these specifications, and the full range of mineral separation methods used in metals and other mining industries is now deployed (Harben and Bates 1990). Almost all operations working solid minerals involve excavation, comminution, sizing, and packaging. To ensure high-purity products, other plants rely on using flotation, density, magnetic, chemical, electrostatic, and other techniques to remove potentially deleterious components. A vast array of commodity-specific techniques has also been developed to optimize product quality and performance. Some industrial minerals and rocks are processed to highly refined forms, even to their elemental chemical components.

Even today, inexpensive, low-technology methods that will still meet stringent quality requirements are needed for many

internationally traded industrial mineral commodities. In Turkey and the Middle East, hand-sorting of K-feldspar is essential to produce the high-quality products used in the European ceramics and glass industries. In China, magnesite, mica, and several other commodities are hand-sorted and exported worldwide. By contrast, industrial minerals products are becoming increasingly sophisticated, and kaolin used in paper manufacture is typically tightly sized at the sub-micron level, and then chemically brightened, delaminated, and rheologically modified. Carbonate fillers for the plastics industry have their naturally hydrophilic calcite surfaces modified so that they are more easily wetted by organic-based formulations. Minerals are increasingly at the cutting edge of materials science.

Because of their generally low value, most industrial minerals and rocks are worked from open-pit operations. Depending on scale and location, the degree of mechanization varies from a multimillion-ton surface mine using large excavators to a hand-dug pit with product transportation by wheelbarrow. Only for higher-value commodities, or when essential cheaper commodities are in extremely short supply, can underground mining usually be justified. There is, however, a trend toward more underground extraction due to perceived environmental benefits and a market for low-cost products such as aggregates and limestone, which are now worked this way in some countries.

Although deposits are generally exploited for single minerals, a significant number are worked together as coproducts, such as fluorite and barite from Mississippi Valley-type lead-zinc deposits, or quartz, feldspar, and mica from pegmatites. In even more cases, by-products such as dimension stone are recovered during aggregate production. This makes the supply-and-demand relationship of these minerals complex because fluctuations in the market for the dominant product will dictate supply of by-product minerals independent of their own demand.

Most industrial minerals and rocks commodities also have multiple uses. For instance, a pure limestone deposit could supply material for lime, aggregate, and cement production, in granular form for flue-gas desulfurization, and in a range of powders for fillers, soil stabilization, and agricultural use. Each of these can command very different prices per ton, so assessing the overall value of the deposit is difficult and involves assessing for multiple quality requirements and variable product splits. In many cases, the evaluation process for an industrial minerals resource is considerably more technically complex than that for metal deposits.

ECONOMICS

Metals and petroleum are largely sold through international exchanges, whereas industrial minerals and rocks producers have to compete directly with each other to gain contracts and develop relationships with customers. Competition between companies is frequently ferocious. It is ultimately the same supply-and-demand market approach of other manufacturing industries but with very different constraints. Without a market for the products, a mineral is effectively worthless. Exploration for new industrial minerals deposits is often initiated because a new niche or emerging market has been identified (Coope 1982; Bristow 1987).

Prices for industrial minerals and rocks generally exhibit greater stability than prices for the more cyclic metals and oil. The growth in the use of most industrial minerals has been accompanied by a decrease or plateau in prices because competition is so intense. It is now technically possible to work at larger scales with consequently lower production costs. More important, over the last 10 to 20 years, the development of exporting capacity from Eastern Europe and especially China, with its massive resources and aggressive pricing policies, has led to cutthroat pricing in the rest

of the world in an attempt to compete. This has ultimately led to import quotas and tariffs being applied to some Chinese products to protect other international sources.

Globalization is an important economic driver in the world industrial minerals sector. Large international corporations such as Imerys of France and Sibelco of Belgium have formed by consolidation and acquisition of smaller companies. This process has led, in some cases, to one or two corporations having dominant control over individual mineral commodities such as diamonds, borates, nepheline syenite, garnet, and talc.

Some parts of the industry simply produce the raw minerals and sell these products to consuming industries, whereas others are more vertically integrated to process a range of intermediate or end-user products. Minerals-producing companies rarely provide minerals to suppliers without a raft of technical support, often involving in-house R&D facilities. To sell their products, larger mineral companies frequently undertake specific or comparative testing for a potential customer to evaluate the impact of changing materials. This often feeds through to improved (tailored or bespoke) products that fit the needs of individual users. This "partnership" approach to industrial minerals supplies is a gain different from that of other mining sectors.

SYNTHETICS AND SUBSTITUTION

As the technical demands on specific minerals increase or supplies are restricted, companies explore the possibilities of making synthetic mineral products. This is especially true for gemstones, but major industries are making synthetic zeolites for use in washing powders, as intermediates such as synthetic rutile for TiO₂ manufacture and in pigments, and in bulk materials such as magnesite, gypsum, and soda ash. In some applications, the boundaries with materials science become blurred, such as in industries making synthetic corundum and silica for laser, military, and electronics applications. Here the mineral structure has been perfected to a point not found in nature. Some of these synthetic minerals are also produced as by-products of upgrading other mineral products, but all affect the demand for primary industrial minerals from new or existing deposits.

More often, a shortage of suitable minerals supplies, or the possibility of cost savings, leads to substitution by function. Other minerals that can perform the same role in a product are then used instead. The increased use of fine-ground or precipitated calcium carbonate at the expense of kaolin in paper coating is a good example. Natural stone businesses also have to consider cultural and architectural trends, whereas colored gemstone demand is controlled by whims and cycles of fashion, which can change rapidly and in ways that are hard to predict.

So in the industrial minerals and rocks supply game, minerals producers must not only strive to supply the best product they can but also must keep an eye on their own market, their customers' markets, and overall product cost structure if they do not wish to be "substituted."

ENVIRONMENTAL CHALLENGES AND CONTRIBUTIONS

Environmental challenges and regulation are an ever-increasing issue that now frequently dictates where deposits can be explored for and developed. This can distort the market. In many countries, it seems less important where the deposits are as opposed to where permission may be obtained for a deposit to be worked. With that said, the industry does "borrow" the land on which the deposits are located, sometimes for considerable periods of time while minerals are worked, and therefore has an important obligation to do this in a sensitive and responsible manner.

Sustainable development and what that means for the industrial minerals sector is still a major area of debate. On a local scale, some deposits will be exhausted, but how does this square with a sustainable mineral supply and environment? Clearly, today's needs for industrial raw materials must be balanced with the needs of future generations to obtain the materials they require (WCE D 1987). Despite depletion of deposits, future industrial minerals professionals will, of course, have improved technology and knowledge in exploration, development, and remediation to guide them, but the environmental consequences of resource use must not be allowed to prejudice the environment that the next generation inherits. This certainly does not mean that natural resources should not be mined and used. The fact that commodity prices are at such low levels strongly indicates that there is no impending shortage of any major industrial minerals and rocks commodity. Although new sources can currently be found apace with consumption rates, this might not always be the case.

Despite centuries of mineral exploitation, only one industrial mineral has actually "run out" (in commercially extractable terms): cryolite, a rare fluoride mineral used in smelting aluminum (and there may well be commercial deposits yet to be found). Cryolite is now made synthetically. Market- and technology-driven substitution has actively prevented exhaustion of individual commodities, and the ability to replace reserves continues to outstrip demand. Because industrial minerals resource depletion is not imminent, the major challenge for the future is the increasing environmental cost of sustaining a growing industrial minerals and rocks supply. Full life-cycle impact analysis, particularly examining the environmental fate of industrial minerals in the consuming industries, is a growing practice.

The industrial minerals and rocks sector actually produces many minerals that are widely used in environmental protection and cleanup, such as bentonite landfill seals, limestone for flue-gas desulfurization, zeolite molecular sieves, and garnet and lime for water treatment. Some notorious enforced reductions in mineral use also occurred in this sector when the health concerns on asbestos emerged, and fluorspar production saw significant reductions in growth when chloro fluorocarbons were removed from many aerosols because of their ozone depletion potential.

Because of their relatively low value and the consequent need for low transport costs, "near market" deposits are required. In practice, this means that many deposits are close to residential centers, and, over time, buildings encroach on and even surround extraction sites. This leads to increasing problems of competition for land use and the environmental impact; the industry continues to make major efforts to be a "good neighbor."

FUTURE TRENDS

Both costs and environmental pressures will ensure more recycling of end products. This will have significant impact on some commodities, but less so than on metals. Higher world population and rising standards of living in the developing countries will drive up demand. Growth rates in China and increasingly in India, Russia, and the Far East have driven markets. Multinational companies will

make greater investment in these areas, and signs are that China will increasingly become a net importer of some of the minerals it formerly aggressively exported.

In recent years, some minerals have gained greater importance, such as the rare earth elements in electronics and mobile phones, and others may fade away because of market changes or environmental problems. No one can predict which will be the growth minerals of this century as new products and markets develop and new raw material challenges are set. Growth of Internet marketing will give global access to small-scale producers capable of supply niche markets.

More waste products, however, will find uses. In the United Kingdom, steel slag and pulverized fly ash are wastes used widely in the construction and cement industries that are, at least in some locations, in short supply. In these cases, the primary products are being made in a way that improves the qualities of the wastes or, more accurately, coproducts.

More "smart" materials technically modified for more efficient use in each application will be developed. Tailoring products using microstructural and surface modification will be more commonplace. Hybrid waste-mineral mixtures will increasingly be exploited and new processing methods, such as microwave-assisted firing, will be perfected to improve energy efficiency.

Whatever the future of the sector, the diversity of industrial minerals and rocks presents a significant challenge for professionals, consumers, educators, and other interested practitioners. It is hoped that the distillation of knowledge and experience presented by the many authors in this book will serve as a useful reference for anyone wishing to learn more about these fascinating industries.

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Classification of Industrial Minerals and Rocks

Kip Jeffrey

INTRODUCTION

In the chapter on characteristics of the industrial minerals sector, a broad definition of industrial minerals and rocks is discussed—a definition that must embrace solids, liquids, gases, minerals, rocks, gems, glasses, wastes, and some manufactured products—each category with its own range of uses. Clearly, industrial minerals and rocks do their utmost to defy simple definition and are linked as closely by their differences as by their similarities.

To bring some order to this disparate field, a classification system is needed to highlight the commonalities and contrasts in a structured way. Any robust classification must address the needs of a wide range of potential users that may include (but is not limited to) academics, industrial geologists, industrial raw material users, specifiers, product formulators, technologists, engineers, managers, and financiers and investors. Given their different priorities, focus of attention, and backgrounds, it is not surprising that no single approach is universally adopted.

CLASSIFICATION SCHEMES

A range of classifications based on a variety of commodity criteria has been used over the past 50 years or more as tools for understanding the geological context, market uses, defining properties, economic contribution, and statistical significance of industrial minerals and rocks. Each approach has its strengths and weaknesses, and any durable scheme in such a dynamic industrial sector will inevitably present only part of the picture. Bates (1975) examined a number of these schemes, and more extensive comparisons have been undertaken by Kuzvart (1984), Noetstaller (1988), and Smith (1999). All of these were drawn on extensively for this review.

Berzelian

The world of systematic mineralogy has a number of classification systems that have also been applied to industrial minerals. Most museum mineral collections are catalogued by the Berzelian classification system, which is based on elements, ions, ionic groups, and compounds such as halides, oxides, carbonates, and silicates, among others. This system was used in early accounts of the non-metallics (such as in Merrill 1904) and also hydrocarbons, but not industrial rocks other than some siliceous and calcareous examples under silica and calcium carbonate, respectively. The classification did not cover waste materials, brines, or most manufactured prod-

ucts because many of these were yet to be recognized as important raw materials or products.

Alphabetic

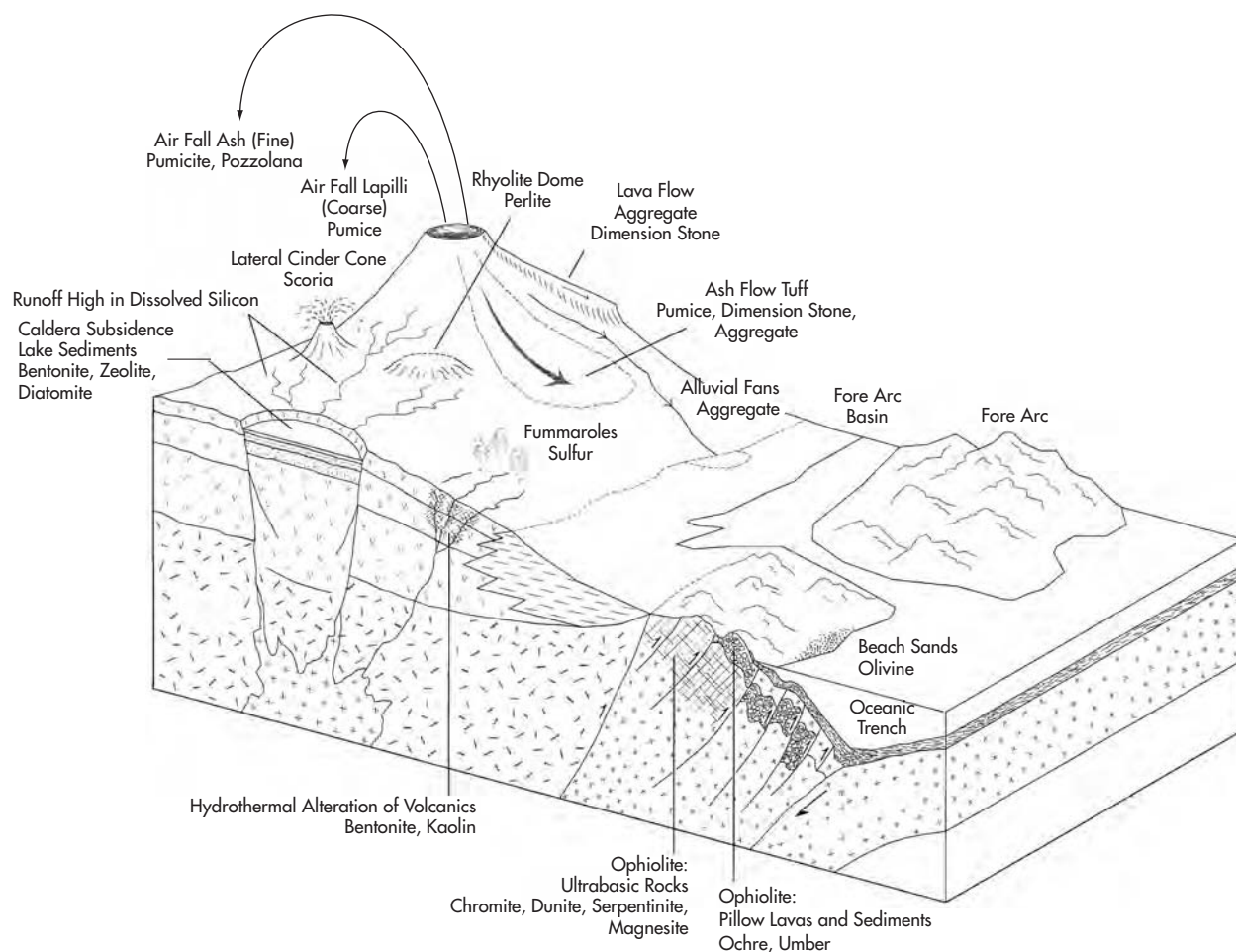
The simplest approach, and certainly the most intuitive and accessible for those from outside the subject seeking commodity-specific information, is nothing more complex than the alphabetical listing of commodities. This has been adopted for systematic commodity reviews in earlier editions of this book (e.g., Lefond 1975; Carr 1994). Indeed, as noted by Harben and Bates (1984), the “alphabetic treatment neatly sidesteps the vexatious matter of classification.”

This edition in part adopts the same approach as it lends itself to simple encyclopedic interrogation once a mineral or commodity is identified. Approximately 60 commodities are typically included in such a listing, but these are always under review. This simplistic compositional approach works reasonably well for industrial minerals but requires a degree of clarification and consistency because subdivisions are often necessary. For example, clays can be divided into bentonites, which can in turn be divided into sodium or calcium smectites. Nomenclature for industrial rocks and other raw materials can also be variable; for example, brick clay, common clay, structural clay, and heavy clay are all common pseudonyms and are based more on application than composition.

Unfortunately, the alphabetic approach to classification obscures many important links between commodities, including similar properties they possess, geological processes that led to their formation, or applications in which they are used. For this reason, the alphabetic classification employed in this edition is supplemented by important reviews of major markets and uses for industrial minerals and rocks. Although this approach may suit those using a book format, other forms of classification have been developed that may be more useful for the consumer or the geologist.

Geological Processes

From the geologist’s perspective, there is much to be gained by trying to place a genetic classification on such a wide variety of materials (Bates 1960; Harben and Bates 1984). There are well-defined categories of geological processes responsible for the formation of all minerals and rocks, and industrial minerals and rocks encompass the complete spectrum. Such a classification parallels standard geological understanding and has exploration relevance because a commodity may be found again in other places where these processes



Source: Anon. 1994.

Figure 1. Industrial mineral deposits found in active continental margins

dominate. Because particular geological processes often result in a range of similar products, there is also some natural grouping of physical properties, although this is far from uniform.

The dominant divisions have been igneous, sedimentary, metamorphic, and surficially altered minerals and rocks (Harben and Bates 1984). Igneous subdivisions were intrusive, extrusive, pegmatitic, and hydrothermal; sedimentary was divided into clastic, biogenic, and chemical. Because this is principally a geological categorization, waste and processed materials were not specifically addressed. In their follow-up account of world deposits (and after much deliberation; P. Harben, personal communication), the same authors reverted to an alphabetic arrangement of commodities, allowing very different deposit types to be discussed under individual commodity headings (Harben and Bates 1990).

Lorenz (1991) produced a more detailed tabulation of geological origins for industrial minerals deposits, along with a similar analysis of deposit sizes and many other economic, technical, and end-use parameters.

Tectonic Models

Although mainly developed as exploration models, these block diagrams have, in effect, produced a tectonic classification of deposit types for particular commodities (Figure 1; Anon. 1994; Highley

1994). They are therefore a development of the geological process classifications and have the major advantage of allowing analysis of the potential spatial, as well as geological, relationship between different industrial minerals. This makes the approach an ideal one for industrial minerals exploration and parallels the earlier work undertaken for metal deposits (e.g., Mitchell and Garson 1981; Sawkins 1984).

Important Properties

As the phrase “industrial minerals and rocks” implies, each commodity has some commercially significant composition or property on which its use is based. Kline (1970) devised a simple twofold division: *chemical minerals*, where their main purpose is as the source of important elements (e.g., industrial minerals and rocks used in the fertilizer, chemical, ceramics, and metallurgical industries); and *physical minerals*, where the minerals do not significantly change in composition during use. Important features of this latter group, which include many construction materials, abrasives, foundry supplies, gems, and fillers, would be their physical properties such as particle-size distribution, brightness, and surface area.

These considerations have become central to many later classifications but usually as one part of a more complex set of classification criteria.

End-Use Classifications

It is a common saying in the industrial minerals and rocks sector that “exploration begins with markets” (Coope 1982). This highlights the essential importance of understanding that the mineral or rock has value only if there is a customer willing and able to pay for it. Minerals are, however, capable of being utilized in many different end uses; limestone, for example, can provide more than 100 separate products that are used in very different applications. Equally, some consuming industries require a suite of different industrial minerals, each of which alone would not meet the needs of the manufacturing process. For these reasons, many classifications have concentrated on either the end uses for minerals and relationships between them, or combined end uses with other important parameters of the industrial minerals and rocks industry.

Following the work of Bates (1959) and Wright and Burnett (1962), Fisher (1969) conducted a detailed analysis and defined six major end-use groupings that were characterized by variation in unit value, production volume, and associated parameters:

1. Bulk construction and building materials
2. Bulk ceramic raw material (in addition to lime and diversified industry raw materials or products)
3. Specialty building products and principal refractories
4. Major industrial chemicals and fertilizer raw materials
5. Industrial minerals and rocks
6. Specialty-grade and precious minerals and rocks

For each group, Fisher also presented a series of graphs showing the typical levels of capital and plant cost, place value, resource spread, enrichment ratios, and fiscal treatment, based on deposits and companies in the United States. Although the groupings are defined on end uses, this represents one of the earliest and most rigorous attempts at a multifaceted classification for industrial minerals and rocks.

In a major review of nonmetallic mineral deposit assessment criteria, Lorenz (1991) produced a detailed tabulation of commodity uses in some 38 products or intermediate products. Highley (1994) adopted a more straightforward graphical attempt to illustrate important sectors with a hierarchical chart of major end users. Chang (2002) also produced an account of the industrial processes and end uses for the main industrial minerals and rocks and noted that they could be allocated into 16 groupings based on their function or final product.

Although not an attempt at a rigorous classification, the end uses for ground (filler and extender) minerals are examined from a “formulator’s” viewpoint in Ciullo (1996). Although this represents only a section of both consuming industries and industrial minerals and rocks, it provides a useful way of examining the diverse roles that different minerals play in products and their ability to substitute for each other.

Economic

As part of their objective to inform Californians about their state’s geology, mineral deposits, and general usefulness of minerals and rocks, Wright and Burnett (1962) proposed a threefold “commercial” classification of industrial minerals and rocks. Based on unit price and production volumes, the groups were

1. Low price–large volume: materials used in construction such as aggregates, gypsum, and common clay
2. High price–high volume: borates, potash, and salt
3. High price–low volume: barite, kyanite, beryl, mica, and talc

Each group was also identified as having a number of common features in terms of their deposit size, distribution, location, mining methods, and treatment.

Table 1. Industrial minerals and rocks classification based on end use and genetic subdivision

Aspect	Group 1	Group 2
Bulk	Large	Small
Unit value	Low	High
Place value	High	Low
Imports and exports	Few	Many
Distribution	Widespread	Restricted
Geology	Simple	Complex
Processing	Simple	Complex
	Industrial Rocks	Industrial Minerals
	Igneous Rocks	Igneous Minerals
	Basalt and diabase	Beryl
	Granite	Feldspar
	Perlite	Lithium minerals
	Pumice and pumicite	Mica
		Nepheline syenite
	Metamorphic Rocks	Vein and Replacement Minerals
	Marble	Barite
	Slate	Fluorspar
		Magnesite
	Sedimentary Rocks	Quartz crystal
	Clay	Metamorphic Minerals
	Gypsum	Asbestos
	Limestone and dolomite	Graphite
	Phosphate rock	Talc
	Salt	Vermiculite
	Sand and gravel	Sedimentary Minerals and Sulfur
	Sandstone	Borates
		Diamond
		Diatomite
		Nitrates
		Potash minerals
		Sodium minerals
		Sulfur

Adapted from Bates 1969.

Bates (1969) developed his own twofold subdivision based on an analysis of similar high and low unit-value commodities. This also involved examining the bulk, place value, imports and exports, and distribution and geological or processing complexity that typified each group. He concluded that because most *industrial minerals* fell into the high unit-value group, while *industrial rocks* mainly fell in the low unit-value group, these should form the basis of a simple classification. In this scheme, rock salt is regarded as a rock, while potash a mineral—a slightly arbitrary attribution that fits better with the typical characteristics of other commodities within each group (Table 1).

From a systematic economic perspective, Noetstaller (1988) produced a highly illuminating analysis of the industrial minerals and rocks sector in his report for the World Bank. Although again not principally for classification purposes, the lists and graphs produced for ranking and economic comparisons offer much insight into the ranges and clustering of industrial minerals and rocks commodities under many economic, trade, technical, and even geological parameters. Examples include commodity lists by unit value, concentration of production in certain countries, the proportion of each commodity’s production that is traded internationally, and a

contrast of commodity production and consumption between the developing and developed world. An update of this World Bank report would be of great service to the industry.

Hybrid and Combined Methods

Bates (1960, 1969) produced a combined end-use and genetic classification incorporating a simple initial division into industrial rocks or industrial minerals, with duplicated geological subdivisions denoting the origin within each (see Table 1).

To attempt to relate geological and economic factors, Dunn (1973) developed a matrix classification in the form of a chart with one axis as uses and processes, and the other as rock types and minerals. The matrix incorporates the split by importance of either physical or chemical property (similar to Kline 1970), with 23 general end-use subdivisions, against which are indicated specific rocks or minerals used and their geological origins (similar to Bates 1969). The main strength of this chart was to visually highlight the versatility of some rock or mineral products, the geological environments that provided a range of economically interesting products, and the end uses that exploit many alternative or complementary mineral raw materials.

Kuzvart (1984) undertook a thorough comparison of different principles on which classifications have been constructed. He favored a classification system based on a combination of genetic, end-use, and economic aspects of industrial minerals. This was achieved despite the observation that an understanding of the genesis, end uses, and economics of deposits develops continually, requiring frequent revision of a classification based on these factors. He did, however, organize his work to encompass the twofold economic classification of Bates (1969), with an alphabetic subdivision of commodities supplemented by separate chapters addressing genetic, prospecting, and technological factors.

As a tool to assist in teaching about industrial minerals and rocks, Smith (1999) developed a classification that defined seven groups of commodities based on the relative importance of physical and chemical applications or a combination of the two. The classification is constructed using a matrix of commodities and uses that are grouped according to application. Clustering of commodities reveals the following groupings:

1. Principal abrasives—diamond, alumina, garnet, and pumice
2. Principal refractories—pyrophyllite, sillimanite group, magnesite, and graphite
3. Principal fillers—wollastonite, titanium minerals, mica, barite, and iron oxide
4. Principal physical and chemical minerals—feldspar and zeolite
5. Mixed-application physical minerals—silica, perlite, clay, and talc
6. Principal chemical minerals—phosphate, salt, and sulfur
7. Mixed-application physical and chemical minerals—olivine, chromite, fluor spar, gypsum, and limestone

The matrix was also supplemented by a schematic representation of the groupings in the form of a set of intersecting circles.

Other Classifications

Industrial minerals are included and subdivided in all manner of other classifications, from depletion allowances to tax rates, under import duties and Bureau of Statistics classifications, and in a multitude of economic categories. These generally do little to illuminate industrial minerals and rocks as a group and will not be considered in any further detail here.

LIMITATION OF THESE APPROACHES

To exploit an industrial mineral deposit successfully, all factors need to be considered, including deposit location, quality, processing amenability, other essential raw materials, power, infrastructure, human resources, competition, marketing, packaging, transportation, technical support, prices, and contractual agreements. It is therefore unreasonable to expect any classification scheme to address the full range of factors that are intrinsic to or affect each commodity or grouping. The industry is dynamic; commodities rise and fall as new applications develop or cheaper and better alternatives surface. Technological advances improve bottom-line performance. A classification system must adapt to these changes. A robust classification system must address the geological, compositional, economic, and end-use properties of each commodity.

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World Distribution of Industrial Minerals Deposits

Peter W. Harben

Although the crust makes up only 0.5% of the earth's total mass, it is obviously where humans live and mine and are in contact with surface waters and the atmosphere, all of which are the reservoirs and production sites for rocks and minerals. Industrial minerals are extracted in commercial quantities from the earth's silicate crust, the biosphere (water, organic substances, and skeletal matter) on land and in the sea, the hydrosphere (fresh and salt water, snow and ice), and even the atmosphere, which contains mainly nitrogen and oxygen as gases plus smaller quantities of hydrogen, carbon dioxide, and inert gases such as argon and helium.

Several methods of classifying mineral deposits have been developed, including a simple alphabetical list of the more than 2,000 identified minerals. This list can be reduced to those nonmetals that are commercially significant, perhaps 50 industrial minerals from asbestos to zircon. Mineralogically, these can be divided into different groups based on their chemical components, broadly, silicate minerals such as quartz, feldspar, and mica, and nonsilicate minerals such as oxides, sulfides, sulfates, halides, carbonates, and native elements (see Table 1). For the purpose of this chapter, however, classification according to geological and tectonic settings and subdivision by a genetic and mineral classification provides a more practical geographical flow that eliminates interference from political boundaries and oceans.

NATURAL DISTRIBUTION

With almost three quarters of the earth's crust comprising oxygen and silicon (Table 2), it stands to reason that minerals based on the SiO_4 tetrahedron—the silicates—dominate most of our surface and near-surface geology. In fact, silicates account for about 30% of all minerals and form an estimated 90% of the earth's crust. These complex silicates, many of which have commercial significance, can be subdivided based on their structures:

- Nesosilicates (single tetrahedrons) that include andalusite, sillimanite, and kyanite; forsterite and olivine; datolite; garnets; staurolite; and zircon
- Sorosilicates (double tetrahedrons) that include bertrandite
- Inosilicates (single and double chains) that include jadeite, spodumene, rhodonite, and wollastonite (all single chain); and actinolite, anthophyllite, riebeckite, and tremolite (double chains)
- Cyclosilicates (rings) that include beryl and cordierite

Table 1. Classification of minerals

Class	Type of Mineral
Elements	Metals and their alloys and the nonmetals
Sulfides	Sulfides, the selenides, the tellurides, the arsenides, the antimonides, the bismuthinides, and the sulfosalts
Halides	Fluorides, the chlorides, and the iodides
Oxides	Oxides and the hydroxides
Carbonates	Carbonates, the nitrates, and the borates
Sulfates	Sulfates, the sulfites, the chromates, the molybdates, the selenates, the selenites, the tellurates, the tellurites, and the tungstates (or the wolframates)
Phosphates	Phosphates, the arsenates, the vanadates, and the antimonates
Silicates	Silicates (the largest class)
Organics	Minerals composed of organic chemicals
Mineraloids	Minerals that lack crystal structure

Table 2. Abundance of elements in the earth's crust

Element	Approximate % by Weight	Cumulative Percentage
Oxygen	46.6	46.6
Silicon	27.7	74.3
Aluminum	8.1	82.4
Iron	5.0	87.4
Calcium	3.6	91.0
Sodium	2.8	93.8
Potassium	2.6	96.4
Magnesium	2.1	98.5
All others	1.5	100.0

- Phyllosilicates (sheets) that include the clay group (chlorite, kaolinite, pyrophyllite, talc), the mica group (muscovite, phlogopite, lepidolite, and zinnwaldite), and serpentine
- Tectosilicates (frameworks) that include the feldspar, feldspathoid, quartz, and zeolite group of minerals

Among the nonsilicates, the most common classes are as follows

- Carbonates with commercial minerals such as calcite, dolomite, and magnesite; trona, nahcolite, and bastnasite; and the various nitrates, borates, and iodates
- Oxides such as anatase, brookite, ilmenite, and rutile; chrysoberyl, corundum, hematite, and magnetite; periclase, pyrochlore, and pyrolusite; stishovite, spinel, and chromite
- Hydroxides such as brucite, gibbsite, goethite, and limonite; and manganite and psilomelane
- Sulfides like pyrite and stibnite
- Sulfates like alunite, anhydrite, and gypsum; barite, celestite, epsomite, kieserite, mirabilite, and thenardite
- Phosphates like the apatite group, brushite, crandallite, amblygonite, montbrasite, wavellite, monazite, and xenotime
- Halides and chlorides like carnallite, cryolite, fluorite, sellaite, and sylvite
- Organics ranging from graphite through coal and amber to diamond
- Mineraloids that include limonite and obsidian

The relatively few elements that occur in pure or native form include gold, silver, and copper. Overall, more than 2,000 natural minerals have been identified in the earth's crust, yet only about 20 can be regarded as common, with less than a handful accounting for more than 90 % of the crust by mass (Shipman, Wilson, and Todd 2003).

Continuing with the obvious theme, Stanton (1972) concluded that most ore deposits appear to be closely related to their geological environments, and since these geological environments vary over time, it follows that particular ores should have been conspicuously concentrated in certain places at certain times during geologic history. In the metallic world, these places are known as metallogenic provinces (Govett and Govett 1976), a concept that can be applied to a more limited degree to nonmetallics. Consequently, the basic distribution pattern of mineral resources is obviously determined by geology, a premise that forms the basis for this chapter.

ANTHROPOGENIC INFLUENCES

There is, however, another layer of classification because the distribution of commercial production—that is, reserves as opposed to resources—is influenced by a diverse host of factors that include mineral grade and consistency, amenability to mineral beneficiation, geographic location, demographics, labor rates, tax and investment incentives, political stability, entrepreneurial skills, transportation options, market demands, research and development, price competitiveness, economic climate, environmental regulations, government intervention, and timing. As a result, natural and anthropogenic factors have combined to produce the distribution pattern.

The industrial minerals category includes almost 50 highly diverse, commercial, nonmetallic and nonfuel materials ranging from sand, gravel, and crushed stone (silicates) used in large tonnage and sold for a few dollars per ton (and so must be produced close to the point of use, i.e., low unit value but a high place value), to ground calcium carbonate (GCC) serving regional markets and sold at middle prices, to industrial diamond (specialized carbon) the occurrence of which in minute quantities that are thousands of kilometers from markets is no deterrent to commercial exploitation (i.e., a high unit value but a low place value). The majority of industrial minerals fall between these extremes of unit and place value—some will be able to service local, regional, and even world markets. As previously outlined, the distribution pattern of these industrial

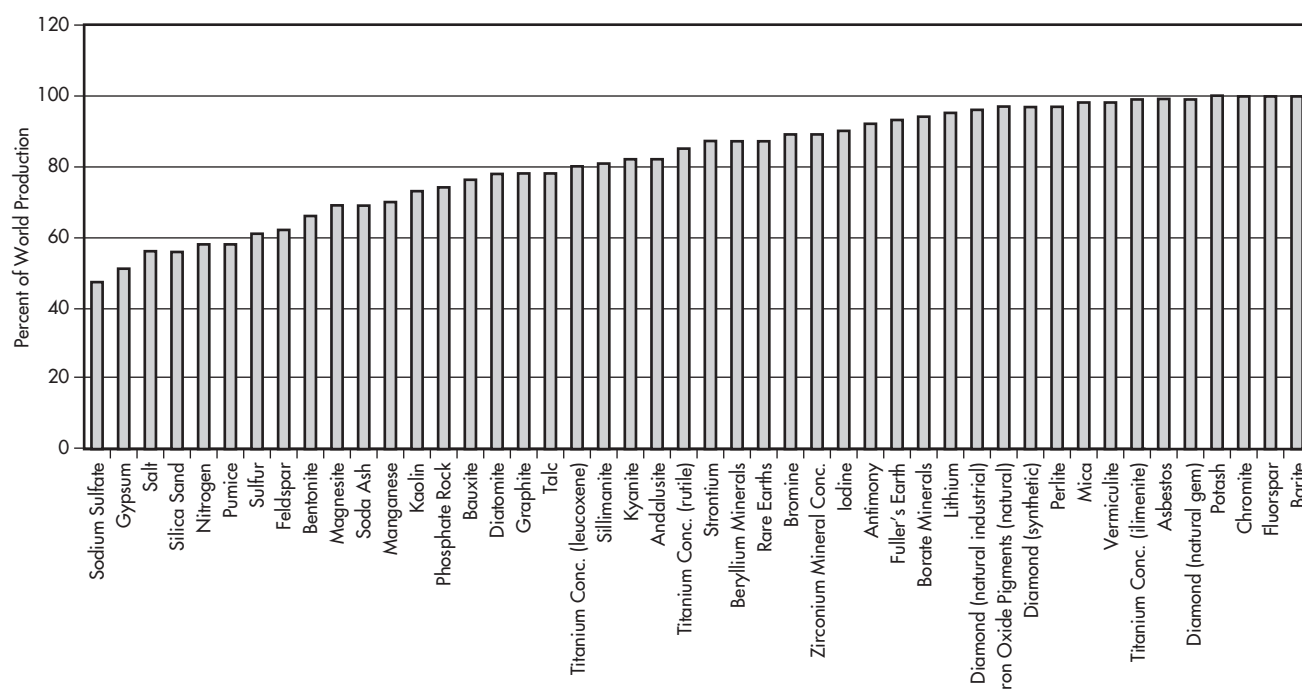
minerals is highly skewed, reflecting the dominance of silicates and, to a lesser extent, carbonates. The distribution of supply is further reduced because commercial extraction is restricted to the land area of the continents or at most the near-shore seawater (even this continental area is distributed rather unevenly: some 65% of the total land area is in the Northern Hemisphere). The chemistry of the rocks that make up the continents and the ocean floor also differs: the mean composition of continents is close to that of granite (acid) whereas the ocean basins are formed mainly of rocks of gabbroic or basaltic (basic) composition. The seawater and atmosphere are a relatively minor but critical source of some industrial minerals such as iodine and magnesium from seawater and ammonia from the atmosphere (Dott and Batten 1988).

Just as significant today is that human resources, and therefore markets, are not distributed equally over the world. This gives rise to some interesting commercial incongruities. In certain regions, raw materials are plentiful but consumers are not, and without a market, a mineral deposit is merely a geological curiosity. Elsewhere, there may be a market but no local raw material supply. For example, despite a huge market, there is no—or virtually no—commercial production of chromite, diamonds, and manganese in the United States and Canada, or phosphate rock, diamonds, rutile, and zirconium minerals in Western Europe. In contrast, Australia with its small domestic market is the world's largest supplier of bauxite, diamonds, ilmenite, natural and synthetic rutile, and zircon. The same is true for South Africa, a leading producer of chromite, manganese, diamonds, andalusite, ilmenite, rutile, and zircon. North America, Western Europe, and parts of Asia, including Japan, Korea, and Taiwan, continue to be the largest consumers of industrial minerals. These regions completely dominate the consumption of high-technology products such as beryllium and rare earths, often importing the raw materials for conversion into specialized products that are then consumed in a local manufacturing process. On the other hand, as manufacturing activity transfers to developing countries, so too does the demand for commodity industrial minerals. Consequently, these conventional industrial minerals markets have become saturated with flat growth prospects compared with the rapid rate of growth in developing regions like parts of Asia, Latin America, and, to a certain degree, the Middle East.

Nature's uneven distribution of minerals is counterbalanced in the commercial world by the continuing growth of deep-sea international trade. More highly developed techniques of materials handling and transportation have been a contributing factor, as has the demand by consumers for materials with special or unique properties, irrespective of where these materials are found. Wyoming bentonite is delivered to oil rigs in the U.S. Gulf Coast region; soda ash from the western United States is transported via dedicated unit trains, port facilities, and ships to glass plants in the Middle East; and caustic soda from the U.S. Gulf Coast region is exported to alumina plants in Australia. Low production costs or exceptional quality products can overcome distance from market and compete successfully with more local products.

PRODUCTION PATTERNS

Contrary to the common concept of being widespread, three quarters of the worldwide supply of industrial minerals and rocks is derived from five or fewer countries (Figure 1). Curiously, even materials that appear to be virtually ubiquitous—like silica sand, gypsum, and common salt—have significant production vacuums where more than half of the world production comes from a mere handful of countries. For example, common solar salt is produced cheaply on a massive scale for export in Australia, Chile, and Mexico, where cargoes of almost 100,000 t cross thousands of miles of



Adapted from U.S. Geological Survey (data for 2000); Harben 2002.

Figure 1. Percentage of world production from five countries or fewer

ocean. The low cost of production and access to deep-water transportation allow silica sand to be exported from Queensland, Australia, to Asian markets. The most often cited example is the use of large-scale production and backhaul transportation to deliver crushed aggregate from Scotland to markets along the U.S. Gulf Coast. The recent period of rationalization has tended to reduce the number and increase the size of some suppliers. A prime example in the second half of the 1990s was when lithium, as the low-cost production of lithium carbonate from brines in Chile, replaced hard-rock mining operations in the United States and therefore severely restricted production elsewhere. Exports from China have forced producers of magnesite and magnesium, barite, fluorspar, and many other minerals, metals, and chemicals to shut down operations because consumers shopped based on price. More recently, China's domestic consumption has increased to the point where China has to import large quantities of celestite, iron ore, potash, and various potassium chemicals.

These examples all underline and expand on the obvious, but acute, truism that "the single most important fact about mineral resources is that they are not distributed equally over the world" (Flawn 1966). Once considered the "country cousins" of those glamorous metallics, industrial minerals are shedding their image of being common.

The industrial minerals can be broadly placed into geological pigeon holes (Table 3), although a number reside comfortably in several slots.

IGNEOUS INTRUSIVE

Chromite

Both olivine and chromite deposits are closely associated with ultramafic plutonic rocks. The bulk of chromite reserves occur in the large, laterally extensive stratiform or Bushveld-type for m occurring in stable shield areas as exemplified by the Bushveld

Igneous Complex in South Africa, the Great Dyke of Zimbabwe, northern Finland, and Bahia State, Brazil. In contrast, the smaller podiform or Alpine-type deposits occur in mobile belts such as the Urals of the former U.S.S.R.; the Tethyan mountain chain of the Balkans, Turkey, and Iran; and the Circum-Pacific belt. Overall, significant chromite reserves and production are restricted to fewer than 10 countries, and no metallurgical grades to still fewer, namely South Africa, the Philippines, Turkey, Greece, Finland, Albania, and India.

Olivine

Commercial olivine and dunite deposits are common in alpine-type ultrabasic terrains. A limited market restricts production to Norway, with 80% of world production; smaller producers are Spain, Italy, Japan, and the United States. The modest U.S. production is from North Carolina and Washington.

Nepheline Syenite

Nepheline syenite is a relatively common, silica-deficient, magmatic intrusive rock. Commercial production, however, is limited to large operations in Canada, Norway, and the former U.S.S.R. because of the limited market size, competition from feldspar, and the requirement for a consistently low iron content. Production from Canada and Norway is virtually all exported; this accounts for 70% and 30%, respectively, of world production, excluding the former U.S.S.R.

Diamonds

The primary geological habitat for natural diamond is kimberlite, an ultrabasic intrusive rock associated with stable shield regions. Diamondiferous kimberlites are concentrated in southern Africa, the Siberian Platform, Brazil, and Western Australia. Ages range from Precambrian in South Africa to Recent in Tanzania. Diamonds are

Table 3. Geological classification of industrial minerals

	Primary Commercial Environment	Alternative Sources
Igneous	Intrusive	
	Olivine	Sedimentary (placer)
	Chromite	Sedimentary (placer)
	Nepheline syenite	
	Granite	
	Pegmatitic and hydrothermal	
	Feldspar	Alteration/sedimentary (sand)
	Mica	
	Quartz crystal	Synthetic
	Lithium minerals	Evaporate
	Beryllium minerals	
	Fluorspar	
	Extrusive	
	Basalt and related rocks	
	Pumice, pumicite, and scoria	
	Perlite	
Sedimentary	Clastic	
	Sand and gravel	
	Sandstone	
	Clays	
	Titanium and zirconium minerals	Intrusive
	Rare-earth minerals	Intrusive
	Diamonds	Intrusive/synthetic
	Biogenetic	
	Limestone and dolomite	
	Diatomite	
	Phosphate	
	Sulfur	Hydrothermal/by-product
	Chemical (evaporate)	
	Barite	Alteration/sedimentary
	Salt	
	Sodium carbonate	Synthetic
	Sodium sulfate	By-product
	Nacholite and dawsonite	
	Gypsum	By-product
	Potassium minerals	
	Borates	
	Celestite	
	Nitrates	Synthetic
	Bromine	
	Iodine	
Surficially altered	Chemical (evaporate)	
	Vermiculite	
	Manganese minerals	Sedimentary
	Bauxite	
	Iron oxide	
	Tripoli and novaculite	
	Zeolites	
Metamorphic	Chemical (evaporate)	
	Marble	
	Slate	
	Asbestos	
	Magnesite and magnesite	Igneous/sedimentary/synthetic
	Graphite	Synthetic
	Corundum and emery	Synthetic
	Garnet	Sedimentary (placer)
	Wollastonite	Synthetic
	Sillimanite minerals	
	Pyrophyllite	

Source: Adapted from Harben and Bates 1984.

also produced commercially from placer deposits such as in Namibia (see Sedimentary section in this chapter). Overall, Africa is a prime region for diamond production, in particular South Africa, Botswana, Namibia, Lesotho, Swaziland, and Angola.

Lithium

Lithium tends to concentrate in silicic rocks and pegmatites containing feldspar, quartz, and mica in places such as Bernic Lake, Manitoba, Canada (spodumene, lepidolite); Greenbushes, Western Australia (spodumene); and Bikita, Zimbabwe (petalite, spodumene, lepidolite, eucryptite). Although lithium-rich pegmatites are separated to form a lithium concentrate plus by-product feldspar, quartz, or mica, these pegmatitic sources of lithium have been strongly challenged by lithium extracted from brines in Chile and Argentina (in fact, the availability of lithium from brines forced the closure of a hard-rock operation in the Kings Mountain area of North Carolina).

Beryllium

Although beryl is also associated with pegmatites in locations such as Brazil, the former U.S.S.R., and western Canada, production of bertrandite in Utah now accounts for 80% of the world's beryllium supply.

Fluorspar

Fluorspar is a "persistent" mineral occurring in various ore deposits, including Mississippi Valley (lead/zinc) type deposits, hydrothermal veins, stratabound or Manto deposits, contact metamorphic terrains, and alkali rock complexes. More than 50% of world production comes from China, with Mexico, Mongolia, South Africa, and Russia adding another 30%. Much of this production is exported, and the availability of attractively priced exports has forced the closure of smaller operations in North America and Europe. Other producers, largely for export, include Brazil, Kenya, Morocco, and Uzbekistan.

SURFICALLY ALTERED

Feldspathic and Silica Sands and Kaolin

Feldspar-rich deposits subject to weathering break down to form feldspathic sand deposits such as those exploited in the western United States and in Spain. Further weathering forms a mixture of feldspar, silica, and kaolin such as that mined in Bavaria. Still further decomposition through weathering or hydrothermal activity eliminates much of the mica and silica and yields premier-quality deposits of kaolin such as those mined in Cornwall in the United Kingdom, Georgia and the Carolinas in the southern United States, and the Amazon Basin of Brazil. These areas produce virtually all the coating-grade material. Other suppliers of quality kaolin include France, Germany, the Czech Republic, Malaysia, and Australia.

Vermiculite

Vermiculite is a supergene alteration product formed by the combined effects of weathering and circulating groundwater. Large-scale commercial production is confined to South Carolina and Virginia in the United States and the Palabora Complex in South Africa, which contributes 70% of world supplies. Minor quantities come from China, Russia, Brazil, Zimbabwe, Japan, Australia, and Egypt.

Bauxite

Because residual bauxite deposits result from the tropical weathering of a variety of source rocks, their distribution is based on clima-

tology rather than lithology. Formation is encouraged by long periods of tectonic stability permitting deep and thorough weathering. Most bauxite deposits are post-Cretaceous in age and many occur in modern tropical regions. Bauxite provinces have been defined as follows:

- Guiana Shield of South America (Venezuela, Guyana, Surinam, Guiana, and parts of Brazil and Colombia)
- Northern Brazilian Shield Province
- Caribbean Shield Province (Costa Rica, Jamaica, Dominican Republic, Haiti, and Puerto Rico)
- Guinea Shield Province (Guinea-Bissau to Togo)
- Cameroon Province (Cameroon, Zaire)
- Australian Province
- European Province (France, Greece, Hungary, and Yugoslavia)
- Others (United States, China, former U.S.S.R., India, and Malaysia).

A dozen countries contribute 95% of world production, with more than 75% coming from Australia, Guinea, Jamaica, China, and Brazil. Nonmetallurgical grades used for refractories, abrasives, chemicals, and aluminum cement are confined to specific deposits in China, Australia, Guinea, Brazil, Guyana, and Suriname.

Manganese

Manganese is found in most geological environments; the commercially more important being sedimentary and residual. Large sedimentary marine deposits of manganese are exploited in Ukraine, the former U.S.S.R., the Kalahari Basin of South Africa, Groote Eylandt in Australia, and Mexico. Residual deposits are important in Ghana and Gabon in West Africa and in Amapá, Brazil. More than 90% of world production comes from eight countries—China, South Africa, Ukraine, Brazil, Gabon, Australia, India, and Kazakhstan. Nonmetallurgical grades constitute a relatively small percentage of output from these major suppliers, plus smaller tonnage producers such as Ghana, Morocco, and Greece.

Iron Oxides

Iron oxides are generally associated with volcanic activity and sulfide deposits combined with subsequent leaching and diagenic alteration. India is the world's largest supplier with more than 70% of production, followed by the United States with an additional 10%. European production is centered in Spain, United Kingdom, France, Italy, and Austria (the last being the main source of natural micaceous oxide). Cyprus is noted for its variety of iron oxides, including ochre andumber.

Tripoli

Tripoli is a microcrystalline, friable, high-silica (98% to 99%) material formed from the weathering of siliceous limestone. The only large-scale commercial producers are in the United States, specifically the southwestern Missouri–northeastern Oklahoma region, southern Illinois, and the Ouachita Mountain region of Arkansas. Deposits in the latter region are associated with novaculite.

Zeolites

Natural zeolites are formed through the reaction of pore water with volcanic glass, clay, feldspar, and a variety of other rocks and minerals. Although zeolites have been recognized in virtually all parts of the world, large-scale commercial production is restricted to the western United States, Cuba, Japan, and several eastern European countries, including Bulgaria.

VOLCANIC EXTRUSIVE

Perlite

Because of susceptibility to devitrification and alteration, commercial deposits of extrusive volcanic rocks like perlite and pumice are generally confined to younger geological terrains. Perlite deposits, which are rarely older than Oligocene, are exploited in the western United States, Mexico, Greece, Turkey, Italy, western Russia, Hungary, the Czech Republic, and Japan. Among them, the United States (particularly Arizona, New Mexico, and Nevada) and Greece account for more than 60% of world production and, in fact, Greece exports product to eastern U.S. markets.

Pumice

Pumice is common on volcanic islands such as Lipari near Sicily, Yali and Nisissos in Greece, and the Canary Islands of Spain. Italy, Greece, and the United States control more than 50% of the world's pumice supply. Smaller tonnages come from Chile, Germany, Spain, Turkey, Italy, New Zealand, France, Ecuador, Ethiopia, Guadeloupe, Iran, Martinique, Argentina, and the Dominican Republic (production from some areas may include volcanic tuff, ash, pumiceous lapilli, or scoria).

SEDIMENTARY

Silica

Sedimentary deposits are formed through the erosion, transportation, and redeposition of minerals that can survive the rigors of transportation. The most common is silica, which forms a number of materials, including silica sand, sand and gravel, and flint. The precursor is igneous quartz (e.g., in granite), and then the sedimentary deposit may undergo metamorphism and recementing to produce quartzite. Sand and gravel for construction use is extremely common, and production is more dependent on local markets than availability. Certain areas are, however, noted for producing industrial sand that is sufficiently pure to be used in the manufacture of glass, ceramics, sodium silicate, and the like. Examples include the midwestern United States; Badgeley Island, Ontario, Canada; Cheshire in northwest England; certain areas of Belgium and the Netherlands; Cape Flattery Island, Queensland, Australia; and Sarawak, Malaysia. In many cases, the use of local sand is based on price rather than quality. The United States is the largest producer of industrial sand, accounting for more than one quarter of world production. Production of flint is much more restricted, based largely on the chalk deposits of southern England and northern France.

Clays

Several clays composed mainly of kaolinite are of sedimentary origin. Premier deposits of ball clay, the carbon content of which indicates that it was deposited in swampy conditions, occur in the Kentucky–Tennessee area of the United States, Devon in southwest England, and the Czech Republic. Flint clay, as produced commercially in the United States, China, Australia, and Argentina, is generally derived from the weathering of soil and deposition in shallow basins. Fire clay or refractory kaolin is a kaolinite material common in many parts of the world, particularly in association with coal deposits. A 400-km belt of kaolinite-rich rocks extends from Aiken, South Carolina, to Eufaula, Alabama, and includes areas supplying high- and medium-quality kaolin and refractory kaolin. Another belt of kaolin, bauxite, and bauxitic and kaolinitic clays extends from western Tennessee into northeastern Mississippi. Other areas include southwest England and over the English Channel in France (kaolin and ball clay); various parts of the Czech Republic (kaolin and ball clay); Spain; the Amazon Basin in Brazil (bauxite,

kaolin); Japan (kaolin, refractory clay, roseki, and tosek i); and Queensland, Australia (bauxite, kaolin).

Volcanic ash deposited as part of a sedimentary sequence eventually forms sodium or calcium bentonite. Important bentonite deposits occur in the United States in the Wyoming–Montana region (sodium-based bentonite) and in the Mississippi–Texas region (calcium-based). Almost 40% of the world's bentonite production is from these and some smaller deposits in the United States. More modest tonnages are produced in Mexico and Canada. In Europe, bentonite is mined on Milos Island in Greece, Turkey, Sardinia in Italy, Bavaria in Germany, southwestern England, Ukraine, and Spain. In Asia, production is centered in Japan, India, and China. Attapulgite and sepiolite (fuller's earth) are more restricted, being produced in Georgia and Florida in the United States (75% of world production), Germany, the United Kingdom, Senegal, and Spain.

Titanium and Zirconium Minerals (and Rare Earths)

Placer and palaeo-placer mineral deposits are important sources of heavy minerals such as ilmenite, rutile, and zircon. The rare earth sources monazite and xenotime are invariably associated with the mineral sands deposits. Many titanium/zirconium/rare earth mineral deposits are Tertiary and Quaternary in age because this was a period of geological uplift that provided the correct conditions for accumulation, plus the fact that older examples have been destroyed. Most placer deposits are in marine sand deposits along or near present coastlines, where they are concentrated by a combination of tidal action, longshore currents, waves, winds, and natural traps such as a cape. Most commercial placer deposits are recent beaches and dunes along coastlines, with some older deposits being stranded by land elevation or ocean withdrawal. Important areas include the east and west coasts of Australia, parts of Florida and Georgia in the southeastern United States, around Richards Bay in South Africa, Sierra Leone in Africa, the coastal areas of Tamil Nadu and Kerala states in southern India extending into eastern Sri Lanka, and the coastal areas of Brazil. Consequently, supplies are dominated by Australia with 45% of the ilmenite supply, 100% of the leucoxene, and more than 50% of the rutile, followed by South Africa, the United States, Ukraine, and India. Hard-rock ilmenite deposits are exploited in Quebec, Canada, and Norway. Except for the United States, most of the production is exported for use in the production of titanium dioxide pigment.

Diamonds

Major diamondiferous beach placers extend along the southwest coast of Africa and are exploited in South Africa and Namibia.

BIOGENIC

Limestone and Dolomite

Limestone is an extremely common rock formed as shell beds on a shallow sea floor. Purity depends on the environment of deposition and the subsequent mineralogical and tectonic history that may include metamorphism to marble. Limestone is exploited for uses ranging from construction aggregates and railroad ballast to cement and lime manufacturing, and glassmaking to GCC used as functional fillers in paper, plastics, and paint. The relatively modest price even for the high-calcium and high-brightness grades of GCC (less than \$200/t) means that consumption is generally close to the point of production (i.e., a local or regional market). In the United States, for example, crushed limestone is produced in all states except for Louisiana (which does produce shell), includes more than 2,500 quarries, and accounts for two thirds of the nation's crushed stone output. High-quality, filler-grade GCC produced in

Vermont, Massachusetts, and Ontario in Canada serves many parts of the United States, including the Northeast, Maryland, the mid-Atlantic states, Georgia, Alabama, Illinois, Texas, California, and Washington. In Western Europe, chalk is important in the United Kingdom, France, and Belgium, whereas crushed marble is often used in Italy and Greece.

Dolomite has many of the uses outlined for limestone, plus several others, including in refractories, in seawater magnesia and magnesium metal production, and as a dimension stone. Although less common than limestone, dolomite production, particularly for aggregates, is extremely widespread. In the United States, nonaggregate production is concentrated in California, Ohio, Michigan, Alabama, Texas, Connecticut, and Pennsylvania. Europe has an active dolomite industry where it is used extensively as a raw material for refractories and seawater magnesia production. The main producers are Spain, the United Kingdom, Belgium, France, Germany, Norway, Sweden, and Finland.

Diatomite

Diatomite deposits are formed through the accumulation of the frustules of diatoms, small animals that thrived after the Cretaceous period. Diatoms require marine or freshwater rich in nutrients like phosphates, nitrates, and silica, and relatively free of sediment. In many cases, the diatomite is associated with volcanic activity, which may be the source of silica. Important diatomite production sites include the western United States—especially California, Nevada, Washington, and Oregon. Almost three quarters of the world's production comes from the United States, China, Japan, and Denmark (although the last produces mainly molar, an impure diatomite product). Other producers are Spain, Germany, Italy, Iceland, and Korea.

Phosphate Rock

The bulk of commercial phosphorus-based compounds are derived from marine sedimentary phosphate rock deposits, with much of the rest derived from igneous deposits. Sedimentary phosphate deposits are concentrated in two main belts, the trade-wind belt that is aligned north-south from the equator to 50° latitude, and the equatorial belt, oriented west to east in low latitudes. In the trade-wind belt, deposits are located in the southeastern and northwestern United States (Florida, North Carolina, and Idaho); Baja California, Mexico; Sechura Desert, Peru; and the Caribbean Sea. In the equatorial belt, deposits are found in North Africa (Morocco, Tunisia, Algeria, Togo); the Middle East (Jordan, Israel, Syria, Senegal, Iran); the former U.S.S.R.; Venezuela; and Colombia.

More than 80% of the world's phosphate rock production comes from the United States, Morocco, China, Russia, Tunisia, and Jordan. Morocco is particularly important because it is the leading exporter. A series of middle-range producers include Brazil, Israel, Togo, and South Africa. The production in Russia, Brazil, and South Africa is largely derived from igneous deposits that may also yield rare earths, vermiculite, or copper.

Sulfur

The discretionary extraction of sulfur has declined as more and more production is based on nondiscretionary by-product sulfur extracted to comply with environmental regulations at nonferrous smelters and roasters, natural gas and crude petroleum processing plants, coking plants, and the like. Native sulfur associated with the cap rock of salt domes and in sedimentary deposits is still mined by the Frasch hot-water method (mainly in Poland but no longer in the United States), and the mining of pyrite as a source of sulfur is restricted to China.

CHEMICAL (EVAPORATE) MINERALS

Certain minerals are found dissolved in seawater and various other brines; evaporate deposits form when the concentration reaches saturation and precipitation occurs. This process requires favorable conditions such as a barred basin or broad shelf environment, plus a hot, dry climate that encourages evaporation. Once formed, the fragile deposit needs to be preserved in subsequent geological events such as burial. Halite, gypsum, and anhydrite, often interbedded with limestone and dolomite, are the most common minerals present in marine evaporates, which often extend over hundreds of square kilometers and attain a thickness greater than several thousand meters. In rarer cases, other evaporate minerals are present, such as potassium minerals, borates, and strontium minerals.

Salt

Common salt lives up to its name by being ubiquitous in most brines and many evaporate deposits. It is exploited commercially from seawater where the modern climate allows evaporation (e.g., in Western Australia, Mexico, Bahamas, Netherlands Antilles, Chile, India, Brazil, Italy, and Spain). Large, buried rock salt and salt dome deposits are important in the northeastern, southern, and midwestern areas of North America; central and northern Europe; parts of the former U.S.S.R.; and the Middle East. Saline lakes are worked in the western United States, for example, the Great Salt Lake in Utah (which yields or has yielded sodium sulfate, potassium minerals, magnesium chloride, bromine, and lithium as well as salt) and Searles Lake in California (sodium sulfate and borates). Despite the widespread production of salt, three quarters of the world's production is accounted for by the United States, China, Germany, India, Canada, Mexico, Australia, France, Brazil, Chile, and the United Kingdom.

Other Sodium Minerals

In addition to salt, other sodium-rich minerals are concentrated in modern brines or evaporate deposits. Vast deposits of natural sodium carbonate or trona around Green River, Wyoming, yield more than 10 Mtpy of refined soda ash and form a soda feedstock for a variety of chemical products. Smaller deposits are known in China and Turkey. Sodium carbonate is also extracted from saline lakes in the western United States, Mexico, China, Russia, and Africa. Lake Magadi, Kenya, which has been producing sodium carbonate for most of the last century, is one of numerous sodium-rich lakes in the 6,030-km rift valley stretching from Turkey through Arabia and East Africa to Tanzania. This valley also includes the Dead Sea (dividing Israel and Jordan), which currently produces salt and potash and has the potential to produce sodium carbonate, magnesium oxide, and bromine. Natural soda ash production constitutes almost 30% of total world production (virtually all from the United States), with the balance produced in Solvay plants using a salt and limestone feedstock.

Sodium sulfate is a common co-product in brine-based operations. In addition, natural sodium sulfate is exploited from lakes in western Canada, in California in the United States, and in Mexico, Russia, and Turkey. Buried deposits are mined in Spain. Sodium sulfate is also a by-product of several industrial processes, including rayon manufacture. Although production is broad based, more than 50% is in China, the United States, Spain, Mexico, and Belgium.

There are three important commercial sulfate minerals—gypsum (calcium), celestine (strontium), and barite (barium). In North America, large deposits of gypsum occur in the Northeast (New York in the United States and Ontario and the Maritime provinces in Canada), Midwest (Michigan, Iowa, and Indiana), and the Southwest and West (Oklahoma, Texas, Kansas, New Mexico, and

California). In the U.S. Gulf Coast region, accumulations of salt, gypsum, and sulfur stretch into Mexico. Overall, the three countries in North America account for a third of world gypsum production. In Australasia, China, Japan, Thailand, and Australia contribute more than 20% of world production; and in Europe, the large evaporate deposits previously outlined also contain gypsum, with the main suppliers being France, Spain, Germany, and the United Kingdom. Production in the Middle East is dominated by Iran. Several countries such as Germany produce gypsum as a by-product from flue-gas desulfurization (FGD) or phosphoric acid plants competing with the natural product in the marketplace. Despite its low unit value, gypsum is often exported on a large scale from coastal locations in Mexico, Canada, and Spain to the United States.

Potassium Minerals

In some cases, potassium minerals are found associated with salt. During the Permian period in Europe, for example, the Zechstein Basin extended from northern Britain through the Netherlands, Denmark, and Germany to Poland. This was a shallow stable sea that allowed thick evaporate sequences to accumulate, resulting in the large potash and salt deposits that are exploited today. To the east, three basins contain vast reserves of potash—Stebnik/Kalush in Ukraine near the border with Poland, Soligorsk near Minsk in Belarus, and Solikamsk/Berezniki west of the Urals. In western Canada during the Silurian to mid-Devonian period, the land subsided to form a large basin stretching southward into the United States. This allowed vast thicknesses of evaporates to be formed, including the potash resources of Saskatchewan, Canada. A large potash/salt-rich basin identified in Thailand has potential for commercial production. Despite its strategic importance as a fertilizer, large-scale potash production is fairly restricted with just 10 countries—Canada, Russia, Germany, Belarus, Israel, the United States, Jordan, the United Kingdom, Spain, and Brazil—accounting for 97% of world production.

Celestite

Virtually all the world's celestite is mined in just six countries—Mexico, Spain, Turkey, Argentina, Iran, and Pakistan. In northern Mexico, the output from several mines accounts for half of the world's production; Spain contributes an additional 40%.

Barite

As mentioned previously, barite can be associated with evaporate minerals such as celestite and gypsum. In addition, barite is also found as a hydrothermal vein filling associated with stratiform massive sulfide deposits and as a residual deposit. China has emerged as the world leader in barite production, accounting for more than 50% of the world total. In contrast, barite production in the United States has declined to 6% of world production because of the availability of imports from China and, to a lesser extent, Mexico and Morocco. Other suppliers are India, Iran, and Turkey.

Borates

About 60% of the world's borate production is controlled by the United States and Turkey, with Argentina, Chile, and Russia supplying most of the balance. Part of the production is based on brines and encrustations in Searles Lake, California, and from small concentrations along a stretch of the Andes Mountains encompassing Argentina, Bolivia, Chile, and Peru. The major source of borate minerals is a buried mass of sodium borate at Boron in the Mojave Desert of California. Other buried and surface borate deposits occur in Death Valley, including the Billie colemanite deposit, which was mined until the mid-1980s. In Turkey, borates are concentrated in

six areas—the most important being the Emet and Kirka areas (both sodium borate) and the Bigadiç area (calcium borates).

Lithium

In addition to hard-rock deposits already described, lithium may be enriched in some geothermal waters (for example, Imperial Valley, California, United States; Reykjanes Field, Iceland; and Wairekei, New Zealand) and oil-field brines (Paradox Basin, Utah; Smackover Formation, Arkansas; and Texas—all in the United States). Brines may be further concentrated in saline lakes or salars if given an enclosed basin close to Tertiary or Recent volcanoes, a desert environment, and time for accumulation and enrichment. Major lithium-producing salars include the Salar de Atacama in Chile (which contributes more than 50% of world production); Salar del Hombre Muerto in Argentina; and Silver Peak, Nevada, in the United States.

Magnesia

In addition to magnesite, dolomite, and olivine, magnesia is concentrated in subterranean and seawater brines. Magnesium-rich brines are exploited on a commercial scale in Michigan in the United States, and in Mexico, the Netherlands, and Israel. Magnesia is also extracted from seawater in Japan, South Korea, the United States, Mexico, the United Kingdom, France, Italy, Ireland, Norway, and Russia.

Nitrates

Natural nitrate production is now confined to an area of northern Chile that has an annual rainfall of less than 1 cm. In addition, iodine is co-produced from the caliche ore and accounts for more than 50% of world production. Elsewhere, commercial iodine production is based on brines largely found in Japan (35% of world production), the United States (Oklahoma), China, Azerbaijan, Russia, and Turkmenistan. Bromine is also extracted from well brines in Arkansas and Michigan in the United States, the Dead Sea in Israel, potash brines in Germany and France, and seawater in the United Kingdom, France, Spain, and Japan. The United States and Israel combine to account for 75% of world production.

METAMORPHIC

Metamorphism produces a range of minerals, many of which have unique properties that are used commercially.

Asbestos

Asbestos is found in several metamorphic environments usually associated with ultramafic rocks and serpentinization. Large deposits are exploited in Quebec, eastern Canada; in the Transvaal and Cape Province of South Africa and in Swaziland and Zimbabwe in Africa; Russia, Italy, and Greece in Europe; New South Wales in Australia; Brazil; Kazakhstan; and India.

Talc

China produces about 50% of the world's talc and is a major exporter. The United States and Canada account for about 12% of world talc production with output from Vermont, upstate New York, Montana, Texas, and California in the United States and Quebec and Ontario in Canada. In Australasia, China is by far the largest producer, followed by India, North and South Korea, Japan, and Australia. In Europe, significant talc producers include France, Italy, Austria, Finland, and Norway, along with Russia. In South America, Brazil is the largest producer. Table 4 shows the major suppliers in the world minerals market.

Table 4. Major suppliers of industrial minerals (more than 20%)*

Country	Mineral	Total	World Production, %
Australia	Titanium concentrates (leucocoxene), <i>t</i>	27,000	100
	Titanium concentrates (rutile), <i>t</i>	237,000	57
	Zirconium mineral concentrates, <i>t</i>	353,000	46
	Titanium concentrates (ilmenite), <i>t</i>	2,156,000	45
	Bauxite, <i>kt</i>	53,802	40
	Diamond (natural industrial), <i>thousand carats</i>	14,684	26
	Lithium (spodumene), <i>t</i>	76,000	40
Botswana	Diamond (natural gem), <i>thousand carats</i>	19,700	31
Canada	Titanium concentrates (titaniferous slag), <i>t</i>	950,000	46
	Potash, <i>kt, K₂O equivalent</i>	8,600	34
Chile	Iodine, <i>t</i>	9,100	51
China	Antimony, <i>kt</i>	100,000	85
	Rare earths, <i>t, REO[†] equivalent</i>	80,600	68
	Barite, <i>kt</i>	3,500,000	56
	Fluorspar, <i>kt</i>	2,450,000	54
	Talc (may include pyrophyllite), <i>t</i>	3,500,000	48
	Graphite, <i>t</i>	220,000	37
	Nitrogen (ammonia), <i>kt</i>	28,000	26
	Soda ash, <i>kt</i>	8,343	24
	Magnesite, <i>t</i>	2,500,000	23
	Sodium sulfate (natural and synthetic), <i>t</i>	800,000	22
	Manganese, <i>kt, gross weight</i>	4,000	20
	Diamond (natural industrial), <i>thousand carats</i>	14,200	26
	Andalusite, <i>t</i>	65,000	26
	Perlite, <i>t</i>	500,000	26
	Iron oxide pigments (natural ochre), <i>t</i>	365,000	72
Congo (Kinshasa)	Sillimanite, <i>t</i>	12,000	60
France	Graphite, <i>t</i>	140,000	23
Greece	Rare earths, <i>t, REO equivalent</i>	27,000	23
India	Bromine, <i>kt</i>	185,000	34
	Pumice (may include volcanic tuff, ash, pumiceous lapilli, scoria, etc.), <i>t</i>	4,000,000	33
	Feldspar, <i>kt</i>	2,600,000	28
Israel	Iodine, <i>t</i>	6,100	34
Italy	Strontium, <i>kt</i>	157,420	50
Japan	Asbestos, <i>kt</i>	750,000	39
Mexico	Mica, <i>t</i>	100,000	34
Russia	Borate minerals, <i>kt</i>	1,000	24
	Diamond (natural industrial), <i>thousand carats</i>	11,600	21
	Andalusite, <i>t</i>	185,055	73
	Titanium concentrates (titaniferous slag), <i>t</i>	1,120,000	54
	Chromite, <i>t, gross weight</i>	6,620,754	46
South Africa	Vermiculite, <i>t</i>	208,835	41
	Zirconium mineral concentrates, <i>t</i>	270,000	36
	Titanium concentrates (rutile), <i>t</i>	100,000	24
	Strontium, <i>kt</i>	130,000	41
	Borate minerals, <i>kt</i>	1,400	33
Spain	Kyanite, <i>t</i>	90,000	94
Turkey	Beryllium minerals, <i>kt</i>	4,510	80
United States	Fuller's earth (attapulgite), <i>t</i>	2,910,000	75
	Diamond (synthetic) <i>thousand carats</i>	248,000	50
	Bromine, <i>kt</i>	228,000	42
	Bentonite, <i>t</i>	3,760,000	38
	Diatomite, <i>kt</i>	677	36
	Perlite, <i>t</i>	672,000	35
	Mica, <i>t</i>	101,000	35
	Soda ash, <i>kt</i>	10,200	30
	Vermiculite, <i>t</i>	150,000	29
	Phosphate rock, <i>kt, gross weight</i>	38,600	29
	Silica sand, <i>kt</i>	28,500	27
	Borate minerals, <i>t</i>	1,070	25
	Kaolin, <i>t</i>	8,800,000	21
	Salt, <i>kt</i>	45,600	21
	Sillimanite, <i>t</i>	4,000	20
	Lithium, <i>t</i>	37,000	20

Adapted from USGS (data for 2000).

* Data for 2000.

† REO = rare earth oxides.

Wollastonite

Wollastonite is formed through the metamorphism of rocks containing silica and calcium. Major producing areas of high-quality wollastonite include the Adirondack Mountains of upstate New York in the United States, southeastern Finland, several provinces in China and India, and Russia.

Garnet

Garnet is associated with some wollastonite deposits, including one at Willsboro, New York. In the same area of the state, a large-scale hard-rock garnet mine is in operation. Elsewhere in the United States, although there are hard-rock garnet deposits in Maine and Nevada, the most important commercially are placer deposits in Idaho. Garnet is also produced as a by-product of mineral sand operations in Western Australia, India, and Sri Lanka.

Kyanite Group

The kyanite group of minerals occurs in aluminous metamorphic rocks and their weathered derivatives. Production is restricted to a handful of countries, including South Africa, Russia, the United States, France, India, Sweden, Spain, China, and Zimbabwe. Like garnet, some are found associated with placer mineral sand deposits, particularly in India.

Pyrophyllite

Weathering may form sericite or pyrophyllite, the hydrous aluminum silicate. The main pyrophyllite deposits, however, are formed through the hydrothermal alteration of acidic volcanic rocks. This is particularly well developed in areas of Japan and the Republic of Korea—accounting for 85% of world production between them. Smaller producers include Canada, the United States, India, China, Thailand, Australia, Brazil, and Argentina.

Corundum

Natural corundum is another alumina-rich mineral formed through metamorphism. The main producers are Zimbabwe and South Africa, the former U.S.S.R., and India. Production of the impure form, emery, is restricted to Turkey and Greece.

Graphite

When certain organic matter is metamorphosed, deposits of graphite can form. Although world production is concentrated in fewer than 20 countries, more than 60% is produced in Asia—China, the Republic of Korea, Sri Lanka, and India. In the Americas, Mexico and Brazil are well-established producers, and Canada is emerging as a major supplier. The main producers are Germany, Austria, the Czech Republic, Norway, Romania, Turkey, and Russia in Europe, and Zimbabwe and Madagascar in Africa.

THE EMERGING PATTERN

The uneven distribution of industrial minerals and rocks and their production counters the concept of a group of common, low-priced commodities destined for local markets (see Tables 5 and 6). Local markets are the most important for some industrial minerals, especially for developing countries, which should adopt simpler approaches to exploiting their domestic resources. Nevertheless, the overall view of industrial minerals is an international one of intriguing complexity.

For instance, production of borates, beryl, iodine, nepheline syenite, celestite, and vermiculite is restricted to just a few countries, and essential materials such as titanium, zirconium, rare earth minerals, sulfur, graphite, phosphates, and potash are extremely

active in deep-sea trade. Even relatively common materials enter international trade as consumers demand higher and more consistent quality (feldspar and silica sand) or find it more cost-effective to import (soda ash, salt, barite, gypsum, and fluorspar). The international supply-and-demand pattern is dynamic as new producers and markets come and go. Twenty years ago, Australia's diamond industry was a kimberlite pipe dream; today it accounts for 20% of gem quality and 30% of industrial quality diamonds. A generation ago, celestite was used solely for pyrotechnics; today the much larger market is dominated by glass for color television screens.

Substitution has always been an important aspect of the industrial minerals scene and continues to be critical for success. For example, in the paper industry, calcium carbonate is a major challenger to kaolin as a filler and coater, and precipitated calcium carbonate competes with GCC in many applications. In certain parts of the world, most notably in Scandinavia, talc is a potential substitute for both carbonate and kaolin. Regional bans on the use of phosphates in detergents encouraged the use of synthetic zeolites that in turn aided sodium silicate producers and therefore silica sand and chloralkali suppliers. Substitution offers opportunities and dangers for potential new suppliers, although regional differences in use patterns need to be considered.

Increasingly, environmental considerations influence the supply of minerals—prime examples include sulfur and sulfuric acid recovered during the refining of crude oil and sour natural gas and gypsum precipitated from an FGD plant attached to a coal-burning power plant or the neutralization of acid in a titanium dioxide pigment plant. By-product minerals are produced as the result of a manufacturing process itself, such as sodium sulfate derived from rayon spinning or calcium chloride from the Solvay soda ash manufacturing process. The need to dispose of these minerals in a responsible and cost-effective manner encourages sale on the merchant market at low prices that in turn depress the price of any commercial equivalent or rival. By-product-generating processes driven more by economics than by environmental concerns include the electrolysis of salt, which produces equal parts of chlorine and caustic soda irrespective of the market conditions; similarly, when feldspar is separated from a granite or alkali by flotation, silica and mica are produced and sold as-is or even upgraded to value-added products. Another example would be the extraction of titanium minerals like ilmenite and rutile from mineral sands, which invariably yields monazite, garnet, zircon, and other heavy minerals. Revenues from these coproducts can be critical for the economic feasibility of the operation, even though the rate of production is not influenced by demand. It is difficult to compete with a by-product or coproduct mineral based on price alone.

Mineral-related environmental and health issues range from simple mineral dusting problems at ports to the need to label mineral content and use specialized containers to address the alleged health hazards associated with certain minerals and mineral-related products. At the very least, these issues can result in additional handling or transportation costs, create barriers to sales, impinge on the prospects for future growth, and even pose a long-term threat to the financial stability of the producing company because of the potential for litigation. Several minerals have been singled out for scrutiny—in particular, silica, asbestos, fluorspar, and bromine. Both recycling and material conservation have reduced the demand for virgin raw materials used to make everything from aluminum and glass containers, paper, and plastics to refractories, steel, and even roadbeds.

The pattern can be influenced by political events such as the opening of trade with China, which promptly became a dominant

Table 5. Distribution of world industrial minerals production by commodity

Mineral and Country	Production	World Production, %	World Production Cumulative, %	Mineral and Country	Production	World Production, %	World Production Cumulative, %
Andalusite, t	252,555			United Kingdom	70,000	1	92
South Africa	185,055	73	73	Russia	60,000	1	93
France	65,000	26	99	Algeria	50,000	1	94
Spain	2,500	1	100	Thailand	49,220	1	94
Antimony, kt	118,000			Brazil	45,000	1	95
United States	W*			Belgium	30,000		
China	100,000	85	85	Burma	29,200		
South Africa	5,000	4	89	Spain	26,000		
Russia	4,500	4	93	Italy	25,000		
Bolivia	2,800	2	95	Pakistan	21,234		
Tajikistan	2,000	2	97	Australia	20,000		
Australia	1,800	2	98	Canada	20,000		
Peru	460			Georgia	15,000		
Guatemala	450			Romania	15,000		
Canada	364			Slovakia	15,000		
Turkey	360			Kazakhstan	14,000		
Kyrgyzstan	150			Malaysia	13,500		
Morocco	150			Peru	11,403		
Thailand	84			Laos	9,000		
Mexico	52			Saudi Arabia	8,000		
Asbestos, kt	1,900,000			Bolivia	6,000		
Russia	750,000	39	39	Nigeria	5,000		
Canada	340,000	18	57	Argentina	4,400		
China	260,000	14	71	Tunisia	3,702		
Brazil	170,000	9	80	Guatemala	2,800		
Kazakhstan	125,000	7	87	Afghanistan	2,000		
Zimbabwe	110,000	6	92	Bosnia and Herzegovina	2,000		
Greece	50,000	3	95	South Africa	1,628		
Swaziland	25,000	1	96	Chile	900		
India	21,000	1	97	Greece	800		
South Africa	18,909	1	98	Colombia	600		
Japan	18,000	1	99	Kenya	10		
United States	5,260			Bauxite, kt	135,000		
Iran	2,000			United States	NA†		
Egypt	2,000			Australia	53,802	40	40
Serbia and Montenegro	550			Guinea	15,000	11	51
Bulgaria	350			Brazil	14,000	10	61
Argentina	350			Jamaica	11,127	8	70
Barite, kt	6,200,000			China	9,000	7	76
China	3,500,000	56	56	India	7,366	5	82
India	550,000	9	65	Russia	4,200	3	85
United States	392,000	6	72	Venezuela	4,200	3	88
Morocco	350,000	6	77	Kazakhstan	3,727	3	91
Iran	185,000	3	80	Suriname	3,610	3	93
Turkey	130,000	2	82	Guyana	2,404	2	95
Mexico	127,688	2	84	Greece	1,991	1	97
Bulgaria	120,000	2	86	Indonesia	1,200	1	98
Germany	120,000	2	88	Hungary	1,047	1	98
France	75,000	1	90	Iran	1,000	1	99
North Korea	70,000	1	91	Serbia and Montenegro	630		

Adapted from USGS (data for 2000); Harben 2002.

(Table continued next page)

* W = Withheld to avoid disclosing proprietary data.

† Not available.

‡ Rare earth oxides.

Table 5. Distribution of world industrial minerals production by commodity (continued)

Mineral and Country	Production	World Production, %	World Production Cumulative, %	Mineral and Country	Production	World Production, %	World Production Cumulative, %
Bauxite (continued)				Beryllium minerals, kt	5,650		
Ghana	504			United States	4,510	80	80
Turkey	459			Russia	1,000	18	98
Malaysia	123			Kazakhstan	100	2	99
Bosnia and Herzegovina	75			Madagascar	30	1	
Pakistan	9			Brazil	10		
Mozambique	8			Portugal	4		
Bentonite, t	9,860,000			Borate minerals, kt	4,220		
United States	3,760,000	38	38	Turkey	1,400	33	33
Greece	950,000	10	48	United States	1,070	25	59
Former U.S.S.R.	750,000	8	55	Russia	1,000	24	82
Turkey	560,000	6	61	Argentina	360	9	91
Germany	500,000	5	66	Chile	200	5	95
Italy	500,000	5	71	China	105	2	98
Japan	445,115	5	76	Peru	40	1	99
Ukraine	300,000	3	79	Kazakhstan	30	1	
Brazil	275,000	3	82	Bolivia	7		
Mexico	269,730	3	84	Iran	4		
Australia	180,000	2	86	Bromine, kt	542,000		
Argentina	150,000	2	88	United States	228,000	42	42
Bulgaria	150,000	2	89	Israel	185,000	34	76
Czech Republic	150,000	2	91	United Kingdom	55,000	10	86
Spain	150,000	2	92	China	45,000	8	95
Zimbabwe	140,000	1	94	Japan	20,000	4	98
Cyprus	126,313	1	95	Ukraine	3,000	1	99
South Africa	85,187	1	96	Azerbaijan	2,000		
Iran	70,000	1	96	France	2,000		
Egypt	50,000	1	97	India	1,500		
Turkmenistan	50,000	1	97	Italy	300		
Romania	35,789			Turkmenistan	150		
Macedonia	30,000			Spain	100		
Pakistan	27,700			Chromite, t, gross weight	14,400,000		
Algeria	22,708			South Africa	6,620,754	46	46
Morocco	21,352			Kazakhstan	2,067,000	14	60
Peru	21,059			India	1,500,000	10	71
Mozambique	16,144			Turkey	1,000,000	7	78
Hungary	15,000			Finland	640,000	4	82
Georgia	12,000			Zimbabwe	640,000	4	87
Croatia	10,013			Brazil	400,000	3	89
New Zealand	10,000			Iran	310,000	2	92
Indonesia	6,000			Australia	130,000	1	92
Poland	6,000			Madagascar	100,000	1	93
Guatemala	3,800			Russia	100,000	1	94
Armenia	2,807			Albania	70,000		
Philippines	2,000			United Arab Emirates	60,000		
Chile	1,314			Vietnam	55,000		
Bosnia and Herzegovina	800			Cuba	40,000		
Burma	600			Pakistan	26,643		
Serbia and Montenegro	75			Oman	15,110		
Tanzania	75			Philippines	15,000		

Adapted from USGS (data for 2000); Harben 2002.

* W = Withheld to avoid disclosing proprietary data.

† Not available.

‡ Rare earth oxides.

(Table continued next page)

Table 5. Distribution of world industrial minerals production by commodity (continued)

Mineral and Country	Production	World Production, %	World Production Cumulative, %	Mineral and Country	Production	World Production, %	World Production Cumulative, %
Chromite (continued)				Japan	33,000	7	85
Greece	12,000			Belarus	25,000	5	90
Sudan	10,000			Sweden	20,000	4	94
Indonesia	6,400			China	16,800	3	98
Macedonia	5,000			Ukraine	8,000	2	99
Burma	3,000			France	3,000	1	
Diamond (natural gem), thousand carats	62,600			Greece	750		
Botswana	19,700	31	31	Diatomite, kt	1,890		
Australia	12,014	19	51	United States	677	36	36
Russia	11,600	19	69	China	350	19	54
Angola	5,400	9	78	Japan	190	10	64
South Africa	4,300	7	85	Denmark	185	10	74
Congo (Kinshasa)	3,500	6	90	Former U.S.S.R.	80	4	78
Canada	2,000	3	93	France	75	4	82
Namibia	1,520	2	96	Mexico	75	4	86
Sierra Leone	450	1	97	Peru	35	2	88
Guinea	410	1	97	Spain	35	2	90
Central African Republic	400	1	98	Republic of Korea	32	2	92
Brazil	300			Romania	30	2	93
China	230			Iceland	26	1	95
Côte d'Ivoire	200			Italy	25	1	96
Ghana	178			Australia	20	1	97
Liberia	120			Chile	15	1	98
Venezuela	60			Brazil	14	1	99
Zimbabwe	7			Argentina	9		
Diamond (natural industrial), thousand carats	55,600			Iran	5		
Australia	14,684	26	26	Macedonia	5		
Congo (Kinshasa)	14,200	26	52	Colombia	4		
Russia	11,600	21	73	Algeria	3		
South Africa	6,480	12	84	Costa Rica	2		
Botswana	4,950	9	93	Poland	2		
China	920	2	95	Portugal	2		
Ghana	712	1	96	Feldspar, kt	9,280,000		
Angola	600	1	97	Italy	2,600,000	28	28
Brazil	600	1	98	Turkey	1,200,000	13	41
Central African Republic	150			United States	790,000	9	49
Sierra Leone	150			France	600,000	6	56
Guinea	140			Thailand	542,991	6	62
Côte d'Ivoire	100			Germany	460,000	5	67
Liberia	80			Spain	425,000	5	71
Namibia	80			Mexico	334,439	4	75
Venezuela	40			Egypt	330,000	4	78
Zimbabwe	13			Republic of Korea	250,000	3	81
Diamond (synthetic), thousand carats	495,000			Brazil	240,000	3	84
United States	248,000	50	50	Iran	240,000	3	86
Russia	80,000	16	66	Venezuela	160,000	2	88
Ireland	60,000	12	78	Portugal	120,000	1	89
				India	110,000	1	91
				Norway	75,000	1	91
				Uzbekistan	70,000	1	92

Adapted from USGS (data for 2000); Harben 2002.

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† Not available.

‡ Rare earth oxides.

Table 5. Distribution of world industrial minerals production by commodity (continued)

Mineral and Country	Production	World Production, %	World Production Cumulative, %	Mineral and Country	Production	World Production, %	World Production Cumulative, %
Feldspar (continued)				Turkey	5,000		
South Africa	66,774	1	93	Thailand	4,745		
Argentina	61,000	1	93	Kyrgyzstan	3,000		
Greece	60,000	1	94	India	850		
Colombia	55,000	1	95	Pakistan	700		
Ecuador	55,000	1	95	Egypt	500		
Japan	52,000	1	96	Fuller's earth (attapulgitite), t	3,870,000		
Poland	50,000	1	96	United States	2,910,000	75	75
Russia	45,000			Germany	500,000	13	88
Sweden	45,000			United Kingdom	140,000	4	92
Finland	40,000			Spain	90,000	2	94
Romania	35,000			Senegal	80,000	2	96
Pakistan	32,000			Mexico	51,685	1	97
Sri Lanka	26,500			Morocco	30,665	1	98
Philippines	25,000			Italy	30,000	1	99
Australia	20,000			Pakistan	15,288		
Burma	12,000			South Africa	7,337		
Guatemala	11,000			Australia	5,000		
Macedonia	10,000			Algeria	3,431		
United Kingdom	8,000			Argentina	1,500		
Peru	5,600			Graphite, t	602,000		
Morocco	5,000			China	220,000	37	37
Algeria	3,000			India	140,000	23	60
Serbia and Montenegro	3,000			Brazil	56,000	9	69
Zimbabwe	2,250			Mexico	30,330	5	74
Uruguay	1,600			Canada	25,000	4	78
Chile	1,500			Czech Republic	25,000	4	82
Nigeria	600			North Korea	25,000	4	87
Kenya	100			Turkey	15,000	2	89
Fluorspar, kt	4,520,000			Madagascar	13,000	2	91
China	2,450,000	54	54	Austria	12,000	2	93
Mexico	635,000	14	68	Zimbabwe	12,000	2	95
South Africa	212,355	5	73	Ukraine	7,500	1	96
Mongolia	198,843	4	77	Russia	6,000	1	97
Russia	160,000	4	81	Sweden	5,000	1	98
Spain	125,000	3	84	Sri Lanka	4,600	1	99
France	100,000	2	86	Norway	2,500		
Morocco	100,000	2	88	Romania	1,500		
Kenya	90,000	2	90	Germany	1,000		
Uzbekistan	80,000	2	92	Republic of Korea	60		
Brazil	72,000	2	93	Uzbekistan	60		
Italy	65,000	1	95	Gypsum, kt	106,000		
Namibia	58,000	1	96	United States	19,500	18	18
United Kingdom	45,000	1	97	Iran	11,000	10	29
Germany	30,000	1	98	Canada	8,548	8	37
North Korea	25,000	1	98	Spain	7,500	7	44
Iran	20,000			Mexico	7,000	7	51
Romania	15,000			China	6,800	6	57
Tajikistan	9,000			Thailand	5,830	6	62
Argentina	7,000			Japan	5,600	5	68

Adapted from USGS (data for 2000); Harben 2002.

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† Not available.

‡ Rare earth oxides.

Table 5. Distribution of world industrial minerals production by commodity (continued)

Mineral and Country	Production	World Production, %	World Production Cumulative, %	Mineral and Country	Production	World Production, %	World Production Cumulative, %
Gypsum (continued)				Azerbaijan	60		
France	4,500	4	72	Bhutan	54		
Australia	3,800	4	76	Peru	52		
Germany	2,500	2	78	Israel	46		
India	2,210	2	80	Tajikistan	35		
Egypt	2,000	2	82	Bosnia and Herzegovina	30		
Poland	1,700	2	83	Honduras	30		
Brazil	1,500	1	85	Guatemala	29		
United Kingdom	1,500	1	86	Macedonia	25		
Italy	1,300	1	88	Mongolia	25		
Austria	1,000	1	88	Venezuela	25		
Uruguay	1,000	1	89	Nicaragua	23		
Chile	890	1	90	Tanzania	21		
Russia	700	1	91	Serbia and Montenegro	15		
Greece	600	1	91	Moldova	14		
Colombia	560	1	92	Slovenia	10		
Argentina	514			Zambia	10		
Portugal	500			El Salvador	6		
Burma	484			Indonesia	5		
Ireland	450			Paraguay	4		
Morocco	450			Sudan	4		
South Africa	413			Afghanistan	3		
Pakistan	377			Lebanon	3		
Saudi Arabia	350			Ecuador	2		
Syria	304			Niger	2		
Nigeria	300			Somalia	2		
Switzerland	300			Kenya	1		
Turkey	300			Mali	1		
Algeria	275			Namibia	1		
Czech Republic	250			Iodine, t	18,000		
Jamaica	240			Chile	9,100	51	51
Bulgaria	180			Japan	6,100	34	84
Hungary	180			United States	1,470	8	93
Jordan	175			China	500	3	95
Libya	175			Azerbaijan	300	2	97
Laos	154			Russia	300	2	99
Cyprus	138			Turkmenistan	150	1	
Cuba	130			Indonesia	70		
Latvia	122			Uzbekistan	2		
Slovakia	120			Iron oxide pigments (natural ochre), t	504,027		
Ethiopia	108			India	365,000	72	72
Croatia	100			United States	57,100	11	84
Mauritania	100			Spain	15,000	3	87
Tunisia	100			Iran	13,500	3	89
Turkmenistan	100			Cyprus	12,258	2	92
Yemen	100			Chile	10,600	2	94
Dominican Republic	90			Spain	7,000	1	95
United Arab Emirates	90			Austria	7,000	1	97
Iraq	80			Brazil	5,500	1	98
Romania	75						

Adapted from USGS (data for 2000); Harben 2002.

(Table continued next page)

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† Not available.

‡ Rare earth oxides.

Table 5. Distribution of world industrial minerals production by commodity (continued)

Mineral and Country	Production	World Production, %	World Production Cumulative, %	Mineral and Country	Production	World Production, %	World Production Cumulative, %
Iron oxide pigments (continued)				Sri Lanka	12,230		
Pakistan	4,700	1	99	Algeria	11,616		
Germany	4,000	1		Italy	10,000		
France	1,000			Bangladesh	7,900		
South Africa	569			Ecuador	7,000		
Italy	500			Hungary	7,000		
Paraguay	300			Chile	6,445		
Kaolin, t	41,200,000			Peru	6,165		
United States	8,800,000	21	21	Bosnia and Herzegovina	3,000		
Colombia	8,000,000	19	41	Denmark	2,500		
Uzbekistan	5,500,000	13	54	Ethiopia	1,654		
Czech Republic	5,200,000	13	67	Vietnam	1,200		
United Kingdom	2,420,000	6	73	Burundi	800		
Republic of Korea	2,098,499	5	78	Kenya	500		
Germany	1,800,000	4	82	Sweden	440		
Brazil	1,500,000	4	86	Eritrea	393		
Iran	800,000	2	88	Madagascar	115		
India	690,000	2	89	Guatemala	100		
Mexico	532,268	1	91	Kyanite, t	95,600		
Turkey	400,000	1	92	United States	90,000	94	94
Spain	365,000	1	92	India	5,000	5	99
Belgium	300,000	1	93	Brazil	600	1	100
France	300,000	1	94	Lithium, t	189,300		
Egypt	290,000	1	95	United States (brines)	W*		
Malaysia	225,139	1	95	Australia (spodumene)	76,000	40	40
Ukraine	225,000	1	96	Zimbabwe	37,000	20	60
Australia	220,000	1	96	Chile (carbonate)	28,500	15	75
Thailand	201,226			Canada (spodumene)	22,500	12	87
Portugal	175,000			China (carbonate)	13,000	7	94
Bulgaria	110,000			Portugal (lepidolite)	7,000	4	97
Nigeria	110,000			Russia	2,000	1	98
Poland	99,382			Brazil (concentrates)	1,600	1	99
South Africa	98,897			Argentina (carbonate)	1,000	1	
Kazakhstan	70,000			Argentina (spodumene and amblygonite)	700		
Taiwan	68,000			Magnesite, t	10,700,000		
Paraguay	66,500			United States	W		
Greece	60,000			China	2,500,000	23	23
Austria	50,000			Turkey	2,000,000	19	42
Pakistan	49,574			North Korea	1,000,000	9	51
Argentina	45,000			Russia	1,000,000	9	61
Russia	45,000			Slovakia	850,000	8	69
Serbia and Montenegro	44,000			Austria	750,000	7	76
Jordan	36,795			Greece	650,000	6	82
Israel	26,700			Spain	500,000	5	86
Japan	26,000			India	365,000	3	90
New Zealand	25,000			Australia	349,783	3	93
Slovakia	25,000			Brazil	310,000	3	96
Indonesia	22,000			Canada	180,000	2	98
Romania	19,007			Iran	141,000	1	99
Slovenia	14,000						

Adapted from USGS (data for 2000); Harben 2002.

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† Not available.

‡ Rare earth oxides.

Table 5. Distribution of world industrial minerals production by commodity (continued)

Mineral and Country	Production	World Production, %	World Production Cumulative, %	Mineral and Country	Production	World Production, %	World Production Cumulative, %
Magnesite (continued)				Trinidad and Tobago	2,686	2	68
South Africa	74,000	1		Netherlands	2,543	2	70
Serbia and Montenegro	40,000			Germany	2,473	2	72
Colombia	10,500			Pakistan	1,884	2	74
Zimbabwe	4,000			Poland	1,862	2	76
Pakistan	3,100			Saudi Arabia	1,743	2	77
Philippines	700			France	1,700	2	79
Mexico	335			Egypt	1,511	1	80
Manganese, kt, gross weight	20,200			Japan	1,405	1	81
China	4,000	20	20	Bangladesh	1,255	1	83
South Africa	3,635	18	38	Qatar	1,097	1	84
Ukraine	2,741	14	51	Romania	1,016	1	84
Brazil	2,000	10	61	Iran	965	1	85
Gabon	1,743	9	70	Brazil	925	1	86
Australia	1,614	8	78	Belgium	863	1	87
India	1,550	8	86	United Kingdom	814	1	88
Kazakhstan	1,136	6	91	Uzbekistan	810	1	88
Ghana	896	4	96	Belarus	730	1	89
Mexico	418	2	98	Mexico	701	1	90
Mica, t	290,000			Malaysia	605	1	90
United States	101,000	35	35	Australia	576	1	91
Russia	100,000	34	69	South Africa	560	1	91
Republic of Korea	30,000	10	80	Libya	552	1	92
Canada	17,500	6	86	Bulgaria	533		
France	10,000	3	89	Austria	500		
Taiwan	7,000	2	92	Algeria	458		
Brazil	5,000	2	93	North Korea	450		
Malaysia	3,700	1	95	Spain	442		
Argentina	3,100	1	96	Lithuania	420		
Spain	2,500	1	96	Ireland	410		
Iran	2,000	1	97	Kuwait	410		
Sri Lanka	1,500	1	98	Italy	408		
India	1,500	1	98	Republic of Korea	400		
Zimbabwe	1,300			Venezuela	377		
Mexico	1,058			Hungary	352		
India	950			Bahrain	350		
South Africa	707			United Arab Emirates	348		
Madagascar	491			Norway	334		
Argentina (sheet)	300			Croatia	325		
Peru	100			Slovakia	271		
Serbia and Montenegro	100			Czech Republic	246		
Nitrogen (ammonia), kt	109,000			Portugal	246		
China	28,000	26	26	Iraq	220		
United States	12,300	11	37	Argentina	199		
India	10,148	9	46	Cuba	135		
Russia	8,735	8	54	Estonia	128		
Canada	4,130	4	58	Greece	121		
Indonesia	4,000	4	62	New Zealand	105		
Ukraine	3,577	3	65	Serbia and Montenegro	100		
				Colombia	93		

Adapted from USGS (data for 2000); Harben 2002.

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* W = Withheld to avoid disclosing proprietary data.

† Not available.

‡ Rare earth oxides.

Table 5. Distribution of world industrial minerals production by commodity (continued)

Mineral and Country	Production	World Production, %	World Production Cumulative, %	Mineral and Country	Production	World Production, %	World Production Cumulative, %
Nitrogen (continued)				Algeria	875	1	96
Syria	91			Vietnam	850	1	97
Burma	78			Finland	700	1	98
Turkmenistan	75			Christmas Island	575		
Zimbabwe	58			Australia	540		
Turkey	53			Nauru	500		
Vietnam	42			Venezuela	375		
Switzerland	33			North Korea	350		
Taiwan	11			Uzbekistan	300		
Albania	10			Peru	104		
Iceland	7			Philippines	100		
Finland	6			Zimbabwe	90		
Afghanistan	5			Colombia	75		
Denmark	2			Sri Lanka	32		
Bosnia and Herzegovina	1			Chile	15		
Georgia	1			Pakistan	11		
Tajikistan	1			Thailand	3		
Perlite, t	1,910,000			Tanzania	2		
United States	672,000	35	35	Albania	1		
Greece	500,000	26	61	Indonesia	1		
Japan	250,000	13	74	Potash, kt, K₂O equivalent	25,400		
Hungary	150,000	8	82	Canada	8,600	34	34
Turkey	130,000	7	89	Russia	3,700	15	48
Mexico	67,001	4	93	Germany	3,409	13	62
Italy	60,000	3	96	Belarus	3,400	13	75
Armenia	35,000	2	98	Israel	1,710	7	82
Slovakia	20,000	1	99	United States	1,300	5	87
Iran	15,000	1	99	Jordan	1,110	4	91
Philippines	10,000	1		United Kingdom	600	2	94
Australia	5,000			Spain	522	2	96
South Africa	400			Brazil	350	1	97
Phosphate rock, kt, gross weight	133,000			France	321	1	99
United States	38,600	29	29	China	250	1	99
Morocco	21,568	16	45	Ukraine	30		
China	19,400	15	60	Chile	23		
Russia	11,100	8	68	Pumice (may include volcanic tuff, ash, pumiceous lapilli, scoria, etc.), t	12,000,000		
Tunisia	8,339	6	74	Italy	4,000,000	33	33
Jordan	5,506	4	79	Greece	1,600,000	13	47
Brazil	4,900	4	82	United States	697,000	6	52
Israel	4,110	3	85	Chile	650,000	5	58
South Africa	2,778	2	87	Germany	600,000	5	63
Syria	2,166	2	89	Spain	600,000	5	68
Senegal	1,800	1	90	Turkey	600,000	5	73
India	1,720	1	92	Italy	600,000	5	78
Togo	1,370	1	93	New Zealand	500,000	4	82
Mexico	1,052	1	94	France	450,000	4	86
Egypt	1,020	1	94	Ecuador	350,000	3	89
Iraq	1,000	1	95	Ethiopia	300,000	3	91
Kazakhstan	1,000	1	96				

Adapted from USGS (data for 2000); Harben 2002.

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* W = Withheld to avoid disclosing proprietary data.

† Not available.

‡ Rare earth oxides.

Table 5. Distribution of world industrial minerals production by commodity (continued)

Mineral and Country	Production	World Production, %	World Production Cumulative, %	Mineral and Country	Production	World Production, %	World Production Cumulative, %
Pumice (continued)				Argentina	1,000		
Guadeloupe	210,000	2	93	Bahamas	900		
Iran	150,000	1	94	Thailand	892		
Martinique	130,000	1	95	Israel	863		
Argentina	120,000	1	96	Republic of Korea	800		
Dominican Republic	100,000	1	97	Vietnam	730		
Cameroon	90,000	1	98	Philippines	705		
Serbia and Montenegro	70,000	1	98	Indonesia	680		
Macedonia	60,000	1	99	Denmark	605		
Slovenia	40,000			Portugal	600		
Iceland	25,000			Jordan	546		
Burkina Faso	10,000			Namibia	510		
Costa Rica	8,000			North Korea	500		
Guatemala	6,300			Netherlands Antilles	500		
Austria	5,000			Tunisia	481		
Cape Verde	1,000			Colombia	460		
Rare earths	119,000			Austria	401		
t, REO[†] equivalent				Belarus	400		
China	80,600	68	68	Senegal	350		
India	27,000	23	90	Venezuela	350		
United States	5,000	4	95	Bangladesh	350		
Kyrgyzstan	2,000	2	96	South Africa	346		
Former U.S.S.R.	2,000	2	98	Iraq	300		
Malaysia	280			Switzerland	300		
Sri Lanka	120			Turkmenistan	215		
Salt, kt	214,000			Guadeloupe	200		
United States	45,600	21	21	Martinique	200		
China	31,280	15	36	Botswana	185		
Germany	15,700	7	43	Cuba	180		
India	14,453	7	50	Algeria	165		
Canada	11,935	6	56	Greece	150		
Mexico	8,884	4	60	Morocco	150		
Australia	8,798	4	64	Syria	150		
France	7,000	3	67	Yemen	150		
Brazil	6,000	3	70	Saudi Arabia	140		
Chile	6,000	3	73	Eritrea	100		
United Kingdom	5,800	3	75	Kuwait	100		
Netherlands	5,000	2	78	Slovakia	100		
Poland	4,200	2	80	Sri Lanka	96		
Italy	3,600	2	81	Ecuador	90		
Russia	3,200	1	83	El Salvador	90		
Spain	3,200	1	84	Peru	80		
Bulgaria	2,500	1	86	Taiwan	80		
Egypt	2,400	1	87	Serbia and Montenegro	78		
Ukraine	2,287	1	88	Dominican Republic	62		
Turkey	2,200	1	89	New Zealand	60		
Romania	2,070	1	90	Mozambique	60		
Iran	1,600	1	91	Bosnia and Herzegovina	50		
Pakistan	1,333	1	91	Ghana	50		
Japan	1,300	1	92	Sudan	50		

Adapted from USGS (data for 2000); Harben 2002.

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* W = Withheld to avoid disclosing proprietary data.

† Not available.

‡ Rare earth oxides.

Table 5. Distribution of world industrial minerals production by commodity (continued)

Mineral and Country	Production	World Production, %	World Production Cumulative, %	Mineral and Country	Production	World Production, %	World Production Cumulative, %
Salt (continued)				Czech Republic	2,000	2	82
Guatemala	49			Canada	1,946	2	84
Kenya	45			Mexico	1,800	2	86
Cambodia	40			Peru	1,600	2	87
Libya	40			India	1,350	1	88
Laos	40			Republic of Korea	1,300	1	90
Costa Rica	37			Turkey	1,100	1	91
Tanzania	36			Eritrea	1,000	1	92
Burma	35			Iran	1,000	1	92
Angola	30			Norway	1,000	1	93
Armenia	30			Bulgaria	900	1	94
Honduras	25			Venezuela	650	1	95
Madagascar	25			Egypt	600	1	95
Panama 23				Malaysia	500		
Croatia	20			Sweden	500		
Guinea	15			Thailand	350		
Jamaica	15			Chile	300		
Benin 15				Cuba	300		
Nicaragua	15			Indonesia	300		
Afghanistan	13			Argentina	250		
Albania	10			Gambia	250		
Azerbaijan	6			Hungary	250		
Mali	6			Poland	250		
Mauritania	6			Israel	225		
Mauritius	6			Slovenia	200		
Nepal	6			Pakistan	162		
Burkina Faso	5			Serbia and Montenegro	100		
Uganda	5			Greece	90		
Iceland	4			Finland	70		
Lebanon	4			Philippines	70		
Cape Verde	2			Bosnia and Herzegovina	50		
Niger	2			Croatia	50		
Slovenia	2			Denmark	50		
Mongolia	1			Guatemala	50		
Somalia	1			Latvia	50		
Ethiopia	1			Ecuador	40		
Silica sand, kt	106,000			New Caledonia	40		
United States	28,500	27	27	Lithuania	30		
Paraguay	10,000	9	36	Estonia	25		
Germany	7,000	7	43	New Zealand	25		
Austria	6,800	6	49	Cameroon	12		
Spain	6,600	6	56	Kenya	12		
France	6,500	6	62	Ethiopia	7		
United Kingdom	4,000	4	65	Jamaica	6		
Italy	3,000	3	68	Ireland	5		
Japan	2,800	3	71	Netherlands	5		
Brazil	2,700	3	73	Portugal	5		
Australia	2,500	2	76	Iceland	4		
Belgium	2,400	2	78	Sillimanite, t	20,000		
South Africa	2,100	2	80	India	12,000	60	60

Adapted from USGS (data for 2000); Harben 2002.

(Table continued next page)

* W = Withheld to avoid disclosing proprietary data.

† Not available.

‡ Rare earth oxides.

Table 5. Distribution of world industrial minerals production by commodity (continued)

Mineral and Country	Production	World Production, %	World Production Cumulative, %	Mineral and Country	Production	World Production, %	World Production Cumulative, %
Sillimanite (continued)				Sweden	100,000	3	86
Zimbabwe	4,000	20	80	Austria	80,000	2	88
China	3,000	15	95	Turkmenistan	70,000	2	90
Australia	1,000	5	100	United Kingdom	70,000	2	92
Soda ash, kt	34,200			Portugal	50,000	1	94
United States	10,200	30	30	Chile	40,000	1	95
China	8,343	24	54	South Africa	30,000	1	95
Russia	2,199	6	61	Finland	30,000	1	96
India	1,500	4	65	Turkey	30,000	1	97
Germany	1,400	4	69	Egypt	25,000	1	98
France	1,000	3	72	Netherlands	20,000	1	98
Italy	1,000	3	75	Chile	15,000		
United Kingdom	1,000	3	78	Brazil	10,000		
Poland	950	3	81	Greece	6,000		
Bulgaria	800	2	83	Hungary	6,000		
Japan	685	2	85	Argentina	5,000		
Romania	550	2	87	Serbia and Montenegro	3,000		
Spain	500	1	88	Macedonia	1,000		
Turkey	500	1	90	Pakistan	1,000		
Ukraine	500	1	91	Strontium, kt	318,000		
Netherlands	400	1	92	Mexico	157,420	50	50
Republic of Korea	310	1	93	Spain	130,000	41	90
Australia	300	1	94	Turkey	25,000	8	98
Canada	300	1	95	Argentina	3,000	1	99
Mexico	290	1	96	Iran	2,000	1	
Kenya	246	1	96	Pakistan	600		
Pakistan	230	1	97	Sulfur, kt	57,200		
Botswana	225	1	98	United States	10,300	18	18
Brazil	200	1	98	Canada	9,900	17	35
Austria	150			Russia	5,900	10	46
Portugal	150			China	5,220	9	55
Taiwan	140			Japan	3,500	6	61
Egypt	50			Venezuela	3,200	6	66
Bosnia and Herzegovina	15			Saudi Arabia	2,400	4	71
Sodium sulfate (natural and synthetic), t	3,668,000			Poland	1,700	3	74
China	800,000	22	22	Kazakhstan	1,500	3	76
United States	491,000	13	35	Iran	1,350	2	79
Spain	250,000	7	42	Mexico	1,310	2	81
Mexico	200,000	5	47	Germany	1,240	2	83
Belgium	200,000	5	53	United Arab Emirates	1,120	2	85
Japan	195,000	5	58	France	1,110	2	87
Canada	150,000	4	62	Chile	1,100	2	89
Iran	150,000	4	66	Finland	850	1	90
Italy	125,000	3	70	Italy	693	1	92
Turkey	100,000	3	73	Australia	689	1	93
Bosnia and Herzegovina	100,000	3	75	Spain	685	1	94
France	100,000	3	78	Kuwait	675	1	95
Germany	100,000	3	81	Netherlands	512	1	96
Spain	100,000	3	83	Republic of Korea	490	1	97
				Uzbekistan	460	1	98

Adapted from USGS (data for 2000); Harben 2002.

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* W = Withheld to avoid disclosing proprietary data.

† Not available.

‡ Rare earth oxides.

Table 5. Distribution of world industrial minerals production by commodity (continued)

Mineral and Country	Production	World Production, %	World Production Cumulative, %	Mineral and Country	Production	World Production, %	World Production Cumulative, %
Sulfur (continued)				Ukraine	576,749	12	70
South Africa	448	1	99	United States	400,000	8	79
Belgium	410	1	99	India	380,000	8	87
Talc (may include pyrophyllite), †	7,244,970			China	185,000	4	91
China	3,500,000	48	48	Egypt	125,000	3	93
United States	851,000	12	60	Malaysia	110,000	2	96
India	460,000	6	66	Vietnam	109,000	2	98
Brazil	452,000	6	73	Brazil	96,000	2	
Finland	360,000	5	78	Titanium concentrates (leucoxene), ‡	27,000		
France	350,000	5	82	Australia	27,000	100	100
Australia	250,000	3	86	Titanium concentrates (rutile), ‡	416,600		
Austria (steatite)	150,000	2	88	United States	W*		
Italy	140,000	2	90	Australia	237,000	57	57
North Korea	120,000	2	92	South Africa	100,000	24	81
Spain	100,000	1	93	Ukraine	58,600	14	95
Russia	100,000	1	94	India	17,000	4	99
Canada	79,000	1	95	Brazil	4,000	1	
Japan	50,000	1	96	Titanium concentrates (titaniferous slag), ‡	2,070,000		
Egypt	40,000	1	97	South Africa	1,120,000	54	54
Norway	27,000			Canada	950,000	46	100
Sweden	26,000			Vermiculite, ‡	512,000		
Iran	20,000			South Africa	208,835	41	41
Morocco	20,000			United States	150,000	29	70
Mexico	19,000			China	40,000	8	78
Republic of Korea	16,000			Russia	25,000	5	83
Colombia	15,000			Brazil	23,000	4	87
Germany	15,000			Zimbabwe	18,935	4	91
Argentina	14,600			Japan	15,000	3	94
Peru	13,000			Australia	12,000	2	96
Macedonia	10,000			Egypt	12,000	2	99
Romania	8,200			India	4,200	1	99
Portugal	8,000			Argentina	2,800	1	
South Africa	5,600			Kenya	165		
Nepal	5,500			Mexico	100		
Turkey	5,000			Zirconium mineral concentrates, ‡	760,000		
United Kingdom	5,000			United States	W		
Chile	3,850			Australia	353,000	46	46
Thailand	2,000			South Africa	270,000	36	82
Hungary	1,200			Ukraine	75,000	10	92
Uruguay	1,000			Brazil	19,500	3	94
Zimbabwe	1,000			India	19,000	3	97
Guatemala	740			China	15,000	2	99
Taiwan	200			Russia	6,500	1	
Zambia	80			Malaysia	2,000		
Titanium concentrates (ilmenite), ‡	4,747,749			Indonesia	250		
Australia	2,156,000	45	45				
Norway	610,000	13	58				

Adapted from USGS (data for 2000); Harben 2002.

* W = Withheld to avoid disclosing proprietary data.

† Not available.

‡ Rare earth oxides.

Table 6. Distribution of world industrial minerals production by country

Country	Mineral	World Distribution	Country	Mineral	World Distribution
Afghanistan	Barite, <i>kt</i>	2,000		Diamond (natural gem), <i>thousand carats</i>	12,014
	Gypsum, <i>kt</i>	3		Diamond (natural industrial)	14,684
	Nitrogen (ammonia), <i>kt</i>	5		<i>thousand carats</i>	
	Salt, <i>kt</i>	13		Diatomite, <i>kt</i>	20
Albania	Chromite, <i>t, gross weight</i>	70,000		Feldspar, <i>kt</i> 2	0,000
	Nitrogen (ammonia), <i>kt</i>	10		Fuller's earth (attapulgitite), <i>t</i>	5,000
	Phosphate rock, <i>kt, gross weight</i>	1		Gypsum, <i>kt</i> 3,800	
	Salt, <i>kt</i>	10		Kaolin (includes ball clay), <i>t</i>	220,000
Algeria	Barite, <i>kt</i> 50,000		M	Lithium (spodumene), <i>t</i>	76,000
	Bentonite, <i>t</i>	22,708		Magnesite, <i>t</i>	349,783
	Diatomite, <i>kt</i>	3		anganese, <i>kt, gross weight</i>	1,614
	Feldspar, <i>kt</i> 3,000			Nitrogen (ammonia), <i>kt</i> 576	
	Fuller's earth, <i>t</i>	3,431		Perlite, <i>t</i>	5,000
	Gypsum, <i>kt</i>	275		Phosphate rock, <i>kt, gross weight</i>	540
	Kaolin, <i>t</i>	11,616		Salt, <i>kt</i> 8,798	
	Nitrogen (ammonia), <i>kt</i> 458			Silica sand, <i>kt</i> 2,500	
	Phosphate rock, <i>kt, gross weight</i>	875		Sillimanite, <i>t</i>	100
	Salt, <i>kt</i> 165			Sillimanite minerals, <i>t</i>	1,000
Angola	Diamond (natural gem), <i>thousand carats</i>	5,400		Soda ash, <i>kt</i> 300	
	Diamond (natural industrial),	600		Sulfur, <i>kt</i> 689	
	<i>thousand carats</i>			Talc, <i>t</i>	250,000
Argentina	Salt, <i>kt</i>	30		Titanium concentrates (ilmenite), <i>t</i>	2,156,000
	Asbestos, <i>kt</i>	350		Titanium concentrates (rutile), <i>t</i>	237,000
	Barite, <i>kt</i>	4,400		Titanium concentrates (leucoxene), <i>t</i>	27,000
	Bentonite, <i>t</i>	150,000		Vermiculite, <i>t</i>	12,000
	Borate minerals, <i>kt</i>	360		Zirconium mineral concentrates, <i>t</i>	353,000
	Diatomite, <i>kt</i>	9	Austria	Graphite, <i>t</i>	12,000
	Feldspar, <i>kt</i>	61,000		Gypsum, <i>kt</i>	1,000
	Fluorspar, <i>kt</i>	7,000		Iron oxide pigments (natural), <i>t</i>	7,000
	Fuller's earth, <i>t</i>	1,500		Kaolin, <i>t</i>	50,000
	Gypsum, <i>kt</i>	514		Magnesite, <i>t</i>	750,000
	Kaolin, <i>t</i>	45,000		Nitrogen (ammonia), <i>kt</i>	500
	Lithium (carbonate), <i>t</i>	1,000		Pumice (trass), <i>t</i>	5,000
	Lithium (spodumene and amblygonite), <i>t</i>	700		Salt, <i>kt</i>	401
	Mica sheet, <i>t</i>	300		Silica sand, <i>kt</i>	6,800
	Mica scrap, <i>t</i>	3,100		Soda ash, <i>kt</i>	150
	Nitrogen (ammonia), <i>kt</i>	199		Sodium sulfate (synthetic), <i>kt</i>	80,000
	Pumice, <i>t</i>	120,000		Talc steatite, <i>t</i>	150,000
	Salt, <i>kt</i>	1,000		Graphite, <i>t</i>	12,000
	Silica sand, <i>kt</i>	250		Gypsum, <i>kt</i>	1,000
	Sodium sulfate (natural), <i>kt</i>	5,000		Iron oxide pigments (natural), <i>t</i>	7,000
	Strontium, <i>kt</i>	3,000		Kaolin, <i>t</i>	50,000
	Talc, <i>t</i>	14,600		Magnesite, <i>t</i>	750,000
	Vermiculite, <i>t</i>	2,800		Nitrogen (ammonia), <i>kt</i>	500
Armenia	Bentonite, <i>t</i>	2,807		Pumice (trass), <i>t</i>	5,000
	Perlite, <i>t</i>	35,000		Salt, <i>kt</i>	401
	Salt, <i>kt</i>	30		Silica sand, <i>kt</i>	6,800
Australia	Antimony, <i>kt</i>	1,800		Soda ash, <i>kt</i>	150
	Barite, <i>kt</i>	20,000		Sodium sulfate (synthetic), <i>kt</i>	80,000
	Bauxite, <i>kt</i>	53,802		Talc steatite, <i>t</i>	150,000
	Bentonite, <i>t</i>	180,000	Azerbaijan	Bromine, <i>kt</i>	2,000
	Chromite <i>t, gross weight</i>	130,000		Gypsum, <i>kt</i>	60

Adapted from USGS (data for 2000); Harben 2002.

* REE = rare earth element.

(Table continued next page)

Table 6. Distribution of world industrial minerals production by country (continued)

Country	Mineral	World Distribution	Country	Mineral	World Distribution
Azerbaijan (continued)	Iodine, <i>t</i>	300		Kaolin, <i>t</i>	1,500,000
	Salt, <i>kt</i>	6		Kyanite, <i>t</i>	600
Bahamas	Salt, <i>kt</i>	900		Lithium (concentrates), <i>t</i>	1,600
Bahrain	Nitrogen (ammonia), <i>kt</i>	350		Magnesite, <i>t</i>	310,000
Bangladesh	Kaolin, <i>t</i>	7,900		Manganese, <i>kt, gross weight</i>	2,000
	Nitrogen (ammonia), <i>kt</i>	1,255		Mica, <i>t</i>	5,000
	Salt (marine salt), <i>kt</i>	350		Nitrogen (ammonia), <i>kt</i>	925
Belarus	Diamond (synthetic), <i>thousand carats</i>	25,000		Phosphate rock, <i>kt, gross weight</i>	4,900
	Nitrogen (ammonia), <i>kt</i>	730		Potash, <i>kt, K₂O equivalent</i>	350
	Potash, <i>kt, K₂O equivalent</i>	3,400		Salt, <i>kt</i>	6,000
	Salt, <i>kt</i>	400		Silica sand, <i>kt</i>	2,700
Belgium	Barite, <i>kt</i>	30,000		Soda ash, <i>kt</i>	200
	Kaolin, <i>t</i>	300,000		Sodium sulfate (synthetic), <i>kt</i>	10,000
	Nitrogen (ammonia), <i>kt</i>	863		Talc (includes pyrophyllite), <i>t</i>	452,000
	Silica sand, <i>kt</i>	2,400		Titanium concentrates (ilmenite), <i>t</i>	96,000
	Sodium sulfate (synthetic), <i>kt</i>	200,000		Titanium concentrates (rutile), <i>t</i>	4,000
	Sulfur, <i>kt</i>	410		Vermiculite, <i>t</i>	23,000
Benin	Salt (marine salt), <i>kt</i>	15		Zirconium mineral concentrates, <i>t</i>	19,500
Bhutan	Gypsum, <i>kt</i>	54	Bulgaria	Asbestos, <i>kt</i>	350
Bolivia	Antimony, <i>kt</i>	2,800		Barite, <i>kt</i>	120,000
	Barite, <i>kt</i>	6,000		Bentonite, <i>t</i>	150,000
	Borate minerals (ulexite), <i>kt</i>	7		Gypsum, <i>kt</i>	180
Bosnia and Herzegovina	Barite, <i>kt</i>	2,000		Kaolin, <i>t</i>	110,000
	Bauxite, <i>kt</i>	75		Nitrogen (ammonia), <i>kt</i>	533
	Bentonite, <i>t</i>	800		Salt, <i>kt</i>	2,500
	Gypsum, <i>kt</i>	30		Silica sand, <i>kt</i>	900
	Kaolin, <i>t</i>	3,000		Soda ash, <i>kt</i>	800
	Nitrogen (ammonia), <i>kt</i>	1	Burkina Faso	Pumice, <i>t</i>	10,000
	Salt, <i>kt</i>	50		Salt, <i>kt</i>	5
	Silica sand, <i>kt</i>	50	Burma	Barite, <i>kt</i>	29,200
	Soda ash, <i>kt</i>	15		Bentonite, <i>t</i>	600
	Sodium sulfate (synthetic), <i>kt</i>	100,000		Chromite, <i>t, gross weight</i>	3,000
Botswana	Diamond (natural gem), <i>thousand carats</i>	19,700		Feldspar, <i>kt</i>	12,000
	Diamond (natural industrial), <i>thousand carats</i>	4,950		Gypsum, <i>kt</i>	484
	Salt, <i>kt</i>	185		Nitrogen (ammonia), <i>kt</i>	78
	Soda ash, <i>kt</i>	225		Salt, <i>kt</i>	35
Brazil	Asbestos, <i>kt</i>	170,000	Burundi	Kaolin, <i>t</i>	800
	Barite, <i>kt</i>	45,000	Cambodia	Salt, <i>kt</i>	40
	Bauxite, <i>kt</i>	14,000	Cameroon	Pumice (pozzolan), <i>t</i>	90,000
	Bentonite, <i>t</i>	275,000		Silica sand, <i>kt</i>	12
	Beryllium minerals, <i>kt</i>	10	Canada	Antimony, <i>kt</i>	364
	Chromite (<i>t, gross weight</i>)	400,000		Asbestos, <i>kt</i>	340,000
	Diamond (natural gem), <i>thousand carats</i>	300		Barite, <i>kt</i>	20,000
	Diamond (natural industrial), <i>thousand carats</i>	600		Diamond (natural gem), <i>thousand carats</i>	2,000
	Diatomite, <i>kt</i>	14		Graphite, <i>t</i>	25,000
	Feldspar, <i>kt</i>	240,000		Gypsum, <i>kt</i>	8,548
	Fluorspar, <i>kt</i>	72,000		Lithium (spodumene), <i>t</i>	22,500
	Graphite, <i>t</i>	56,000		Magnesite, <i>t</i>	180,000
	Gypsum, <i>kt</i>	1,500		Mica, <i>t</i>	17,500
	Iron oxide pigments (natural), <i>t</i>	5,500		Nitrogen (ammonia), <i>kt</i>	4,130
				Potash, <i>kt, K₂O equivalent</i>	8,600
				Salt, <i>kt</i>	11,935

Adapted from USGS (data for 2000); Harben 2002.

* REE = rare earth element.

(Table continued next page)

Table 6. Distribution of world industrial minerals production by country (continued)

Country	Mineral	World Distribution	Country	Mineral	World Distribution
Canada (continued)	Silica sand, <i>kt</i>	1,946		Rare earths, <i>t</i> , REE*	73,000
	Soda ash, <i>kt</i>	300		Salt, <i>kt</i>	31,280
	Sodium sulfate (natural), <i>kt</i>	150,000		Sillimanite minerals, <i>t</i>	3,000
	Sulfur, <i>kt</i>	9,900		Soda ash, <i>kt</i>	8,343
	Talc, <i>t</i>	79,000		Sodium sulfate (natural), <i>kt</i>	800,000
	Titanium concentrates (titaniferous slag), <i>t</i>	950,000		Sulfur, <i>kt</i>	5,220
Cape Verde	Pumice (pozzolan), <i>t</i>	1,000		Talc, <i>t</i>	3,500,000
	Salt, <i>kt</i>	2		Titanium concentrates (ilmenite), <i>t</i>	185,000
Central African Republic	Diamond (natural gem), <i>thousand carats</i>	400		Vermiculite, <i>t</i>	40,000
	Diamond (natural industrial), <i>thousand carats</i>	150		Zirconium mineral concentrates, <i>t</i>	15,000
Chile			Christmas Island	Phosphate rock, <i>kt, gross weight</i>	575
	Barite, <i>kt</i>	900	Colombia	Barite, <i>kt</i>	600
	Bentonite, <i>t</i>	1,314		Diatomite, <i>kt</i>	4
	Borate minerals (ulexite), <i>kt</i>	200		Feldspar, <i>kt</i>	55,000
	Diatomite, <i>kt</i>	15		Gypsum, <i>kt</i>	560
	Feldspar, <i>kt</i>	1,500		Kaolin (includes common clay), <i>t</i>	8,000,000
	Gypsum, <i>kt</i>	890		Magnesite, <i>t</i>	10,500
	Iodine, <i>t</i>	9,100		Nitrogen (ammonia), <i>kt</i>	93
	Iron oxide pigments (natural), <i>t</i>	10,600		Phosphate rock, <i>kt, gross weight</i>	75
	Kaolin, <i>t</i>	6,445		Salt, <i>kt</i>	460
	Lithium (carbonate), <i>t</i>	28,500		Talc (includes pyrophyllite), <i>t</i>	15,000
	Phosphate rock, <i>kt, gross weight</i>	15	Congo (Kinshasa)	Diamond (natural gem), <i>thousand carats</i>	3,500
	Potash, <i>kt, K₂O equivalent</i>	23		Diamond (natural industrial), <i>thousand carats</i>	14,200
	Pumice (pozzolan), <i>t</i>	650,000	Costa Rica	Diatomite, <i>kt</i>	2
	Salt, <i>kt</i>	6,000		Pumice, <i>t</i>	8,000
	Silica sand, <i>kt</i>	300		Salt (marine salt), <i>kt</i>	37
	Sodium sulfate (natural), <i>kt</i>	15,000	Côte d'Ivoire	Diamond (natural gem), <i>thousand carats</i>	200
	Sodium sulfate (synthetic), <i>kt</i>	40,000		Diamond (natural industrial), <i>thousand carats</i>	100
	Sulfur, <i>kt</i>	1,100			10,013
	Talc, <i>t</i>	3,850	Croatia	Bentonite, <i>t</i>	100
China	Antimony, <i>kt</i>	100,000		Gypsum, <i>kt</i>	325
	Asbestos, <i>kt</i>	260,000		Nitrogen (ammonia), <i>kt</i>	20
	Barite, <i>kt</i>	3,500,000		Salt, <i>kt</i>	50
	Bauxite, <i>kt</i>	9,000		Silica sand, <i>kt</i>	40,000
	Borate minerals, <i>kt</i>	105	Cuba	Chromite <i>t, gross weight</i>	130
	Bromine, <i>kt</i>	45,000		Gypsum, <i>kt</i>	135
	Diamond (natural gem), <i>thousand carats</i>	230		Nitrogen (ammonia), <i>kt</i>	180
	Diamond (natural industrial), <i>thousand carats</i>	920		Salt, <i>kt</i>	300
	Diamond (synthetic), <i>thousand carats</i>	16,800		Silica sand, <i>kt</i>	126,313
	Diatomite, <i>kt</i>	350	Cyprus	Bentonite, <i>t</i>	138
	Fluorspar, <i>kt</i>	2,450,000		Gypsum, <i>kt</i>	12,258
	Graphite, <i>t</i>	220,000		Iron oxide pigments (natural umber), <i>t</i>	150,000
	Gypsum, <i>kt</i>	6,800	Czech Republic	Bentonite, <i>t</i>	25,000
	Iodine, <i>t</i>	500		Graphite, <i>t</i>	250
	Lithium (carbonate), <i>t</i>	13,000		Gypsum, <i>kt</i>	5,200,000
	Magnesite, <i>t</i>	2,500,000		Kaolin, <i>t</i>	246
	Manganese, <i>kt, gross weight</i>	4,000		Nitrogen (ammonia), <i>kt</i>	2,000
	Nitrogen (ammonia), <i>kt</i>	28,000		Silica sand, <i>kt</i>	2,000
	Phosphate rock, <i>kt, gross weight</i>	19,400	Denmark	Diatomite, <i>kt</i>	2,500
	Potash, <i>kt, K₂O equivalent</i>	250		Kaolin, <i>t</i>	2
				Nitrogen (ammonia), <i>kt</i>	2

Adapted from USGS (data for 2000); Harben 2002.

* REE = rare earth element.

(Table continued next page)

Table 6. Distribution of world industrial minerals production by country (continued)

Country	Mineral	World Distribution	Country	Mineral	World Distribution
Denmark (continued)	Salt, <i>kt</i> 605			Fluorspar, <i>kt</i> 10	0,000
	Silica sand, <i>kt</i> 50			Gypsum, <i>kt</i> 4,500	
Dominican Republic	Gypsum, <i>kt</i>	90		Iron oxide pigments (natural), <i>t</i>	1,000
	Pumice and volcanic ash, <i>t</i>	100,000		Kaolin, <i>t</i>	300,000
	Salt, <i>kt</i> 62			Mica, <i>t</i>	10,000
Ecuador	Feldspar, <i>kt</i> 55,000			Nitrogen (ammonia), <i>kt</i> 1,700	
	Gypsum, <i>kt</i>	2	P	otash, <i>kt</i> , <i>K₂O equivalent</i>	321
	Kaolin, <i>t</i>	7,000		Pumice (pozzolan and lapilli), <i>t</i>	450,000
	Pumice, <i>t</i>	350,000		Salt, <i>kt</i> 7,000	
	Salt, <i>kt</i> 90			Silica sand, <i>kt</i> 6,500	
	Silica sand, <i>kt</i> 40			Soda ash, <i>kt</i> 1,000	
Egypt	Asbestos, <i>kt</i>	2,000		Sodium sulfate (synthetic), <i>kt</i> 10	0,000
	Bentonite, <i>t</i>	50,000		Sulfur, <i>kt</i> 1,110	
	Feldspar, <i>kt</i> 330,000			Talc, <i>t</i>	350,000
	Fluorspar, <i>kt</i> 500		Gabon	Manganese, <i>kt</i> , gross weight	1,743
	Gypsum, <i>kt</i> 2,000		Gambia	Silica sand, <i>kt</i> 250	
	Kaolin, <i>t</i>	290,000	Georgia	Barite, <i>kt</i> 1	5,000
	Nitrogen (ammonia), <i>kt</i> 1,511			Bentonite, <i>t</i>	12,000
	Phosphate rock, <i>kt</i> , gross weight	1,020		Nitrogen (ammonia), <i>kt</i>	1
	Salt, <i>kt</i> 2,400		Germany	Barite, <i>kt</i> 12	0,000
	Silica sand, <i>kt</i> 600			Bentonite, <i>t</i>	500,000
	Soda ash, <i>kt</i>	50		Borate minerals (borax), <i>kt</i>	1
	Sodium sulfate (natural), <i>kt</i> 25,000			Feldspar, <i>kt</i> 46	0,000
	Talc (includes pyrophyllite), <i>t</i>	40,000		Fluorspar, <i>kt</i> 3	0,000
	Titanium concentrates (ilmenite), <i>t</i>	125,000		Fuller's earth, <i>t</i>	500,000
	Vermiculite, <i>t</i>	12,000		Graphite, <i>t</i>	1,000
El Salvador	Gypsum, <i>kt</i>	6	G	ypsum, <i>kt</i> 2,500	
	Salt (marine salt), <i>kt</i>	90		Iron oxide pigments (natural), <i>t</i>	4,000
Eritrea	Kaolin, <i>t</i>	393		Kaolin, <i>t</i>	1,800,000
	Salt, <i>kt</i> 100			Nitrogen (ammonia), <i>kt</i> 2,473	
	Silica sand, <i>kt</i> 1,000			Potash, <i>kt</i> , <i>K₂O equivalent</i>	3,409
Estonia	Nitrogen (ammonia), <i>kt</i> 128			Pumice, <i>t</i>	600,000
	Silica sand, <i>kt</i> 25			Salt, <i>kt</i> 1	5,700
Ethiopia	Gypsum, <i>kt</i> 108			Silica sand, <i>kt</i> 7,000	
	Kaolin, <i>t</i>	1,654		Soda ash, <i>kt</i> 1,400	
	Pumice, <i>t</i>	300,000		Sodium sulfate (synthetic), <i>kt</i> 10	0,000
	Salt (rock salt), <i>kt</i>	1		Sulfur, <i>kt</i> 1,240	
	Silica sand, <i>kt</i>	7	T	alc, <i>t</i>	15,000
Finland	Chromite, <i>t</i> , gross weight	640,000	Ghana	Bauxite, <i>kt</i> 504	
	Feldspar, <i>kt</i>	40,000		Diamond (natural gem), <i>thousand carats</i>	178
	Nitrogen (ammonia), <i>kt</i>	6		Diamond (natural industrial), <i>thousand carats</i>	712
	Phosphate rock, <i>kt</i> , gross weight	700		Manganese, <i>kt</i> , gross weight	896
	Silica sand, <i>kt</i> 70			Salt, <i>kt</i> 50	
	Sodium sulfate (synthetic), <i>kt</i> 30,000		Greece	Asbestos, <i>kt</i> 5	0,000
	Sulfur, <i>kt</i> 850			Barite, <i>kt</i> 800	
	Talc, <i>t</i>	360,000		Bauxite, <i>kt</i> 1,991	
France	Andalusite, <i>t</i>	65,000		Bentonite, <i>t</i>	950,000
	Barite, <i>kt</i> 75,000			Chromite, <i>t</i> , gross weight	12,000
	Bromine, <i>kt</i> 2,000			Diamond (synthetic), <i>thousand carats</i>	750
	Diamond (synthetic), <i>thousand carats</i>	3,000		Feldspar, <i>kt</i> 6	0,000
	Diatomite, <i>kt</i> 75			Gypsum, <i>kt</i> 600	
	Feldspar, <i>kt</i> 600,000				

Adapted from USGS (data for 2000); Harben 2002.

* REE = rare earth element.

(Table continued next page)

Table 6. Distribution of world industrial minerals production by country (continued)

Country	Mineral	World Distribution	Country	Mineral	World Distribution
Greece (continued)	Kaolin, <i>t</i>	60,000		Iron oxide pigments (natural ocher), <i>t</i>	365,000
	Magnesite, <i>t</i>	650,000		Kaolin, <i>t</i>	690,000
	Nitrogen (ammonia), <i>kt</i> 121			Kyanite, <i>t</i>	5,000
	Perlite, <i>t</i>	500,000		Magnesite, <i>t</i>	365,000
	Pumice, <i>t</i>	850,000		Manganese, <i>kt, gross weight</i>	1,550
	Pumice (pozzolan), <i>t</i>	750,000		Mica, <i>t</i>	1,500
	Salt, <i>kt</i>	150		Mica scrap and waste, <i>t</i>	950
	Silica sand, <i>kt</i>	90		Nitrogen (as ammonia), <i>kt</i> 1	0,148
	Sodium sulfate (synthetic), <i>kt</i> 6,000			Phosphate rock, <i>kt, gross weight</i>	1,720
Guadeloupe	Pumice, <i>t</i>	210,000		Rare earths (monazite concentrate), <i>t, gross weight</i>	5,000
Guatemala	Salt, <i>kt</i> 200			Rare earths, <i>t, REE*</i>	2,700
	Antimony, <i>kt</i> 450			Salt, <i>kt</i> 1	4,453
	Barite, <i>kt</i> 2,800			Silica sand, <i>kt</i> 1,350	
	Bentonite, <i>t</i>	3,800		Sillimanite, <i>t</i>	12,000
	Feldspar, <i>kt</i> 11,000			Soda ash, <i>kt</i> 1,500	
	Gypsum, <i>kt</i> 29			Talc, <i>t</i>	460,000
	Kaolin, <i>t</i>	100		Titanium concentrates (ilmenite), <i>t</i>	380,000
	Pumice, <i>t</i>	6,300		Titanium concentrates (rutile), <i>t</i>	17,000
	Salt, <i>kt</i>	49		Vermiculite, <i>t</i>	4,200
Guinea	Silica sand, <i>kt</i> 50		Indonesia	Zirconium mineral concentrates, <i>t</i>	19,000
	Talc, <i>t</i>	740		Bauxite, <i>kt</i> 1,200	
	Bauxite, <i>kt</i> 15,000			Bentonite, <i>t</i>	6,000
	Diamond (natural gem), <i>thousand carats</i>	410		Chromite, <i>t, gross weight</i>	6,400
	Diamond (natural industrial), <i>thousand carats</i>	140		Gypsum, <i>kt</i>	5
	Salt, <i>kt</i> 15			Iodine, <i>t</i>	70
	Bauxite, <i>kt</i> 2,404			Kaolin, <i>t</i>	22,000
Guyana	Gypsum, <i>kt</i>	30		Nitrogen (as ammonia), <i>kt</i> 4,000	
Honduras	Salt, <i>kt</i> 25			Phosphate rock, <i>kt, gross weight</i>	1
Hungary	Bauxite, <i>kt</i> 1,047		Iran	Salt, <i>kt</i> 680	
	Bentonite, <i>t</i>	15,000		Silica sand, <i>kt</i> 300	
	Gypsum, <i>kt</i>	180		Zirconium mineral concentrates, <i>t</i>	250
	Kaolin, <i>t</i>	7,000		Asbestos, <i>kt</i> 2,000	
	Nitrogen (as ammonia), <i>kt</i> 352			Barite, <i>kt</i> 18	5,000
	Perlite, <i>t</i>	150,000		Bauxite, <i>kt</i> 1,000	
	Silica sand, <i>kt</i> 250			Bentonite, <i>t</i>	70,000
	Sodium sulfate (synthetic), <i>kt</i>	6,000		Borate minerals (borax), <i>kt</i>	4
	Talc, <i>t</i>	1,200		Chromite, <i>t, gross weight</i>	310,000
Iceland	Diatomite, <i>kt</i> 26		G	Diatomite, <i>kt</i>	5
	Nitrogen (as ammonia), <i>kt</i> 7			Feldspar, <i>kt</i> 24	0,000
	Pumice and scoria, <i>t</i>	25,000		Fluorspar, <i>kt</i> 2	0,000
	Salt, <i>kt</i>	4		Gypsum, <i>kt</i> 1	1,000
	Silica sand, <i>kt</i>	4		Iron oxide pigments (natural), <i>t</i>	13,500
	Asbestos, <i>kt</i> 21,000			Kaolin, <i>t</i>	800,000
	Barite, <i>kt</i> 550,000			Magnesite, <i>t</i>	141,000
	Bauxite, <i>kt</i> 7,366			Mica, <i>t</i>	2,000
	Bromine, <i>kt</i>	1,500		Nitrogen (as ammonia), <i>kt</i> 965	
India	Chromite, <i>t, gross weight</i>	1,500,000		Perlite, <i>t</i>	15,000
	Feldspar, <i>kt</i> 110,000			Pumice, <i>t</i>	150,000
	Fluorspar, <i>kt</i> 850			Salt, <i>kt</i> 1,600	
	Graphite, <i>t</i>	140,000		Silica sand, <i>kt</i> 1,000	
	Gypsum, <i>kt</i>	2,210		Sodium sulfate (natural), <i>kt</i> 15	0,000

Adapted from USGS (data for 2000); Harben 2002.

* REE = rare earth element.

(Table continued next page)

Table 6. Distribution of world industrial minerals production by country (continued)

Country	Mineral	World Distribution	Country	Mineral	World Distribution
Iran (continued)	Strontium, <i>kt</i> 2,000			Perlite, <i>t</i>	250,000
	Sulfur, <i>kt</i> 1,350			Salt, <i>kt</i> 1,300	
	Talc, <i>t</i>	20,000		Silica sand, <i>kt</i> 2,800	
Iraq	Gypsum, <i>kt</i> 80			Soda ash, <i>kt</i> 685	
	Nitrogen (as ammonia), <i>kt</i>	220		Sodium sulfate (synthetic), <i>kt</i> 19	5,000
	Phosphate rock, <i>kt, gross weight</i>	1,000		Sulfur, <i>kt</i> 3,500	
	Salt, <i>kt</i> 300			Talc, <i>t</i>	50,000
Ireland	Diamond (synthetic), <i>thousand carats</i>	60,000		Vermiculite, <i>t</i>	15,000
	Gypsum, <i>kt</i> 450		Jordan	Gypsum, <i>kt</i> 175	
	Nitrogen (as ammonia), <i>kt</i> 410			Kaolin, <i>t</i>	36,795
Israel	Silica sand, <i>kt</i>	5		Phosphate rock, <i>kt, gross weight</i>	5,506
	Bromine, <i>kt</i> 185,000			Potash, <i>kt, K₂O equivalent</i>	1,110
	Gypsum, <i>kt</i> 46			Salt, <i>kt</i> 546	
	Kaolin, <i>t</i>	26,700	Kazakhstan	Asbestos, <i>kt</i> 12	5,000
	Phosphate rock, <i>kt, gross weight</i>	4,110		Barite, <i>kt</i> 1	4,000
	Potash, <i>kt, K₂O equivalent</i>	1,710		Bauxite, <i>kt</i> 3,727	
	Salt, <i>kt</i> 863			Beryllium minerals, <i>kt</i> 100	
	Silica sand, <i>kt</i> 225			Borate minerals, <i>kt</i> 30	
	Barite, <i>kt</i> 25,000			Chromite, <i>t, gross weight</i>	2,067,000
	Bentonite, <i>t</i>	500,000		Kaolin, <i>t</i>	70,000
	Bromine, <i>kt</i> 300			Manganese, <i>kt, gross weight</i>	1,136
	Diatomite, <i>kt</i> 25			Phosphate rock, <i>kt, gross weight</i>	1,000
	Feldspar, <i>kt</i> 2,600,000			Sulfur, <i>kt</i> 1,500	
	Fluorspar, <i>kt</i> 65,000		Kenya	Barite, <i>kt</i> 10	
	Fuller's earth, <i>t</i>	30,000		Feldspar, <i>kt</i> 100	
	Gypsum, <i>kt</i> 1,300			Fluorspar, <i>kt</i> 9	0,000
	Iron oxide pigments (natural), <i>t</i>	500		Gypsum, <i>kt</i>	1
	Kaolin (kaolinitic earth), <i>t</i>	10,000		Kaolin, <i>t</i>	500
	Nitrogen (as ammonia), <i>kt</i> 408			Silica sand, <i>kt</i> 12	
	Perlite, <i>t</i>	60,000		Soda ash, <i>kt</i> 246	
	Pumice and pumiceous lapilli, <i>t</i>	600,000		Vermiculite, <i>t</i>	165
	Pumice (pozzolan), <i>t</i>	4,000,000		Salt, <i>kt</i> 45	
	Salt, <i>kt</i> 3,600		North Korea	Barite, <i>kt</i> 7	0,000
	Silica sand, <i>kt</i> 3,000			Fluorspar, <i>kt</i> 2	5,000
	Soda ash, <i>kt</i> 1,000			Graphite, <i>t</i>	25,000
	Sodium sulfate (synthetic), <i>kt</i> 125,000			Magnesite, <i>t</i>	1,000,000
	Sulfur, <i>kt</i>	693		Nitrogen (as ammonia), <i>kt</i> 450	
	Talc, <i>t</i>	140,000		Phosphate rock, <i>kt, gross weight</i>	350
				Salt, <i>kt</i> 500	
Jamaica	Bauxite, <i>kt</i> 11,127			Talc, <i>t</i>	120,000
	Gypsum, <i>kt</i> 240		Korea, Republic of	Diatomite, <i>kt</i> 32	
	Salt, <i>kt</i> 15			Feldspar, <i>kt</i> 25	0,000
	Silica sand, <i>kt</i> 6			Graphite, <i>t</i>	60
	Asbestos, <i>kt</i> 18,000			Kaolin, <i>t</i>	2,098,499
	Bentonite, <i>t</i>	445,115		Mica, <i>t</i>	30,000
	Bromine, <i>kt</i> 20,000			Nitrogen (as ammonia), <i>kt</i> 400	
	Diamond (synthetic), <i>thousand carats</i>	33,000		Salt, <i>kt</i> 800	
	Diatomite, <i>kt</i> 190			Silica sand, <i>kt</i> 1,300	
	Feldspar, <i>kt</i> 52,000			Soda ash, <i>kt</i> 310	
	Gypsum, <i>kt</i> 5,600			Sulfur, <i>kt</i> 490	
	Iodine, <i>t</i>	6,100		Talc, <i>t</i>	16,000
	Kaolin, <i>t</i>	26,000	Kuwait	Nitrogen (as ammonia), <i>kt</i> 410	
	Nitrogen (as ammonia), <i>kt</i> 1,405				

Adapted from USGS (data for 2000); Harben 2002.

* REE = rare earth element.

(Table continued next page)

Table 6. Distribution of world industrial minerals production by country (continued)

Country	Mineral	World Distribution	Country	Mineral	World Distribution
Kuwait (continued)	Salt, kt 100			Barite, kt 12	7,688
	Sulfur, kt 675			Bentonite, t	269,730
Kyrgyzstan	Antimony, kt 150			Diatomite, kt 75	
	Fluorspar, kt 3,000			Feldspar, kt 33	4,439
Laos	Barite, kt 9,000			Fluorspar, kt 63	5,000
	Gypsum, kt 154			Fuller's earth, t	51,685
	Salt (rock salt), kt 40			Graphite, t	30,330
Latvia	Gypsum, kt 122			Gypsum, kt 7,000	
	Silica sand, kt 50			Kaolin, t	532,268
Lebanon	Gypsum, kt	3	M	agnesite, t	335
	Salt, kt	4	M	anganese, kt, gross weight	418
Liberia	Diamond (natural gem), thousand carats	120		Mica, t	1,058
	Diamond (natural industrial), thousand carats	80		Nitrogen (as ammonia), kt 701	
				Perlite, t	67,001
Libya	Gypsum, kt 175			Phosphate rock, kt, gross weight	1,052
	Nitrogen (as ammonia), kt 552			Salt, kt 8,884	
	Salt, kt 40			Silica sand, kt 1,800	
Lithuania	Nitrogen (as ammonia), kt 420			Soda ash, kt 290	
	Silica sand, kt	30		Sodium sulfate (natural), kt 20	0,000
Macedonia	Bentonite, t	30,000		Strontium, kt 15	7,420
	Chromite, t, gross weight	5,000		Sulfur, kt 1,310	
	Diatomite, kt	5	T	alc, t	19,000
	Feldspar, kt 10,000			Vermiculite, t	100
	Gypsum, kt 25		Moldova	Gypsum, kt 14	
	Pumice (volcanic tuff), t	60,000	Mongolia	Fluorspar, kt 19	8,843
	Sodium sulfate (synthetic), kt 1,000			Gypsum, kt 25	
	Talc, t	10,000		Salt, kt	1
Madagascar	Beryllium minerals, kt 30		Morocco	Antimony, kt 150	
	Chromite, t, gross weight	100,000		Barite, kt 35	0,000
	Graphite, t	13,000		Bentonite, t	21,352
	Kaolin, t	115		Feldspar, kt 5,000	
	Mica (phlogopite), t	491		Fluorspar, kt 10	0,000
	Salt, kt	25		Fuller's earth (smectite), t	30,665
Malaysia	Barite, kt 13,500			Gypsum, kt 450	
	Bauxite, kt 123			Phosphate rock, kt, gross weight	21,568
	Kaolin, t	225,139		Salt, kt 150	
	Mica, t	3,700		Talc, t	20,000
	Nitrogen (as ammonia), kt 605		Mozambique	Bauxite, kt	8
	Rare earths (monazite concentrate), t, gross weight	1,000		Bentonite, t	16,144
	Rare earths, t, REE*	450		Salt (marine salt), kt 60	
	Silica sand, kt	500	Namibia	Diamond (natural gem), thousand carats	1,520
	Titanium concentrates (ilmenite), t	110,000		Diamond (natural industrial), thousand carats	80
	Zirconium mineral concentrates, t	2,000		Fluorspar, kt 5	8,000
Mali	Gypsum, kt	1	G	ypsum, kt	1
	Salt, kt	6		Salt marine alt), kt 510	(s
Martinique	Pumice, t	130,000	Nauru	Phosphate rock, kt, gross weight	500
	Salt, kt 200		Nepal	Salt, kt	6
Mauritania	Gypsum, kt 100			Talc, t	5,500
	Salt, kt	6	Netherlands	Nitrogen (as ammonia), kt 2,543	
Mauritius	Salt, kt	6	S	alt, kt 5,000	
Mexico	Antimony, kt 52			Silica sand, kt	5

Adapted from USGS (data for 2000); Harben 2002.

* REE = rare earth element.

(Table continued next page)

Table 6. Distribution of world industrial minerals production by country (continued)

Country	Mineral	World Distribution	Country	Mineral	World Distribution
Netherlands (continued)	Soda ash, <i>kt</i> 400			Bentonite, <i>t</i>	21,059
	Sodium sulfate (natural), <i>kt</i> 20,000			Borate minerals, <i>kt</i> 40	
	Sodium sulfate (synthetic), <i>kt</i> 15,000			Diatomite, <i>kt</i> 35	
	Sulfur, <i>kt</i> 512			Feldspar, <i>kt</i> 5,600	
Netherlands Antilles	Salt, <i>kt</i> 500			Gypsum, <i>kt</i> 52	
New Caledonia	Silica sand, <i>kt</i> 40			Kaolin, <i>t</i>	6,165
New Zealand	Bentonite, <i>t</i>	10,000		Mica, <i>t</i>	100
	Kaolin, <i>t</i>	25,000		Phosphate rock, <i>kt, gross weight</i>	104
	Nitrogen (as ammonia), <i>kt</i> 105			Salt, <i>kt</i> 80	
	Pumice, <i>t</i>	500,000		Silica sand, <i>kt</i> 1,600	
	Salt, <i>kt</i> 60			Talc, <i>t</i>	13,000
	Silica sand, <i>kt</i> 25		Philippines	Bentonite, <i>t</i>	2,000
Nicaragua	Gypsum, <i>kt</i> 23			Chromite, <i>t, gross weight</i>	15,000
	Salt (marine salt), <i>kt</i> 15			Feldspar, <i>kt</i> 2	5,000
Niger	Gypsum, <i>kt</i>	2	M	agnesite, <i>t</i>	700
	Salt, <i>kt</i>	2	P	erlite, <i>t</i>	10,000
Nigeria	Barite, <i>kt</i> 5,000			Phosphate rock, <i>kt, gross weight</i>	100
	Feldspar, <i>kt</i>	600		Salt (marine salt), <i>kt</i> 705	
	Gypsum, <i>kt</i> 300			Silica sand, <i>kt</i> 70	
	Kaolin, <i>t</i>	110,000	Poland	Bentonite, <i>t</i>	6,000
Norway	Feldspar, <i>kt</i> 75,000			Diatomite, <i>kt</i>	2
	Graphite, <i>t</i>	2,500		Feldspar, <i>kt</i> 5	0,000
	Nitrogen (as ammonia), <i>kt</i> 334			Gypsum, <i>kt</i> 1,700	
	Silica sand, <i>kt</i> 1,000			Kaolin, <i>t</i>	99,382
	Talc, <i>t</i>	27,000		Nitrogen (as ammonia), <i>kt</i> 1,862	
	Titanium concentrates (ilmenite), <i>t</i>	610,000		Salt, <i>kt</i> 4,200	
Oman	Chromite, <i>t, gross weight</i>	15,110		Silica sand, <i>kt</i> 250	
Pakistan	Barite, <i>kt</i> 21,234			Soda ash, <i>kt</i> 950	
	Bauxite, <i>kt</i>	9	S	ulfur, <i>kt</i> 1,700	
	Bentonite, <i>t</i>	27,700	Portugal	Beryllium minerals, <i>kt</i>	4
	Chromite, <i>t, gross weight</i>	26,643		Diatomite, <i>kt</i>	2
	Feldspar, <i>kt</i> 32,000			Feldspar, <i>kt</i> 12	0,000
	Fluorspar, <i>kt</i> 700			Gypsum, <i>kt</i> 500	
	Fuller's earth, <i>t</i>	15,288		Kaolin, <i>t</i>	175,000
	Gypsum, <i>kt</i> 377			Lithium (lepidolite), <i>t</i>	7,000
	Iron oxide pigments (natural ocher), <i>t</i>	4,700		Nitrogen (as ammonia), <i>kt</i> 246	
	Kaolin, <i>t</i>	49,574		Salt (rock salt), <i>kt</i> 600	
	Magnesite, <i>t</i>	3,100		Silica sand, <i>kt</i>	5
	Nitrogen (as ammonia), <i>kt</i> 1,884			Soda ash, <i>kt</i> 150	
	Phosphate rock, <i>kt, gross weight</i>	11		Sodium sulfate (synthetic), <i>kt</i> 5	0,000
	Salt, <i>kt</i> 1,333			Talc, <i>t</i>	8,000
	Silica sand, <i>kt</i> 162		Qatar	Nitrogen (as ammonia), <i>kt</i> 1,097	
	Soda ash, <i>kt</i> 230		Romania	Barite, <i>kt</i> 1	5,000
	Sodium sulfate (synthetic), <i>kt</i> 1,000			Bentonite, <i>t</i>	35,789
	Strontium, <i>kt</i> 600			Diatomite, <i>kt</i> 30	
	Salt (marine salt), <i>kt</i> 23			Feldspar, <i>kt</i> 3	5,000
Panama	Gypsum, <i>kt</i> 4			Fluorspar, <i>kt</i> 1	5,000
Paraguay	Iron oxide pigments (natural ocher), <i>t</i>	300		Graphite, <i>t</i>	1,500
	Kaolin, <i>t</i>	66,500		Gypsum, <i>kt</i> 75	
	Silica sand, <i>kt</i> 10,000			Kaolin, <i>t</i>	19,007
Peru	Antimony, <i>kt</i>	460		Nitrogen (as ammonia), <i>kt</i> 1,016	
	Barite, <i>kt</i> 11,403			Salt, <i>kt</i> 2,070	

Adapted from USGS (data for 2000); Harben 2002.

* REE = rare earth element.

(Table continued next page)

Table 6. Distribution of world industrial minerals production by country (continued)

Country	Mineral	World Distribution	Country	Mineral	World Distribution
Romania (continued)	Soda ash, <i>kt</i> 550		Sierra Leone	Diamond (natural gem), <i>thousand carats</i>	450
	Talc, <i>t</i>	8,200		Diamond (natural industrial), <i>thousand carats</i>	150
Russia	Antimony, <i>kt</i> 4,500		Slovakia	Gypsum, <i>kt</i> 120	
	Asbestos, <i>kt</i> 750,000			Barite, <i>kt</i> 1	5,000
	Barite, <i>kt</i> 60,000			Kaolin, <i>t</i>	25,000
	Bauxite, <i>kt</i> 4,200			Magnesite, <i>t</i>	850,000
	Beryllium minerals, <i>kt</i> 1,000			Nitrogen (as ammonia), <i>kt</i> 271	
	Borate minerals, <i>kt</i>	1,000		Perlite, <i>t</i>	20,000
	Chromite (<i>t</i> , gross weight)	100,000		Salt, <i>kt</i> 100	
	Diamond (natural gem), <i>thousand carats</i>	11,600	Slovenia	Gypsum, <i>kt</i> 10	
	Diamond (natural industrial), <i>thousand carats</i>	11,600		Kaolin, <i>t</i>	14,000
	Diamond (synthetic), <i>thousand carats</i>	80,000		Pumice (volcanic tuff), <i>t</i>	40,000
	Feldspar, <i>kt</i> 45,000			Salt, <i>kt</i>	2
	Fluorspar, <i>kt</i> 160,000			Silica sand, <i>kt</i> 200	
	Graphite, <i>t</i>	6,000	Somalia	Gypsum, <i>kt</i>	2
	Gypsum, <i>kt</i> 700			Salt, <i>kt</i>	1
	Iodine, <i>t</i>	300		Silica sand, <i>kt</i> 100	
	Kaolin, <i>t</i>	45,000		Sodium sulfate (synthetic), <i>kt</i> 3,000	
	Lithium, <i>t</i>	2,000	South Africa	Andalusite, <i>t</i>	185,055
	Magnesite, <i>t</i>	1,000,000		Antimony, <i>kt</i> 5,000	
	Mica, <i>t</i>	100,000		Asbestos, <i>kt</i> 1	8,909
	Nitrogen (as ammonia), <i>kt</i> 8,735			Barite, <i>kt</i> 1,628	
	Phosphate rock, <i>kt</i> , gross weight	11,100		Bentonite, <i>t</i>	85,187
	Potash, <i>kt</i> , K ₂ O equivalent	3,700		Chromite, <i>t</i> , gross weight	6,620,754
	Salt, <i>kt</i>	3,200		Diamond (natural gem), <i>thousand carats</i>	4,300
	Soda ash, <i>kt</i>	2,199		Diamond (natural industrial), <i>thousand carats</i>	6,480
	Sulfur, <i>kt</i> 5,900			Feldspar, <i>kt</i>	66,774
	Talc, <i>t</i>	100,000		Fluorspar, <i>kt</i>	212,355
	Vermiculite, <i>t</i>	25,000		Fuller's earth (attapulgit), <i>t</i>	7,337
	Zirconium mineral concentrates, <i>t</i>	6,500		Gypsum, <i>kt</i> 413	
Saudi Arabia	Barite, <i>kt</i> 8,000			Iron oxide pigments (natural), <i>t</i>	569
	Gypsum, <i>kt</i>	350		Kaolin, <i>t</i>	98,897
	Nitrogen (as ammonia), <i>kt</i> 1,743			Magnesite, <i>t</i>	74,000
	Salt, <i>kt</i> 140			Manganese, <i>kt</i> , gross weight	3,635
	Sulfur, <i>kt</i> 2,400			Mica (ground and scrap), <i>t</i>	707
Senegal	Fuller's earth (attapulgit), <i>t</i>	80,000		Nitrogen (as ammonia), <i>kt</i> 560	
	Phosphate rock, <i>kt</i> , gross weight	1,800		Perlite, <i>t</i>	400
	Salt, <i>kt</i> 350			Phosphate rock, <i>kt</i> , gross weight	2,778
Serbia and Montenegro	Asbestos, <i>kt</i> 550			Salt, <i>kt</i> 346	
	Bauxite, <i>kt</i> 630			Silica sand, <i>kt</i> 2,100	
	Bentonite, <i>t</i>	75		Sodium sulfate (natural), <i>kt</i>	30,000
	Feldspar, <i>kt</i>	3,000		Sulfur, <i>kt</i> 448	
	Gypsum, <i>kt</i> 15			Talc, <i>t</i>	5,600
	Kaolin, <i>t</i>	44,000		Titanium concentrates (rutile), <i>t</i>	100,000
	Magnesite, <i>t</i>	40,000		Titanium concentrates (titaniferous slag), <i>t</i>	1,120,000
	Mica, <i>t</i>	100		Vermiculite, <i>t</i>	208,835
	Nitrogen (as ammonia), <i>kt</i> 100			Zirconium mineral concentrates, <i>t</i>	270,000
	Pumice (volcanic tuff), <i>t</i>	70,000	Spain	Andalusite, <i>t</i>	2,500
	Salt, <i>kt</i>	78		Barite, <i>kt</i> 2	6,000
	Silica sand, <i>kt</i> 100				
	Sodium sulfate (synthetic), <i>kt</i> 3,000				

Adapted from USGS (data for 2000); Harben 2002.

* REE = rare earth element.

(Table continued next page)

Table 6. Distribution of world industrial minerals production by country (continued)

Country	Mineral	World Distribution	Country	Mineral	World Distribution
Spain (continued)	Bentonite, <i>t</i>	150,000	Taiwan	Kaolin, <i>t</i>	68,000
	Bromine, <i>kt</i> 100			Mica, <i>t</i>	7,000
	Diatomite, <i>kt</i>	35		Nitrogen (as ammonia), <i>kt</i> 11	
	Feldspar, <i>kt</i>	425,000		Salt (marine salt), <i>kt</i> 80	
	Fluorspar, <i>kt</i> 125,000		Tajikistan	Soda ash, <i>kt</i> 140	
	Fuller's earth (attapulgate), <i>t</i>	90,000		Talc, <i>t</i>	200
	Gypsum, <i>kt</i> 7,500			Antimony, <i>kt</i> 2,000	
	Iron oxide pigments (natural ochre), <i>t</i>	7,000		Fluorspar, <i>kt</i> 9,000	
	Iron oxide pigments (natural red iron oxide), <i>t</i>	15,000	Tanzania	Gypsum, <i>kt</i> 35	
	Kaolin, <i>t</i>	365,000		Nitrogen (as ammonia), <i>kt</i>	1
	Magnesite, <i>t</i>	500,000		Bentonite, <i>t</i>	75
	Mica, <i>t</i>	2,500		Gypsum, <i>kt</i> 21	
	Nitrogen (as ammonia), <i>kt</i> 442		Thailand	Phosphate rock, <i>kt, gross weight</i>	2
	Potash, <i>kt, K₂O equivalent</i>	522		Salt, <i>kt</i> 36	
	Pumice, <i>t</i>	600,000		Antimony, <i>kt</i> 84	
	Salt, <i>kt</i> 3,200			Barite, <i>kt</i> 4	9,220
	Silica sand, <i>kt</i> 6,600			Feldspar, <i>kt</i> 54	2,991
	Soda ash, <i>kt</i> 500			Fluorspar, <i>kt</i> 4,745	
	Sodium sulfate (natural), <i>kt</i> 250,000			Gypsum, <i>kt</i> 5,830	
	Sodium sulfate (synthetic), <i>kt</i> 100,000			Kaolin, <i>t</i>	201,226
	Strontium, <i>kt</i> 130,000			Phosphate rock, <i>kt, gross weight</i>	3
	Sulfur, <i>kt</i> 685			Salt, <i>kt</i> 892	
	Talc (steatite), <i>t</i>	100,000		Silica sand, <i>kt</i> 350	
Sri Lanka	Feldspar, <i>kt</i> 26,500			Talc, <i>t</i>	2,000
	Graphite, <i>t</i>	4,600	Togo	Phosphate rock, <i>kt, gross weight</i>	1,370
	Kaolin, <i>t</i>	12,230	Trinidad and Tobago	Nitrogen (as ammonia), <i>kt</i> 2,686	
	Mica (scrap), <i>t</i>	1,500	Tunisia	Barite, <i>kt</i> 3,702	
	Phosphate rock, <i>kt, gross weight</i>	32		Gypsum, <i>kt</i> 100	
	Rare earths (monazite concentrate), <i>t, gross weight</i>	200		Phosphate rock, <i>kt, gross weight</i>	8,339
	Rare earths, <i>t, REE*</i>	120		Salt (marine salt), <i>kt</i> 481	
	Salt, <i>kt</i> 96		Turkey	Antimony, <i>kt</i> 360	
Sudan	Chromite, <i>t, gross weight</i>	10,000		Barite, <i>kt</i> 13	0,000
	Gypsum, <i>kt</i>	4		Bauxite, <i>kt</i> 459	
	Salt, <i>kt</i> 50			Bentonite, <i>t</i>	560,000
Suriname	Bauxite, <i>kt</i> 3,610			osphate minerals, <i>kt</i> 1,400	
	Asbestos, <i>kt</i> 25,000			Chromite, <i>t, gross weight</i>	1,000,000
Swaziland	Diamond (synthetic), <i>thousand carats</i>	20,000		Feldspar, <i>kt</i> 1,20	0,000
	Feldspar, <i>kt</i> 45,000			Fluorspar, <i>kt</i> 5,000	
Sweden	Graphite, <i>t</i>	5,000		Graphite, <i>t</i>	15,000
	Kaolin, <i>t</i>	440		Gypsum, <i>kt</i> 300	
	Silica sand, <i>kt</i>	500		Kaolin, <i>t</i>	400,000
	Sodium sulfate (synthetic), <i>kt</i> 100,000			Magnesite, <i>t</i>	2,000,000
	Talc, <i>t</i>	26,000		Nitrogen (as ammonia), <i>kt</i> 53	
	Gypsum, <i>kt</i> 300			Perlite, <i>t</i>	130,000
Switzerland	Nitrogen (as ammonia), <i>kt</i> 33			Pumice, <i>t</i>	600,000
	Salt, <i>kt</i> 300			Salt, <i>kt</i> 2,200	
	Gypsum, <i>kt</i>	304		Silica sand, <i>kt</i> 1,100	
Syria	Nitrogen (as ammonia), <i>kt</i>	91		Soda ash, <i>kt</i> 500	
	Phosphate rock, <i>kt, gross weight</i>	2,166		Sodium sulfate (natural), <i>kt</i> 10	0,000
	Salt, <i>kt</i> 150			Sodium sulfate (synthetic), <i>kt</i> 3	0,000
				Strontium, <i>kt</i> 2	5,000
				Talc, <i>t</i>	5,000

Adapted from USGS (data for 2000); Harben 2002.

* REE = rare earth element.

(Table continued next page)

Table 6. Distribution of world industrial minerals production by country (continued)

Country	Mineral	World Distribution	Country	Mineral	World Distribution
Turkmenistan	Bentonite, <i>t</i>	50,000	M	Diamond (synthetic), <i>thousand carats</i>	248,000
	Bromine, <i>kt</i> 150			Diatomite, <i>kt</i> 677	
	Gypsum, <i>kt</i> 100			Feldspar, <i>kt</i> 79	0,000
	Iodine, <i>t</i>	150		Fuller's earth, <i>t</i>	2,910,000
	Nitrogen (as ammonia), <i>kt</i> 75			Gypsum, <i>kt</i> 1	9,500
	Salt, <i>kt</i> 215			Iodine, <i>t</i>	1,470
U.S.S.R., former	Sodium sulfate (natural), <i>kt</i>	70,000		Iron oxide pigments (natural), <i>t</i>	57,100
	Bentonite, <i>t</i>	750,000		Kaolin, <i>t</i>	8,800,000
	Diatomite, <i>kt</i> 80			Kyanite, <i>t</i>	90,000
Uganda	Rare earths (t, REE*)	2,000		Lithium (brines), <i>t</i>	W
	Salt, <i>kt</i>	5		agnesite, <i>t</i>	W
Ukraine	Bentonite, <i>t</i>	300,000		Mica (scrap and flake), <i>t</i>	101,000
	Bromine, <i>kt</i> 3,000			Mullite, (synthetic), <i>t</i>	40,000
	Diamond (synthetic), <i>thousand carats</i>	8,000		Nitrogen (as ammonia), <i>kt</i> 1	2,300
	Graphite, <i>t</i>	7,500		Perlite, <i>t</i>	672,000
	Kaolin, <i>t</i>	225,000		Phosphate rock, <i>kt, gross weight</i>	38,600
	Manganese, <i>kt, gross weight</i>	2,741		Potash, <i>kt, K₂O equivalent</i>	1,300
	Nitrogen (as ammonia), <i>kt</i> 3,577			Pumice, <i>t</i>	697,000
	Potash, <i>kt, K₂O equivalent</i>	30		Rare earths, <i>t, REE*</i>	5,000
	Salt, <i>kt</i> 2,287			Salt, <i>kt</i> 4	5,600
	Soda ash, <i>kt</i> 500			Silica sand, <i>kt</i> 2	8,500
	Titanium concentrates (ilmenite), <i>t</i>	576,749		Soda ash, <i>kt</i> 1	0,200
	Titanium concentrates (rutile), <i>t</i>	58,600		Sodium sulfate (natural), <i>kt</i> 20	0,000
	Zirconium mineral concentrates, <i>t</i>	75,000		Sodium sulfate (synthetic), <i>kt</i> 29	1,000
United Arab Emirates	Gypsum, <i>kt</i> 90		Uruguay	Sulfur, <i>kt</i> 1	0,300
	Chromite, <i>t, gross weight</i>	60,000		Talc, <i>t</i>	851,000
	Nitrogen (as ammonia), <i>kt</i>	348		Titanium concentrates (ilmenite), <i>t</i>	400,000
	Sulfur, <i>kt</i>	1,120		Titanium concentrates (rutile), <i>t</i>	W
United Kingdom	Barite, <i>kt</i> 70,000			Vermiculite, <i>t</i>	150,000
	Bromine, <i>kt</i>	55,000		Zirconium mineral concentrates, <i>t</i>	W
	Feldspar, <i>kt</i> 8,000		Uzbekistan	Feldspar, <i>kt</i> 1,600	
	Fluorspar, <i>kt</i> 45,000			Gypsum, <i>kt</i> 1,000	
	Fuller's earth, <i>t</i>	140,000		Talc, <i>t</i>	1,000
	Gypsum, <i>kt</i> 1,500			Feldspar, <i>kt</i> 7	0,000
	Kaolin, <i>t</i>	2,420,000	Venezuela	Fluorspar, <i>kt</i> 8	0,000
	Nitrogen (as ammonia), <i>kt</i> 814			Graphite, <i>t</i>	60
	Potash, <i>kt, K₂O equivalent</i>	600		Iodine, <i>t</i>	2
	Salt, <i>kt</i> 5,800			Kaolin, <i>t</i>	5,500,000
	Silica sand, <i>kt</i>	4,000		Nitrogen (as ammonia), <i>kt</i> 810	
	Soda ash, <i>kt</i> 1,000			Phosphate rock, <i>kt, gross weight</i>	300
	Sodium sulfate (synthetic), <i>kt</i> 70,000			Sulfur, <i>kt</i>	460
	Talc, <i>t</i>	5,000		Bauxite, <i>kt</i> 4,200	
United States	Antimony, <i>kt</i>	W†		Diamond (natural gem), <i>thousand carats</i>	60
	Asbestos, <i>kt</i>	5,260		Diamond (natural industrial), <i>thousand carats</i>	40
	Barite, <i>kt</i> 392,000			Feldspar, <i>kt</i> 16	0,000
	Bauxite, <i>kt</i> NA	‡		Gypsum, <i>kt</i> 25	
	Bentonite, <i>t</i>	3,760,000		Nitrogen (as ammonia), <i>kt</i> 377	
	Beryllium minerals, <i>kt</i>	4,510		Phosphate rock, <i>kt, gross weight</i>	375
	Borate minerals, <i>kt</i> 1,070			Salt, <i>kt</i>	350
	Bromine, <i>kt</i> 228,000				

Adapted from USGS (data for 2000); Harben 2002.

* REE = rare earth element.

† W = Withheld to avoid disclosing proprietary data.

‡ NA = not available.

(Table continued next page)

Table 6. Distribution of world industrial minerals production by country (continued)

Country	Mineral	World Distribution	Country	Mineral	World Distribution
Venezuela (continued)	Silica sand, kt	650		Chromite, t, gross weight	640,000
	Sulfur, kt	3,200		Diamond (natural gem), thousand carats	7
Vietnam	Chromite, t, gross weight	55,000		Diamond (natural industrial), thousand carats	13
	Kaolin, t	1,200		Feldspar, kt 2,250	
	Nitrogen (as ammonia), kt 42			Graphite, t	12,000
	Phosphate rock, kt, gross weight	850		Lithium, t	37,000
	Salt, kt 730			Magnesite, t	4,000
	Titanium concentrates (ilmenite), t	109,000		Mica, t	1,300
Yemen	Gypsum, kt 100			Nitrogen (as ammonia), kt 58	
	Salt, kt	150		Phosphate rock, kt, gross weight	90
Zambia	Gypsum, kt 10			Sillimanite minerals, t	4,000
	Talc, t	80		Talc, t	1,000
Zimbabwe	Asbestos, kt 110,000			Vermiculite, t	18,935
	Bentonite, t	140,000			

Adapted from USGS (data for 2000); Harben 2002.

* REE = rare earth element.

force in world markets for magnesite, talc, barite, bauxite, rare earths, and graphite. This shifting pattern of supply and demand will continue to offer future opportunities and challenges to the increasingly sophisticated industrial minerals industry. The streets of the 21st century are paved with industrial minerals, not gold. There will be more of them, and the traffic promises to be heavy.

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International Trade in Industrial Minerals

Mike O'Driscoll

INTRODUCTION

From the outset, any analysis of the definition of industrial minerals at once reveals the essential dynamic that drives trade in industrial minerals; that is, market demand = mineral supply. As a consultant in the field once said, "Without a market, an industrial mineral deposit is merely a geological curiosity." So, put simply, no market demand = no mineral development = no mineral trade.

According to statistics published by the United Nations (Anon. 2004), the total value of world minerals and metal exports in 2001 was US\$166,631 million; for imports, the total value was US\$191,032 million. Industrial minerals trade contained within these figures can be roughly calculated as US\$36,452 million for world exports and US\$42,160 million for imports. These figures underline the importance and value of international minerals trade, but why are industrial minerals traded, and what influences that trade?

Industrial minerals can be defined as minerals mined and processed (either from natural sources or synthetically processed) for the value of their non metallurgical properties, which determine their use in an extremely wide range of industrial and domestic applications. In essence, wherever there is demand for these industrial and domestic applications (i.e., a market), this will create a trading business specific to that market. The crucial point is that the pattern of industrial minerals trade is dictated by the needs of the population and the performance of the economy, and then combined with mineral availability.

This chapter considers the overall nature of international trade in industrial minerals by examining the economic importance of industrial minerals, market geography, the structure of the mine-to-market supply route, pricing, and the main factors influencing mineral trade today.

THE ECONOMIC IMPORTANCE OF INDUSTRIAL MINERALS

If demand is the driver of industrial minerals trade, one must ask: Why are industrial minerals so important and where do they go? Certain industrial minerals may have 1, 2, or maybe up to 10 domestic or industrial applications; others such as lime may have more than 50 uses. To bring some coherence to industrial minerals markets, the main consuming mineral market sectors that require industrial minerals as raw materials are summarized as

- | | |
|----------------|--------------------|
| • Abrasives | • Metallurgy |
| • Absorbents | • Paint |
| • Agricultural | • Paper |
| • Cement | • Pigments |
| • Ceramics | • Plastics |
| • Chemicals | • Refractories |
| | • Synthetic fibers |
- Construction
 - Drilling mud
 - Electronics
 - Filtration
 - Flame retardants
 - Foundry
 - Glass

The individual mineral chapters detail each mineral's main application and use, but for completeness, it should be noted that the trade route of a mineral from mine to market can involve more than one stage (i.e., its consumption in manufacturing an intermediate mineral or end product), which is then consumed in the manufacture of another end product, which is then sold to an end-use market (for examples, see Figure 1).

The other aspect of many industrial minerals—that they can serve a range of markets—also affects the pattern of minerals trade, in that a single mineral source can supply several different customers because of market type and geography. For example, bentonite sourced in Wyoming travels to domestic and overseas population centers because of its widespread use as an absorbent in cat litter products. Its equally important use as a major component in drilling fluids, however, means that it is also freighted to centers of oil and gas drilling activity (e.g., the Gulf of Mexico).

MARKET GEOGRAPHY

Some of these mineral-consuming market sectors represent certain heavy industries responsible for products fundamental to a modern lifestyle. These markets can easily be identified as those that thrive in developed economies serving their populations. So, no matter where industrial minerals occur, there is a natural geoeconomic trend as to where industrial minerals are destined to be shipped and traded for use because of their economic importance. Thus, the major post-World War II modern industrial centers of North America and Europe, followed later by Japan and Republic of Korea, have been well-established market centers for minerals trade for the last half century or so.

Where there is evidence of a growing population combined with a developing economy hosting such mineral-consuming markets, these countries and regions become earmarked as growing and future markets for industrial minerals, and therefore beacons for minerals trade.

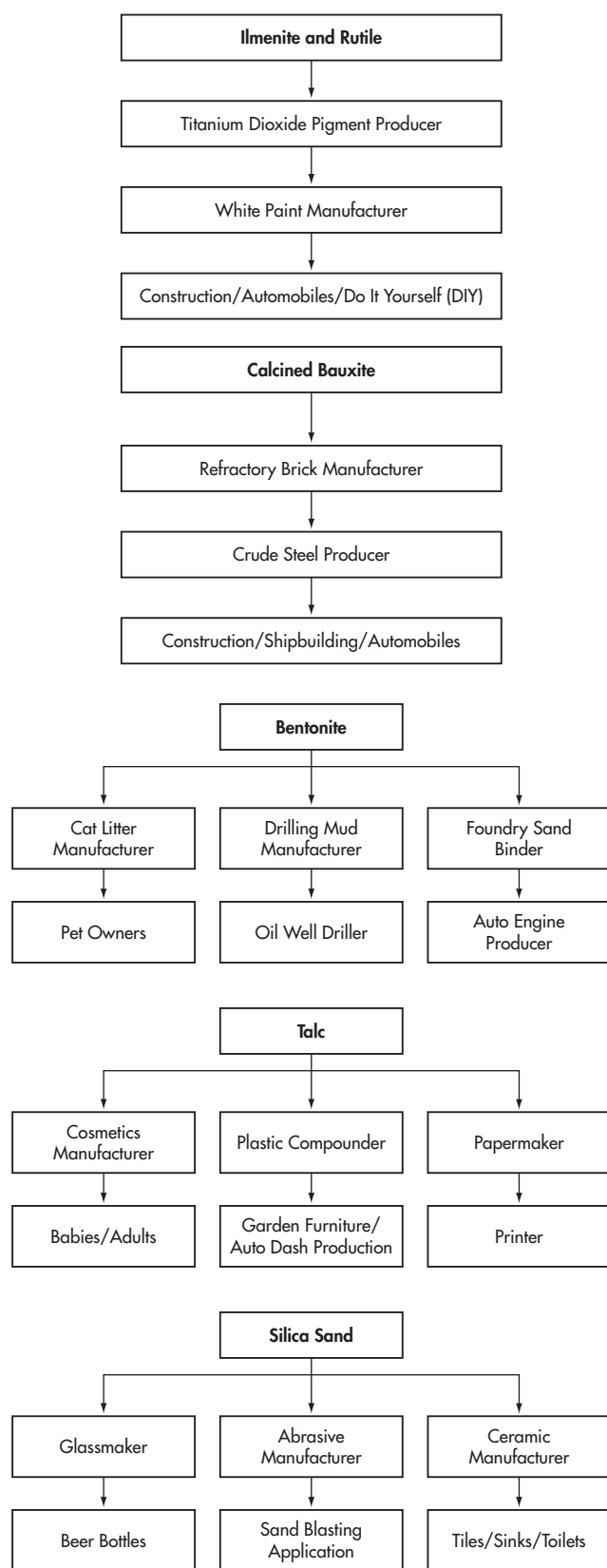


Figure 1. Examples of the trade routes for selected industrial minerals

In the 1980s and 1990s, the established markets for minerals were joined by the emerging “Asian Tiger” and Pacific Rim economies of Indonesia, Malaysia, Singapore, Taiwan, and Thailand. Since the mid-1990s, China has all but dominated world trade in commodities. India and East Asian economies, and now Vietnam, continue to grow in stature. Elsewhere, despite conflict in the Middle East, countries such as Iran are becoming stabilized as its economy flourishes and foreign investment increases. In Europe, with the breakup of the Soviet Union, it is the central and eastern European countries that are now showing good prospects for growth and demand for industrial minerals.

Once the widespread use and economic importance of industrial minerals are appreciated, it is possible to understand the chief and overriding principle of industrial minerals trade: mineral-consuming market existence and its performance directly affect demand and, therefore, trade for mineral raw materials.

Therefore, demand feeds back from the end-use market to the end product, to the intermediate end product, and finally back to the mineral supplier. Thus, the performance of the industrial minerals industry and international trade in industrial minerals is inextricably linked to three related factors: (1) centers of high population—the consumers; (2) their economies—the driver; (3) availability and occurrence of mineral resources—the source.

STRUCTURE OF MINE-TO-MARKET SUPPLY ROUTE

Once a market is established, the mineral must be sourced, a supply route can be enacted, and international trade, if appropriate, is engaged. The best way to see what really makes mineral trade function is to look at who is involved in the mine-to-market supply chain of industrial minerals.

All industrial minerals are mined (surface and under ground) and then undergo processing to refine the crude mineral ore into a processed grade or range of grades for sale to the desired market. The minerals are then transported from their source, sometimes to another plant for further processing, possibly via a complex freight route employing a raft of services, or directly to the consuming markets. In general, three broad sectors facilitate the route of a mineral from mine to market: (1) the supply sector, (2) the logistics sector, and (3) the consuming market sector.

Within each of these sectors are subsectors that have specific functions in the supply chain, employ certain types of businesses, and are influenced by different factors. Figure 1 illustrates these sectors and subsectors, and the overall mine-to-market supply chain. Take note of the influential direction of supply from the top and demand from the bottom. Other key notes to highlight are the activities and objectives of the main players in the industrial minerals market:

- **Mineral producers** seek to maintain supply to current markets and, where possible, diversify into new markets.
- **Mineral producers/processors** seek to employ and develop new processing methods to economically produce superior products for new market applications.
- **Traders, logistics companies, and consuming market mineral buyers** seek to source low-cost, high-quality minerals and alternative or new suppliers.
- **Freight and logistics** costs can be 50% to 70% of delivered cost of mineral to customer; therefore, suppliers and customers strive to secure the most cost-effective and -efficient logistics systems and companies.

The mine-to-market supply route described in Figure 2 is tailored to suit different mineral types for a range of different markets.

INDUSTRIAL MINERALS PRICING

Another important aspect of industrial minerals that requires appreciation when discussing international trade is the trade value of the minerals. Most industrial minerals are essentially high-volume, low-value commodities, whereas metals, for example, are the reverse, especially precious metals. Table 1 compares current (2005) prices.

Apart from the obvious difference in scale of value between the two sets of commodities, a key issue is the fact that unlike the metal markets whose prices are set by an exchange system (London Metal Exchange), no such facility operates for industrial minerals—despite a few ill-fated attempts made by various organizations in recent years, particularly with the advent of the Internet and e-commerce. For the reasons outlined here, it is unlikely that any kind of industrial minerals pricing exchange will be created in the foreseeable future.

Basically, the price of an industrial minerals shipment is negotiated between the mineral buyer (trader/consumer) and the seller (trader/producer). Although that might seem to be a simple concept at the outset, there is far more to industrial minerals pricing than meets the eye, and it is subject to a complex mosaic of interchangeable forces. A range of highly influential factors come into play that can affect this negotiated price and contribute to the difficulties of structuring a price exchange for industrial minerals:

- Source of mineral
- Cost of processing
- Market destination
- Volume of shipment
- Bulk or bagged
- Grade of mineral and its end use—i.e., quality of mineral, dictated by desired end use of the mineral (some minerals boast up to 50 or more grades for as many end uses; e.g., limestone used in cement is much cheaper than limestone used in paper, by approximately >\$150/t)
- Any further processing required between source and customer
- Freight and shipping—can be up to 50% to 70% of final delivered cost of mineral
- Port handling (at loading/discharge)
- Warehousing and storage
- Mineral inspection (at loading/discharge)
- Insurance
- Currency exchange rates
- Spot or long-term contracts
- Relationship between buyer and seller

There are simply too many variables to indicate a set price per grade. That said, with research and investigation, it is possible to calculate an average range of prices that largely indicate current market trading prices. For these reasons, industrial minerals prices quoted in *Industrial Minerals* and *Mineral PriceWatch*, for example, are a range of minimum to maximum prices currently traded for certain mineral grades. Minerals prices are not normally as volatile as metals prices, and price changes may be more subtle and infrequent.

The desired end use of the mineral really underlines the difference in price between grades of a single mineral. This largely reflects the degree of complexity, cost of processing, and perhaps storage of the mineral grade. Three of the examples in Table 2 (for calcium carbonate, kaolin, and zircon) illustrate the differences in pricing that result from market application.



Figure 2. Anatomy of industrial minerals trade by route of mineral from mine to market

Table 1. Price comparison of metals and industrial minerals, in US\$/t, unless otherwise indicated

Metals	Price	Industrial Minerals	Price
Gold	426.3/oz	Salt	15–18
Silver	6.78/oz	Silica sand	14–25
Aluminum HG	1,827	Olivine	50–117
Copper A	3,228	Dead-burned magnesia	157–210
Zinc SHG	1,271	Zircon	420–600

Source: *Metal Bulletin* 2005.

Table 2. Industrial mineral grade price comparisons

Mineral	Grade	Price
Ground calcium carbonate	f.o.b.* United States, US\$/st	
	5–7 µm	110–160
	1.5 µm, high brightness for paper	170–180
Kaolin	United States, EXW,† US\$/st	
	Filler bulk	80–100
	Paper coating	85–185
	Calcined bulk	320–375
	Sanitaryware grade, bagged	65–75
Magnesite	Tableware grade, bagged	125
	Greece, raw <3.5% SiO ₂ , f.o.b.	50–55
	Eastern Mediterranean, Euro/t	
	European caustic calcined, CIF,‡ Euro/t, agricultural grade	145–160
	China, f.o.b.t.,§ US\$/t	
Perlite	Dead burned, 94–95% MgO, refractory grade	195–210
	Caustic calcined, 90–92% MgO	140–165
	Turkey, f.o.b., US\$/t	
	Raw, crushed, graded, bulk/big bags	32–60
	Raw, bulk	14–17
Zircon	United States, EXW, US\$/t	
	Expanded, filter aid grade	210–410
	Australia, bulk, f.o.b., US\$/t	
	Ceramic grade	490–600
	Refractory grade	430–525
	Foundry sand grade	420–530

Source: *Industrial Minerals* 2005.

* f.o.b. = free on board; see Table 3.

† EXW = ex works; see Table 3.

‡ CIF = cost, insurance, and freight; see Table 3.

§ f.o.b.t. = free on board truck; see Table 3.

Table 3. Incoterms used in international minerals trade

CFR	<i>Cost and freight:</i> Title, risk, and insurance cost pass to buyer when delivered on board the ship by seller who pays the transportation cost to the destination port. Used for sea or inland waterway transportation.
CIF	<i>Cost, insurance, and freight:</i> Title and risk pass to buyer when delivered on board the ship by seller who pays transportation and insurance cost to destination port. Used for sea or inland waterway transportation.
CIP	<i>Carriage and insurance paid to:</i> Title and risk pass to buyer when delivered to carrier by seller who pays transportation and insurance cost to destination. Used for any mode of transportation.
CPT	<i>Carriage paid to:</i> Title, risk, and insurance cost pass to buyer when delivered to carrier by seller who pays transportation cost to destination. Used for any mode of transportation.
DAF	<i>Delivered at frontier:</i> Title, risk, and responsibility for import clearance pass to buyer when delivered to named border point by seller. Used for any mode of transportation.
DDP	<i>Delivered duty paid:</i> Title and risk pass to buyer when seller delivers goods to named destination point cleared for import. Used for any mode of transportation.
DDU	<i>Delivered duty unpaid:</i> Title, risk, and responsibility of import clearance pass to buyer when seller delivers goods to named destination point. Used for any mode of transportation. Buyer is obligated for import clearance. Seller fulfills his obligation when goods have been made available at the named place in the country of importation.
DEQ	<i>Delivered ex quay (duty paid):</i> Title and risk pass to buyer when delivered on board the ship at the destination point by the seller who delivers goods on dock at destination point cleared for import. Used for sea or inland waterway transportation.
DES	<i>Delivered ex ship:</i> Title, risk, and responsibility for vessel discharge and import clearance pass to buyer when seller delivers goods on board the ship to destination port. Used for sea or inland waterway transportation.
EXW	<i>Ex works:</i> Title and risk pass to buyer, including payment of all transportation and insurance cost from the seller's door. Used for any mode of transportation.
FAS	<i>Free alongside ship:</i> Title and risk pass to buyer, including payment of all transportation and insurance cost once delivered alongside ship by the seller. Used for sea or inland waterway transportation. The export clearance obligation rests with the seller.
FCA	<i>Free carrier:</i> Title and risk pass to buyer, including transportation and insurance cost when the seller delivers goods cleared for export to the carrier. Seller is obligated to load the goods on the buyer's collecting vehicle; it is the buyer's obligation to receive the seller's arriving vehicle unloaded.
FOB	<i>Free on board:</i> Title and risk passes to buyer, including payment of all transportation and insurance cost once delivered on board the ship (or truck—FOBT) by the seller. Used for sea or inland waterway transportation.

Aside from different units of currency and measurement (although most are now quoted in US\$/t) industrial minerals prices are quoted with several clarifying terms to determine as precisely as possible on what basis the price has been calculated. These can be taken from a plethora of abbreviated shipping terms or standardized *Incoterms*.

Incoterms are standard trade definitions most commonly used in international sales contracts. Devised and published by the International Chamber of Commerce (ICC), Incoterms is short for International Commercial Terms, which are at the heart of world trade. ICC introduced the first version of Incoterms in 1936. Since then, ICC expert lawyers and trade practitioners have updated the terms six times to keep pace with the development of international trade; the last update was on January 1, 2000. EXW, f.o.b., and CIF are

among the most frequently used Incoterms in minerals trade; Table 3 defines these and other applicable terms.

In terms of nomenclature for industrial minerals quotes, consider the following examples of price quotes:

- *Bentonite, Wyoming, EXW, USA per short ton, rail hopper cars, crude, bulk all grades US\$26–\$63* details the source of the mineral, its price in U.S. dollars per short ton as it stands ready to leave the plant (i.e., ex-works, indicating no cost yet included for freight, insurance, etc.) as a crude raw material to be shipped in bulk by rail hopper cars by the buyer.
- *Chromite, Transvaal, 46% Cr₂O₃ wet bulk, f.o.b., chemical grade US\$125–150/t* indicates chromite from Transvaal in South Africa, possessing a minimum chromia content as wet bulk material, free on board, and for chemical applications in U.S. dollars per metric ton.
- *Fluorspar, acid spar filtercake, Chinese, dry basis, CIF, US Gulf Port US\$200–210/t* indicates fluorspar from China processed as dry filtercake, with cost, insurance, and freight included in the price, delivered to a U.S. Gulf port in U.S. dollars per metric ton.
- *Refractory bauxite, Chinese, minimum 87% Al₂O₃, f.o.b., (0–50 mm, undried), Shanxi, rotary lump, BD 3.25 US\$150–160/t* indicates refractory grade bauxite sourced from Shanxi Province, China, calcined in a rotary kiln with a minimum alumina content (in percent) and bulk density value (normally expressed as grams per cubic centimeter), undried at specified lump size, free on board truck, at U.S. dollars per metric ton.

The point to note is that each mineral has its own particular set of pricing criteria that characterize a specific grade for a particular market. Often the price quote will include minimum chemical or physical properties required, depending on the mineral and its desired end use, such as the percentage content of the key performing chemical compound (as in the chromite and bauxite examples) and perhaps the bulk density (e.g., bauxite) or brightness (e.g., calcium carbonate used in paper). The price quote is normally one that is commercially recognized as standard in that specific market but may not be transferable across different grades and even less so across minerals in general.

In international minerals trade, then, each industrial mineral has not only its own tailored mine-to-market supply chain structure but also its own specific pricing criteria. Above all, because of the significance of the dynamic relationship between industrial minerals and the economy, any change in the performance of the latter can have a very strong effect on prices.

MINERALS MOVEMENT

The physical movement of minerals across the globe is naturally determined by the location of the mineral source and that of the consuming market. As has been established, market demand is a key factor in the exploitation of an industrial mineral. But because freight logistics account for such a large proportion of an industrial mineral's price tag, it is economically unfeasible for many industrial minerals to be shipped long distances. This is especially so for low-value minerals required in very large volumes (e.g., carbonate rocks for construction materials, roadstone, and cement, and the main batch materials for glass making, such as silica sand, soda ash, and limestone). As a result, many consuming markets adapt their raw material needs to the mineral sources in closest proximity.

The exception to this rule is when there are limited sources of a particular mineral in demand and few substitute materials (e.g., in early 2005, refractory-grade bauxite could only be sourced from

Shanxi and Guizhou provinces in China, and from Guyana, and the main sources of celestite are only in Mexico, Spain, and China).

Industrial mineral occurrence and distribution are covered in detail in the chapter titled World Distribution of Industrial Mineral Deposits, and individual mineral chapters highlight the main sources of minerals supply. It is not always possible to have mineral resources near centers of market demand, since nature and economic development unfortunately do not always coexist to each other's benefit. Because of this, there will always be international trade in industrial minerals. Table 4 gives examples of industrial minerals that are in constant demand worldwide but that have limited sources and thus enter the global trade network on a regular basis. The source countries, as major exporters, are highly influential in the trade of these minerals.

The one country that crops up the most is of course China, which hosts vast mineral resources and is self-sufficient in most industrial minerals; exceptions include zircon and chromite. Supply of minerals from China to world markets increased markedly during the 1980s and into the 1990s. Therise of China and East Asia as a major consuming market center in its own right, however, somewhat slowed this trade flow since about 2002.

There is another exception to the rule regarding a number of important industrial minerals that are fairly widespread in occurrence and, although produced to serve local and regional markets, still maintain a significant level of international trade. This is frequently the result of their low production costs, low labor rates, and cheap energy, which can translate to a low price per ton of final product, and thus is still competitive to ship overseas. Solar-dried salt produced in Australia is a good example. Some of the other minerals in this category are feldspar, gypsum, refractory clays, sulfur, and certain grades of calcium carbonate and silica sand.

Fused minerals such as fused alumina, fused silica, and silicon carbide are processed from natural feedstock minerals by fusion in high-temperature electric arc furnaces that consume vast amounts of electrical energy. As a result, fused mineral producers locate themselves close to low-cost sources of electrical energy, such as hydroelectric power stations. Thus, Washington Mills Electro Minerals Corp. (fused alumina, fused magnesia, silicon carbide) is based at Niagara Falls, and C-E Minerals (fused silica) and Minco (fused magnesia) are based in Tennessee. Fused materials are high-value minerals that can be shipped great distances to their end-use markets but are still profitable.

INFLUENCING FACTORS AND TRADE TRENDS

We have already highlighted some major influencing factors that affect the mine-to-market supply route and mineral pricing in international trade. In this final section, we look at some specific issues and trends that illustrate examples of interrelated factors that have had and continue to have a direct effect on industrial minerals trade.

Changing Supply Sources

If minerals are in short supply or have few worldwide sources of supply, conditions of high demand for a mineral will normally stimulate exploration and development of alternative sources, especially if older sources have matured and become exhausted or uneconomic. Once these new sources have been established, new trading routes will open.

Recent examples have included the evaluation and development of the Seqi olivine deposit in Greenland by Crew Development Corp. and Minelco AB. Interestingly, Crew already had a gold mine up and running in Greenland—a simple example of the difference in “value” between metals and minerals, whereby the price of gold ensured the success and swift fruition of the gold mining

Table 4. Examples of industrial minerals in global trade with limited sources of supply

Mineral	Source Country*
Andalusite	France, South Africa
Attapulgit	Greece, Senegal, Spain, United States
Baddeleyite	Russia
Barite	China, Morocco, Turkey
Bentonite	Greece, India, Turkey, United States
Bauxite, refractory	China, Guyana
Borates	Argentina, Chile, Turkey, United States
Chromite	South Africa
Fluorspar	China, Mexico, South Africa
Garnet	Australia, China, United States
Graphite	China
Halloysite	New Zealand
Hectorite	United States
Huntite-hydromagnesite	Greece, Turkey
Kaolin, refined	Brazil, United States
Kyanite	India, United States
Lithium minerals	Australia, Canada, Chile, Zimbabwe
Magnesite	China
Mica	China, India
Mullite, sintered	China, United States
Nepheline syenite	Canada, Norway
Nitrates	Chile
Olivine	Norway
Perlite	Greece
Phosphates	Jordan, Morocco, Russia
Potash	Belarus, Canada, Israel, Jordan, Russia
Pumice	Greece, Italy, Spain, Turkey
Rare earths	China
Sepiolite	Spain
Soda ash	United States
Talc	China, France
Titanium minerals	Australia, Canada, South Africa
Wollastonite	China, Finland, India
Vermiculite	China, South Africa
Zircon	Australia, South Africa

* Main supply sources and exporters of industrial mineral grade that influence global trade in that mineral.

project, whereas Crew's olivine project required more thoughtful evaluation of its market value (i.e., Was it economically viable? Where is the market?). With only a single major commercial source of olivine for markets in North America and Europe (i.e., A/S Olvin in Norway) and declining or small-scale production elsewhere, Crew considered that its high-quality olivine deposit might well have a chance.

Evaluation of Seqi olivine began in early 2003, and before the year was out, Minelco AB—the minerals arm of Swedish iron ore giant and large olivine user LKAB—had commissioned a bankable feasibility study from Crew and signed an agreement for an option to buy 51% of the project by funding capital development. A mining license was granted in early 2005, and mining is set to commence to bring a 1- to 2-Mtpy olivine project onstream. The site of the olivine source in Greenland means that Minelco can ship a

range of olivine grades to both European and North American markets. The European markets had been reliant on Norway (and served to a lesser extent by Italy and Turkey), whereas in the United States, in the absence of a major olivine source, iron ore pelletizing and steelmaking had switched to using dolomite as a slag conditioner. The opening and shipping of Seqi olivine is likely to change these market climates.

Elsewhere, other examples include andalusite deposits being evaluated and developed in western China and Peru as an alternative to the dominance of France and South Africa. Canadian gold miner Cambior Inc. has revived refractory-grade bauxite production in Guyana, once the leader in the field. Cambior's timing in 2004 was ideal in that the new millennium witnessed the market being hit by the double impact of refractory bauxite production ceasing in Brazil in 2003 and Chinese suppliers suffering shortages and price hikes during 2003–2005. Outside of China, Guyana is now the only other source of refractory-grade bauxite.

Zircon is another mineral whose development worldwide will create new supply routes across the globe by 2006–2010. As a high-value coproduct to titanium minerals mining, zircon is normally held hostage to the fortunes of the titanium dioxide pigment market, for which titanium minerals are supplied as raw material feedstock and thus the driver for mineral sands development. Growth in zircon markets, however, especially in ceramics, have sparked a raft of zircon-rich deposit evaluations and developments, with projects set to come on-stream in Australia, India, Kenya, Mozambique, the Gambia, and Senegal.

Economy and Market Performance—the China Factor

As ever, industrial minerals demand is shaped by national and regional economic performance. Without a doubt the dominant factor affecting industrial minerals supply and markets since the early 1990s has been China. With its opening up to the world market in 1978, the country has never looked back, and within just 25 years has evolved from a leading supplier of industrial minerals for world markets to a leading consumer and supplier of minerals. China has had a momentous effect on international trade of industrial minerals. The market growth of China and East Asia superbly illustrates the influence of new consuming market development on mineral trade routes.

Key minerals with which China bangs the world-trade drum include bauxite, barite, fused alumina, fluorspar, silicon carbide, flint clay, graphite, magnesite, talc, and wollastonite. Initially, during the mid- to late 1980s, China started to dominate world supply in these minerals, frequently triggering antidumping duties with its low-cost exports (discussed in the section on Antidumping Duties in this chapter). In the early years, Chinese minerals were not only low cost but also rather inconsistent in quality, often leading to insurance claims. This quality problem was mainly a function of outdated mineral processing equipment and techniques, a lack of independent inspection procedures, and an unstructured minerals industry that was ignorant (wittingly and unwittingly) of the risks of mixing and matching material from different sources for a single shipment. This was a gamble that consumers in the West had to take, and many, but not all, did. In the meantime, Western minerals producers would focus on maintaining customers by supplying quality-consistent, high-purity grades, but could do little about the low prices of Chinese material.

The early 1990s—with the Asian Tiger economies in full swing (albeit temporarily stalled by the financial crash of 1997)—saw a major shift in minerals-consuming manufacturing centers to East Asia. Refractories, foundry, steel, ceramics, glass, paper, paint, and plastics markets were all developing rapidly (but, at least to

begin with, at a slower pace in China itself). Leading Western manufacturers in these sectors began to set up joint-venture plants to serve these growth markets. Chinese minerals soon began to supply these East Asian countries in addition to the Western developed countries. At the same time, Western mineral companies, traders, and entrepreneurs began to establish themselves in China and Southeast Asian countries to secure and develop raw material sources to feed these markets.

The mid-1990s also witnessed a significant change in China's mineral exports in that minerals were now being exported as semi-processed or processed materials—adding value to the exports and meeting customers' requirements before shipping. This was enabled by the growth of foreign-owned minerals processors located at or near the main Chinese ports, guaranteeing Western standard processing and quality controls and minimizing the problems of inconsistent sourcing of raw material (this trend also greatly affected the traders and processors located at ports in Europe, who were used to handling and treating imports of crude material from China before distributing to customers). The emergence of Western minerals inspection companies allowed to operate independently in China also greatly facilitated the increase in quality of China's mineral exports. China's central government also introduced controls on export prices and volumes, which had an immediate and lasting effect on minerals trade from China.

By the start of the new millennium, China's economy was starting to take off. Private mining enterprises were allowed to flourish, Chinese minerals producers (and end-product manufacturers) were operating with imported technology and equipment, overseas companies could run wholly owned operations in China, foreign investment increased, and the China trading outpost of Hong Kong became redundant as Shanghai, Dalian, Tianjin, Zhangjian, and Qingdao became the trading hubs of modern China and welcomed overseas businesses.

The result was that Chinese minerals supply increased in quality as well as quantity, and Western minerals producers were now being squeezed out. This was no better exemplified than in the magnesite market, where Western and East Asian refractory producers were able to substitute Western high-purity, dead-burned magnesite supplied with lower-cost fused magnesite from China. This caused Western producers to rethink their grade portfolios and prompted the exit of some big names in magnesite (and fused alumina) in the West and in Japan. China was all dominant.

In early 2005, China's economy was growing at 9.5% per annum (in spite of efforts to cool it down). But in 2003–2004, China's soaring market growth triggered a major shift in world minerals trade. Although China will remain an important exporter of industrial minerals, its ravenous domestic consuming markets became the priority for China's minerals producers. The incentive to export raw material became less attractive (and was replaced by the incentive to export lower-cost finished products such as refractories and ceramics). In fact, the Chinese government took formal steps to conserve its mineral resources, such as reducing mineral export volumes. This prompted a major shortage of Chinese-sourced minerals worldwide. High domestic market demand, limited energy sources, and rising costs, plus a creaking internal freight network, all contributed to a major increase in Chinese minerals prices. As a result of this, Western minerals producers became very much in demand to fill the gap left by Chinese suppliers, and the pattern of mine-to-market supply swung yet again.

Elsewhere, other regions of market growth include central and eastern Europe, where former Eastern Bloc countries and former Soviet Union republics are stabilizing their economies and developing industry and infrastructure. These countries are new targets for

Table 5. Industrial minerals incurring European Commission (EC) antidumping duties, 1996–2005

Mineral	Origin	EC Duty*	Imposed	Expiration Date
Dead burned magnesite	China	Min. CIF € 120 ADV† 63.3%	February 2000	January 2005
Caustic calcined magnesite	China	Min. CIF 112 ADV 27.1%	August 1999	July 2004
Fused alumina	China	Min. CIF € 204	October 1997	October 2002
	Commonwealth of Independent States	ADV 9.8% of CIF price	Expired October 1997	
	Ukraine	ADV 9.8%	Expired October 1997	
	Hungary	Min. price undertaking	Expired October 1997	
	Poland	Min. price undertaking	Expired October 1997	
	Czech Republic/Slovakia	Min. price undertaking	Expired October 1997	
	Brazil	Min. price undertaking	Expired October 1997	
	Former Yugoslavia	Min. price undertaking	Expired October 1997	
Silicon carbide	China	ADV 52.6% of CIF price	June 2000	May 2005
	Russia	ADV 23.3% of CIF price	June 2000	May 2005
	Ukraine	ADV 24% of CIF price	June 2000	May 2005
	Poland	ADV 3.8% duty	Expired June 2000	
Fluorspar	China	Min. CIF € 113.50	November 2000	October 2005
Chamotte	China	Min. CIF € 75	January 1996	January 2001

* Prices in euros per ton; when a minimum price is stipulated, this indicates that the antidumping duty has been determined as the difference between this minimum price of the mineral (as stipulated by the EC) and the net free-at-EU-frontier price of imported mineral from country of origin.

† ADV = ad valorem duty expressed as a percentage duty.

industrial minerals supply and in certain cases hosts to new mineral sources themselves.

Government Trade Policies

A major influence in trade is the role of national governments, which continually strive to encourage investment in their economy and defend their industries from unfair trade practices. A number of particular issues have directly affected industrial minerals trade.

Antidumping Duties

Perhaps the issue most frequently mentioned in terms of trade practice and government influence is *dumping*, which refers to the practice of selling goods overseas (exports) below their normal market value or below the price charged for the same goods in the domestic market of the exporting country. Dumping can be a predatory trade practice whereby the international market, or a certain national market, is flooded with dumped goods to force competitors out of the market and establish a monopoly position.

Reactions to dumping by the importing government can include government subsidies to the threatened domestic industry to temporarily help absorb the losses caused—although this can lead to friction among trade partners. Dumping and predation are considered to be unfair trade practices and, as such, are prohibited under many national trade laws. Although there are variations on this theme, the most common antidumping measure is an added import duty (an antidumping duty) calculated to offset the dumping margin, that is, the discrepancy between home market price (importer's market) and the export price.

Regarding industrial minerals trade, China has been at the center of many dumping issues involving magnesite, fluorspar, silicon carbide, fused alumina, barium carbonate, and titanium dioxide pigment (and, more recently, mineral end products such as magnesia-carbon refractory bricks) exported to European Union (EU) countries, the United States, and the Republic of Korea. Other

countries accused of dumping minerals are Russia and Ukraine for silicon carbide. Table 5 summarizes EU antidumping measures that were in place in early 2005.

India has been the target of dumping for many minerals; those from China include borates, soda ash, fused magnesite, barium carbonate, strontium carbonate, and hydrofluoric acid. In 2003, India instigated antidumping duties on borates from Turkey.

Dumping issues normally take several months to a year to resolve (and longer in some cases), involving investigation by the importing country or trade coalition (e.g., the EC for EU countries) in response to a filed complaint from one or more members of an industry sector (e.g., magnesite producers of Europe, or fused alumina producers of the United States, or a trade association representing its members). The allegation is investigated, including visits to the sources of the exports; a similar market in an unconnected third country may also be evaluated as an example of a typical market for reference; and all parties concerned have an opportunity to comment by a given deadline. A decision is then made to establish if an industry has been materially injured and, if so, what measures should be taken and when. These are then implemented and reviewed, normally after 5 years. The main types of antidumping duties and tariffs can be summarized as follows:

- *Countervailing duty* differs from antidumping duty because it is applied in situations where foreign governments subsidize their industries by providing financial assistance to benefit the production, manufacture, or export of goods. These subsidies can take many forms, such as direct cash payments, credits against taxes, and loans at terms that do not reflect market conditions. Most trade anti-dumping determination bodies have standards for determining when an unfair subsidy has been conferred. The amount of subsidies the foreign producer receives from the government is the basis for the subsidy rate by which the subsidy is offset, or "countervailed," through higher import duties.

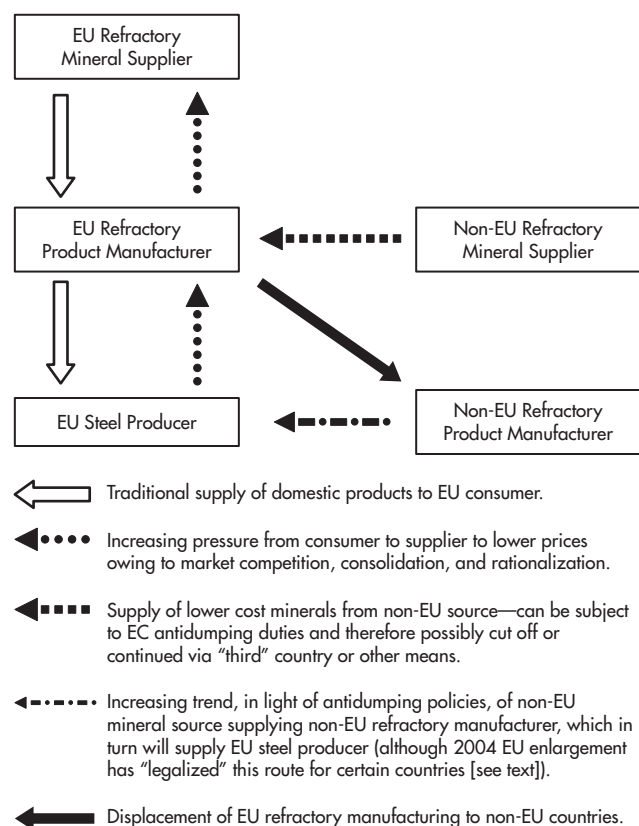


Figure 3. Interrelationships among supplier and consumer in EU refractories sector and influence of EC antidumping policies

- *Minimum import price (MIP)* is one type of antidumping measure. It has drawbacks, however, because it can become irrelevant if across-the-board prices for a particular product area decrease or increase significantly. In addition, it can be bypassed or circumvented through agreements between related exporters and importers, where the exporter supplies the product at an inflated price above or equal to the MIP, then makes the discount after clearing customs. Circumvention can also occur through exporting via a third country to change the country of origin. There are various ways to correct this, and in 2003, the EC altered its policy on an MIP applied to Chinese magnesite imports to the EU because of these types of problems.
- *Ad valorem duty* is the most common form of antidumping duty and is based on the dumping margin, being imposed as either a percentage equal to the dumping margin or a percentage equal to the proportion of the dumping margin that is causing injury. It is imposed as that percentage of the landed price.
- *Tariffs* are completely different to antidumping duties in that they are customs duties that are applied independently, and antidumping duties are applied in addition to any existing tariffs. They are either safeguards against imports that are in such increased quantities to cause or threaten to cause serious injury to domestic producers or simply a means of the home government to raise fiscal revenue. Thus, they do not depend on dumping having been established and do not necessarily apply to a specific exporting country.

Dumping issues are perhaps the most contentious of all mineral trade issues. Basic business rules dictate that as long as there is a free market, there will always be a customer for low-cost goods. Moreover, spurred on by today's increasingly competitive markets, in spite of the best efforts of antidumping policies, it seems there may always be alternative routes for such imports to reach their target market. Unfortunately, the term *free market* may be the subject of debate for some buyers and consumers of minerals. The nub of the debate surrounding the dumping issue has centered on calling into question just who is being protected and whether it is to the greater benefit of the country or region or just for a few threatened producers.

The supply chain involving the European refractories market may be taken as an example that highlights the issues at stake here. Figure 3 illustrates in crude terms the interrelationships between suppliers and consumers, and the influence of EC antidumping policies.

During 2001, the end-consuming market, the steelmaking sector, was facing increased consolidation and rationalization in the EU. As a result, the steel sector imposed intense pressure on refractory manufacturers (and its other suppliers) to lower their prices.

In turn, under pressure to meet the demands of their steel customers, the refractory manufacturers found ways to cut the costs of their raw material purchasing. For example, blast furnace runners are largely composed of silicon carbide (SiC) or brown fused alumina (BFA)—thus, low-cost sources of these materials were sought.

EC antidumping practices, however, instigated to protect the business of EU SiC and BFA producers, cut down the opportunity for EU refractory manufacturers to secure low-cost non-EU supply sources, with no option left but to buy domestic supplies. Furthermore, the European supply market for certain minerals has shrunk dramatically in some cases, such as with BFA and SiC, with just one or two producers remaining in Europe. This has been the upshot of a combination of mergers and strategic withdrawals from these businesses in recent years. Naturally, any EU buyer of these minerals is thus left with little alternative in terms of domestic supply.

Therefore, the policy of antidumping duties on competitive materials outside the EU to protect just one or two producers might start to look a little hard to justify. This is not to say that European producers are taking advantage of the situation, but all the same, this question is being asked more and more.

Two primary consequences have resulted from this situation:

1. Suppliers of low-cost minerals from non-EU sources may be encouraged to find alternative ways of getting their products into the EU market.
2. EU refractory product manufacturing may shift to non-EU countries or be displaced altogether by refractory product supply from non-EU countries that can import low-cost minerals free from antidumping duties and use lower costs of production.

On the first point, certain buyers and traders in the business of sourcing mineral imports will find ways and means, which may be quite legal, to circumvent antidumping policies. Although such practices are nothing new, because of the intense competition in mineral markets today, their implementation over the last few years in particular seems to have grown in frequency and profile.

The most common method seems to be that of routing mineral imports through a third country that is not subject to antidumping duties. Each country has its own set of regulations governing what minimum treatment and enhancement in value an imported product must undergo in order for it to adopt a new country-of-origin label.

As long as traders or mineral suppliers keep within these requirements, there is little to prevent their subsequent export free of anti-dumping duties.

From the consumers' viewpoint this can be an obvious advantage in reopening a source of lower cost material. It may, however, also make it less clear what the original source of the material is, and thus could be subject to possible problems of quality inconsistency if material from different sources is blended without prior knowledge. Examples in recent years have included EU imports of BFA from China via South Africa or Poland, and silicon carbide via Norway, Czech Republic, or Romania.

The second point, that of the threat of increasing production of refractory products from non-EU countries, is indeed a very real concern for the EU refractories sector.

Certain companies have already shifted production facilities to non-EU countries (e.g., Vesuvius International shifting refractory brick production from Whitecross, United Kingdom, to Skawina, Poland). Meanwhile, it is generally considered that the first wave of Chinese refractory raw materials into Europe over the last decade or so is going to be followed by a second wave of low-cost Chinese refractory products, and it is on its way—indeed, in late 2004 the EC was investigating allegations of Chinese MgO-C brick dumping.

So, although some EU minerals producers are being protected from low-cost imports, the manufacturers of the intermediate product (refractories) and the end consumer market (steel) appear to bear the cost of this policy—even though they are trying to eke out a living in the same geographical market (i.e., the EU).

Export Licenses

This initiative is unique to China but has transformed the trade in certain minerals from China to the West. China's central government, through the China Chamber of Commerce of Metals, Minerals & Chemicals Importers & Exporters, implemented its export license system in April 1994. The move was largely to enable stricter control of export volumes and prices, reduce smuggling, and minimize allegations of dumping. Although initially focused on magnesite and fluorspar, by early 2005 export licenses were also required for exports of talc, silicon carbide, bauxite, and brucite.

The concept of the Chinese export license system is generally sound, even if it meant that traders and overseas consumers, having enjoyed relatively low-cost Chinese minerals for a decade or so, now have to accommodate a higher price tag. The problem, however, has been in the administration and subsequent tinkering of the system's rules and regulations on an almost annual basis, and with little or no consistency.

For example, in 2004, bauxite exports were subject to a flat fee of RMB230 (US\$28)/t, but in 2005 the system changed to the notorious bidding and quota system, as used for magnesite exports. In this procedure, suitably qualified parties (i.e., those with a stipulated past record of exporting) bid to secure a limited number of export licenses and volume quotas set for the year's total exports. Officially, those unsuccessful in securing export licenses cannot therefore export, and those that have export licenses but fail to fulfill them are subject to a penalty fee and relinquish their right to bid in the following year.

In reality, an underground market for export licenses develops, and inevitably there is some collusion in bidding among prospective exporters. Concerning magnesite exports, there have been at least five successive versions of an exporters' syndicate since 2000, each with laudable aims but lasting only a few months to a year before breaking up over disagreements on prices and procedures or because of apathy. The magnesite export associations have generally tended to increase the price of exported grades.

Smuggling also has become a problem, with unqualified exporters either doctoring export documents or exporting via "third" ports in China or Republic of Korea. Any smuggled shipments of bauxite or magnesite that are suddenly confiscated or impounded by the Chinese authorities naturally have a major effect on waiting consumers overseas.

A very frustrated and confused trading community has been trying to keep up to date with the continually changing export license system and its disruptive impact on prices and material availability. For 2005, in its efforts to conserve its raw material resources, the Chinese government issued reduced export quotas of certain minerals such as bauxite and increased its prices. Although this disrupts supply of minerals from China, it does give impetus to overseas producers to plug the gap with their products.

Other Taxes

In addition to export taxes, countries can impose so-called resource taxes on certain minerals, and China has implemented this with magnesite mined in Liaoning Province. The resource tax thus adds to the overall price of the mineral and has been approximately US\$10 to \$40/t.

Removal and reduction of tax rebates on mineral exports is another issue that has ramifications in world minerals trade. In October 2003, China announced reductions or cancellations of a range of mineral exports, including bauxite, silicon carbide, BFA, magnesite, fluorspar, talc, rare earths, graphite, and barite. Rebates ranging from 13% to 17% were cancelled or reduced to 5%. For most mineral exporters, this resulted in at least a \$2/t increase in prices.

Trade Bans

One obvious measure that has a direct effect on minerals trade is any government or intergovernmental ban on trade in a particular mineral. Perhaps unsurprisingly, asbestos has been the mineral whose trade has been most affected in this way. Trade in asbestos-containing products has already been curbed between most developed countries, and in late 2003, an intergovernmental committee agreed that the four asbestos minerals—amosite, actinolite, anthophyllite, and tremolite—should be added to the Rotterdam Convention Prior Informed Consent (PIC) list. In 2004, however, leading asbestos-producing countries such as Canada, Brazil, Russia, China, and Zimbabwe successfully challenged the addition of the asbestos mineral chrysotile to the PIC list.

Initiated in the 1980s, the voluntary PIC procedure required exporters trading in a list of hazardous substances (such as asbestos) to obtain the prior informed consent of importers before proceeding with the trade. In 1998, governments decided to strengthen the procedure by adopting the Rotterdam Convention, which makes PIC legally binding.

It is likely, however, that chrysotile will eventually meet the same fate as that of the other asbestos minerals, and asbestos mineral trade will cease altogether. In late 2004, Canada's largest chrysotile producer, LAB Chrysotile, indefinitely shut its Black Lake mine near Thetford Mines, Quebec. Among other reasons, the company cited exaggerated standards set by the provincial health and safety board, and numerous studies about the dangers of asbestos, as issues that prompted its decision to close the mine.

Trade Agreements

In contrast to trade bans, there are intergovernmental initiatives on international trade that can greatly enhance minerals trade. There are basically three levels of international trade agreements: bilateral relationships (e.g., Canada–United States Free Trade Agreement); multilateral arrangements (General Agreement on Tariffs and Trade

[GATT] and the World Trade Organization [WTO]); and regional agreements (North American Free Trade Agreement [NAFTA], Southern Cone Common Market [Mercado Comun del Cono Sur, or MERCOSUR], Caribbean Community and Common Market [CARICOM], and ASEAN Free Trade Area [AFTA]). Each aims to generally improve and facilitate trade among countries signed up for the agreement and normally will assist international trade in industrial minerals. The proliferation of regional trade agreements has been instrumental in changing the framework of world trade; more than one third of global trade takes place between countries that have some form of reciprocal regional trade agreement.

Two of the most significant developments in recent years include China's accession to the WTO and the enlargement of the EU. By 2005, the full impact of China's recent admission to the WTO remained to be seen, but one of the main ramifications of WTO membership for China will be its having to adopt WTO rules and regulations and the effect of this on China's current trading practices. For example, WTO membership might now signal the end of the mineral export license system that China initiated in 1994, which may have a profound effect on trade in certain minerals.

At midnight on April 30, 2004, the EU formally accepted 10 new member states into its fold: Cyprus, Czech Republic, Estonia, Hungary, Latvia, Lithuania, Malta, Poland, Slovakia, and Slovenia. Enlargement Day on May 1, 2004, concluded several years of tough negotiations and is one of the most important opportunities for the EU at the beginning of the 21st century. Significantly for industrial minerals trade and markets, enlargement has increased the EU's aggregate population from 378 million to 450 million—second only to China and India—and 160 million more than that of the United States.

With regard to the effect on industrial minerals, there are several issues to keep track of:

1. Expanded markets: An enlarged population equals expanded markets for industrial minerals in general.
2. Demand for modern products: Certain countries' markets are demanding Western standard manufactured products; this will drive existing EU minerals producers to supply them and prompt new member-state producers to develop and supply required grades to manufacturing plants.
3. New sources developed: The potential exists to develop new mineral deposits within new member states to supply EU markets, with possible reduction of reliance on imports.
4. Shift in manufacturing: Potential increase in shift of manufacturing plants to areas of cheaper labor could in turn influence development of mineral deposits, supply bases, and EU trade.

Clearly, for countries like the Czech Republic, Slovakia, Slovenia, Hungary, and Poland, accession to the EU has lifted any anti-dumping duties and other tariffs previously legislated against them by the EU and will be welcome by mineral suppliers of those countries (but perhaps not by those of other EU countries). Another factor that will influence trade relations is that many of the accession countries retain strong industrial links with Commonwealth of Independent States (CIS) countries, particularly Russia and Ukraine. These relationships should work to the advantage of the EU by strengthening or opening up new trading links among the existing EU-15 and the CIS.

Shipping and Freight Rates

The influence of shipping and freight rates on global trade and prices for industrial minerals cannot be overstressed. One of the most frequently cited reasons for producers and traders increasing

raw material prices is cost of freight, along with rising energy prices. Changes in the global freight market can have a profound effect on minerals trade, and this was starkly illustrated by events in late 2003, when a turnaround in global freight conditions hit the market with particular severity.

The freight market in 2002 witnessed such historical lows that almost every transport user within most commodity groups, shipping providers, and even shipbrokers had no inkling as to the severity of change that was to occur in 2003, which would have ramifications for the next few years. The significance of the turnaround lies in the phenomenal price increases experienced in every sector of the dry cargo market during the second half of 2003.

Usually, buyers and sellers of higher-valued commodities have not worried greatly about the movements within the freight market, because these changes represented a small percentage of the delivered price (unlike for industrial minerals). The freight market appreciation in 2003 changed all this because low-value inputs were especially affected (i.e., such as industrial minerals). Producers seeking to maintain market share in an oversupplied market are at the mercy of these changes unless the buyer is prepared to accept the gravity of change and reflect this in the price. Now, more than ever, low-value commodity suppliers such as mineral exporters are selling freight.

The key drivers of the freight market's strength included:

- Massive demand for raw materials in China (the country recorded record imports of grain, coal, iron ore, and steel)
- An upturn in key global economies (Organisation for Economic Co-Operation and Development [OECD] 5%, Europe 1.8%, Japan 1.8%, United States 3%, and India 6% to 7%)
- Slowdown in fleet regeneration
- Increased regional trade (stemming from the Asian crisis, growing interdependence, and more efficient employment of shipping)
- Surge demand (resulting from unforeseen demand bubbles)
- Port congestion

All these factors contributed to what many have considered to be the most significant shift ever in the bulk shipping market (container rates were also affected). Mainly because of a shortage of vessels and soaring demand for raw materials in China, freight rates almost doubled in just 1 month in late 2003. The effect was increased pricing for a number of key industrial minerals, including barite, bauxite, fluorspar, magnesite, and zircon. For example, Chinese barite prices (CIF U.S. Gulf Coast) rose to US\$62.50 to \$64.50/t from US\$42 to \$47/t. Also, because of congestion at ports, the cost of demurrage (the extra charge levied by shipowners as compensation for delays in loading/discharge) rose sharply.

The degree of change and the influence of huge demand for raw materials to feed Chinese growth have made suppliers reexamine the profitability of competing in distant markets where freight has the propensity to erode profitability. Similarly, consumers are reexamining their usual sourcing of product to reduce their delivered costs. These changes may result in a realignment of trades (as consumers source minerals from elsewhere to reduce shipping costs) or simply a reduction in the dependence on bulk shipping and increased usage of containers as a mode of transport because of their competitive pricing.

In 2004 and 2005, the container market witnessed a massive increase in capacity with new and larger container vessels on order. The container lines will want to fill the slots and acquire the economies of scale demanded by the new generation of large container-capacity vessels (some 4,100 teu [20-ft equivalent unit] compared

to the existing fleet average of 1,900 teu). By late 2004, certain bulk trade routes had become so expensive that containers had been able to capture certain commodity trades that logically should have been conducted onboard Handysize or Panamax vessels.

The changes will stimulate a reexamination of key elements within the supply chain, including:

- The freight economics of variable tonnages
- Storage—the ability to handle larger volumes and attract economies of scale
- Production scheduling

A classic example of the influence of a combination of freight and tax factors on the barite market took place in mid-2004. Rising prices for Chinese drilling-grade barite as a result of high ocean freight rates, Chinese port congestion, hampered overland logistics, and the lowering of the value-added-tax (VAT) rebate on barite exports from China enabled barite sourced from Nevada to be competitive again in the Gulf of Mexico drilling mud market. It became much more expensive and time consuming to get Chinese barite to key ports because trucks that previously carried 30 t were limited, almost overnight, to 20 t after a government crackdown on overloading. In many cases, this one factor increased the cost of getting material to the port by 10% or more.

This had the effect of prompting key Gulf consumers to look at renewed investment at their Nevada barite mine and grinding plant operations. The long period of dominance by imported Chinese barite in the Gulf of Mexico market began in the mid-1980s, when the domestic mining operations in Nevada were cut back from their 1982–1983 peak production of 5–6 million tpy to 1.5–2 million tpy, which is where they have stayed to date. Until mid-2004, the cost of shipping barite from Nevada to the southeastern United States by rail had simply priced it out of the Gulf market, and, incredibly, it was more economical to ship barite from China. This 20-year status quo is now changing, however, and the Gulf of Mexico drilling market will be seeing an increase in supply of barite from Nevada, a weakening of dominance from Chinese imports, and perhaps a rejuvenation of supply from other sources such as India and Morocco, which had also been priced out by the Chinese.

OUTLOOK

World trade growth averaged 10.2% in 2004, reflecting rapid increases in industrial production and investment activity. More than 20% of the increase in world trade volumes was accounted for by China, whose imports increased by 30% in 2004. Although China's growth economy will slacken off somewhat, the country is expected to remain a strengthening powerhouse in the overall growth region of East Asia at least until 2010. Overall, world trade was expected to slow slightly to 8.5% growth in 2005.

Industrial minerals trade patterns will continue to react to the performance of the leading world economies and the global freight market. The developing markets in China, East Asia, and eastern and central Europe will continue to attract minerals trade as they grow. In time and with continuing overseas investment, these regions may develop their own mineral sources that will join the world export market.

The Middle East region has very good prospects for attracting increasing minerals supply, but continuing conflict and political uncertainty will naturally stifle any rapid growth in this region for the time being. Perhaps the great unknown market and trade influence in waiting is Russia. At present, much of Russia's supply and demand of minerals is contained within this huge country. As Russian demand for superior end products grows and its manufacturing technology develops, however, increased overseas interest and investment may open markets for imports and even unlock mineral sources for export.

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Applying Industrial Marketing Concepts to Industrial Minerals

Todd Harris

Industrial products such as industrial minerals are for the most part distinctly different from those that consumers purchase for their own uses. It follows, then, that industrial marketing—which involves marketing industrial goods and services to commercial enterprises, governments, and other non-profit institutions for resale to industrial customers, or for use in goods and services that they produce—is also different from consumer goods marketing. The distinction is that the latter involves the marketing of goods and services to individuals and families for personal consumption and to wholesalers and retailers in the distribution system. The key to industrial minerals marketing is identifying the intended customer and the nature of that customer. This gives rise to different challenges and approaches in understanding and applying marketing concepts to industrial minerals. Table 1 illustrates some of these challenges in industrial marketing research compared to consumer marketing research.

CLASSIFICATION OF INDUSTRIAL MINERALS

Basically, all industrial minerals can be classified by their use or performance as either chemical or physical minerals. These classifications are simplistic but often determine how a product is marketed: as a commodity that is sold on price or as a specialty product or material sold on performance in its use. Chemical products are those employed primarily as sources of specific chemical elements or compounds. Five basic end uses consume almost all chemical minerals, as shown in Table 2. A major use of these minerals is as chemical raw materials. Such minerals as salt, lime, soda ash, and fluorspar are primary sources of chlorine, calcium, sodium, or fluorine.

An even larger category is fertilizer raw materials, of which phosphates, sulfur, and potash represent more than 90% of demand. A smaller category is chemical process aids, primarily water treatment minerals such as salt, lime, and caustic soda. Another smaller category is ceramic raw materials, most notably industrial sand, soda ash, and fire clay. The basic characteristic of all these chemical minerals is that they are marketed on chemical content and specifications of purity. As a result, they tend to be more like commodities, with similar products available from several sources at comparable prices. Minerals used for metallurgical fluxes are an example.

Physical minerals, the other major classification, are products sold to performance specifications, mainly for their ability to enhance the value and properties of the end product and not as much for their composition (although chemical compatibility with the end-use product is essential). Similar to chemical minerals,

Table 1. Characteristics of industrial versus consumer marketing research

Key Element	Industrial	Consumer
Sample size	Small	Large
Sampling method	Selective for largest consumers 80/20 rule	Random sample
Sample type	Consumers, competitors, government, other factors	Consumers only
Data processing	Computer-based but often unstructured	Highly structured, using statistical analysis software
Statistical significance	Low due to small sample sizes	High
Cross-checking against other factors	Extensive	Little or none
Key factors	Based on expert judgment	Based on statistical selection techniques

Table 2. Major types of chemical industrial minerals

Market Segment	Major Minerals
Chemical raw materials	Salt, phosphates, soda ash, sulfur
Fertilizer raw materials	Phosphates, sulfur, potash
Chemical process aids	Salt, lime, salt cake
Ceramic raw materials	Sand, soda ash, fire clay
Metallurgical fluxes	Lime, sulfur, fluorspar

Table 3. Major types of physical industrial minerals

Market Segment	Major Minerals
Structural minerals	Sand and gravel, crushed stone
Performance minerals	Kaolin, calcium carbonate, talc, mica
Process aids and absorbents	Attapulgite, bentonite, barites, diatomite
Foundry minerals	Industrial sand, bentonite, zircon

these physical minerals have several basic end-use markets, as shown in Table 3. Important mineral properties required in these applications are brightness, particle size, particle shape, specific gravity, hardness, color, absorption characteristics (e.g., ranging from absorption of polymer resins to various fluids), and electrical

Table 4. Business characteristics of various types of industrial minerals

Characteristic	Chemical Minerals			Physical Minerals		
	Chemical Raw Materials	Fertilizer Raw Materials	Ceramic Raw Materials	Performance Minerals	Structural Minerals	Absorbents/Process Aids
Cyclicality	High/Large	High/Large	High/Large	Low/Small	High/Large	Medium/Moderate
Company size	High/Large	High/Large	Medium/Moderate	Medium/Moderate	Medium/Moderate	Medium/Moderate
Number of customers	Medium/Moderate	High/Large	High/Large	High/Large	High/Large	Medium/Moderate
Captive production	High/Large	High/Large	High/Large	Low/Small	Low/Small	Medium/Moderate
Technical service	Low/Small	Low/Small	Low/Small	High/Large	Low/Small	Medium/Moderate
Capital intensity	High/Large	High/Large	Low/Small	Medium/Moderate	Low/Small	Medium/Moderate
Research and development	Low/Small	Low/Small	Low/Small	Medium/Moderate	Low/Small	Low/Small
Marketing intensity	Low/Small	Medium/Moderate	Low/Small	High/Large	Low/Small	Medium/Moderate

conductivity. Except for structural minerals (e.g., construction materials), virtually all categories of physical minerals are smaller markets than those listed under chemical minerals.

Structural minerals are the largest subgroup in the physical minerals category. Sand and gravel and crushed stone are the major products in this market segment. Although sold to specific performance specifications (e.g., American Society for Testing and Materials, U.S. Department of Transportation), the markets for these materials tend to be defined regionally because of their low unit value and broad availability. In addition, because of their volume, structural minerals often are considered a separate segment of the industrial minerals industry.

Performance minerals are the largest segment in terms of the number of different products available, with roughly 15 major sub-product categories. This is the group that often is associated with the use of marketing practices in industrial minerals businesses because of the unique nature of how these products perform and are sold. Key products in this segment include kaolin, ground calcium carbonate, and talc.

Process aids and absorbents are minerals primarily used in drilling fluids or as filter aids and suspension aids; but they also include such end uses as iron-ore pelletizing and animal litter. Consequently, minerals such as attapulgite, bentonite, barite, diatomite, and perlite are the major types of products sold in these markets. Foundry minerals include products such as industrial sand, bentonite, and zircon used in castings and parts for the automotive and aerospace industries. Table 4 gives a comparison of business characteristics of various types of chemical minerals and physical minerals.

If one accepts the notion that specialty businesses are relatively small in volume but with high value added and good growth potential, then such physical mineral businesses as performance minerals, process aids, and absorbents are the most specialized and attractive of industrial minerals from a marketing perspective. Conversely, chemical and fertilizer raw materials, owing to their large market size and relatively low historical growth, are most like commodities and therefore least likely to benefit from added marketing other than to promote the beneficial nature of these materials as part of a consumer awareness campaign.

ADDING VALUE TO INDUSTRIAL MINERALS

Added value is a term often associated with certain classes of industrial minerals. But what does it take to provide a value-added product and, equally important, how does a producer obtain the value it delivers to its customers? Most companies mistakenly look at the value-added portion of a product from a cost-plus perspective, that is, the price that can be obtained above the production cost for that

material. This approach, however, does not ensure that a product can be produced or maintained profitably. It is important to understand how to produce a value-added product, but it is equally important to appreciate how market forces can affect the value added. Four factors generally influence added-value opportunities for industrial minerals: the mineral deposit, the processing method, marketing and market price, and competition.

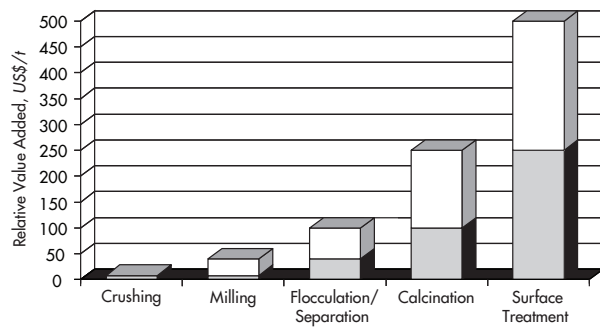
The Mineral Deposit

All opportunities to add value to an industrial mineral begin with the deposit. The geologic environment determines the physical and chemical characteristics of a mineral, which in turn determine the extent that value can be added to it. If a deposit can yield unique products for specialty applications, then the location of that deposit relative to its market is less critical; if, however, a deposit can be used only to produce commodity grades, then production cost and proximity to market are more critical.

Calcium carbonate is a prime example of how quality and location of a deposit can affect a company's ability to add value to its products. Limestone, or calcium carbonate, is one of the most widely occurring industrial minerals in North America, yet only a few high-quality (typically defined as high brightness) deposits are mined at present. The natural whiteness or brightness of calcium carbonate from these deposits gives producers a unique advantage for such color-critical markets as paper, paint, sealants, and plastics.

Processing Method

The second factor to consider in developing a value-added material is the processing method employed. If a mineral has the essential geologic characteristics and can be mined economically, then the next step to adding value is through processing techniques such as crushing, grinding, separation, classification, and surface treatment, as illustrated in Figure 1. The degree of processing will increase the production cost of the material as well as the value of the material, but not always in direct proportion. Reducing the particle size of a mineral is the most common way to derive additional value, but for certain performance industrial minerals, including calcium carbonate, adhering to strict physical parameters such as particle size, shape, and distribution is equally important. These products may also have fairly rigorous chemical or color specifications in addition to physical sizing requirements. The form in which the product is delivered (e.g., slurried, densified, pelletized), the package size, and method of delivery also can contribute greatly to the value-added benefit of the material to the consumer. In many cases, through unique or proprietary processing and delivery systems, suppliers tailor their products to specific customers and end uses to derive the added value.



Courtesy of MineSet Partners LLC.

Figure 1. Relative value-added contribution from the processing of industrial minerals, by stage (unshaded portions of bars represent potential ranges of value that can be obtained from each process)

Marketing and Market Price

The industries purchasing and using these products are diverse, and each has its own specification requirements. In general, however, there is some compatibility among customers within specific industry classifications. For example, paint, plastics, and rubber applications may all use a 3.0- μm ground calcium carbonate product, but raw material specifications for all three industries may be different on several specific chemical or physical parameters. Furthermore, within a given industry group, individual customers' sensitivities relative to specification tolerances and variations from mean datum points can be significantly different (Freas 2002).

The capacity to derive added value from a product often is determined by the market price that a firm can obtain for that material. The market price depends on the supplier's ability to price the product on its value to the customer or end-use product, not the cost to produce it. An important marketing factor that affects a company's ability to price for value is product differentiation. "Sales and service" is one of the key marketing tools commonly used to add value and differentiate a product from competitive offerings. Such techniques include improving packaging and handling, offering application data and other technical information, advertising, and providing reliable and knowledgeable technical service and support. Sales and service is only one aspect of marketing. Marketing value-added industrial minerals involves a strong commitment to research and development and corporate support from the start, followed by the combined efforts of technical service, quality control, sales, and customer service staff. The supplier must be able to demonstrate its products' benefits and unique qualities, and then ensure support for those products. All this rarely is achieved overnight. Companies successful at developing value-added industrial minerals—for example, Nyco Minerals (wollastonite) and Suzorite/Zemex (mica)—spent years researching and developing their product offerings for plastics and other markets before any significant sales were realized.

Competition

Market competition is the other critical factor in the value-added equation. Companies must be innovative in their product development efforts to add value to their products but also stay ahead of their competitors, or the "me too" suppliers. Competition from these in-kind suppliers, and from substitute products, is what ultimately leads to lower prices, reduced profitability, and the subsequent erosion of value added. Suppliers that have the benefits of a quality raw material resource, a unique and cost-efficient process-

ing technology, and a reliable sales and R&D capability occupy the best position to withstand any threats from these competitors.

BUILDING AN INDUSTRIAL MARKETING STRATEGY

The key variables in any marketing scheme include (1) product planning/positioning, (2) pricing, (3) distribution, (4) advertising and promotion, and (5) customer relations and sales. Depending on the nature of the product, the market, and the competition, there may be many other strategic variables such as resource and plant locations, technical service, customer service, and sales schemes. Strategic planning involves making choices in each of these areas and in allocating resources—labor, capital, physical assets—to such elements of the marketing program as new product development, field sales, advertising, and inventories.

In general, suppliers commit more resources proportionally to field sales and technical service elements in an industrial marketing campaign than to media and print advertising when compared to a consumer-goods marketing campaign. This is because industrial customers for any given product, whether an industrial mineral or a piece of equipment, often (but not always) are small in number, readily identifiable, and reached directly and personally more economically. Another consideration is the nature of communications required. Industrial customers may need technical education in the use or application of the product, and sometimes the performance and benefits of that product in the customer's final product. In addition, suppliers need continuous and detailed feedback from their customers on any problems dealing with product quality and performance in order to troubleshoot and also to offer new product innovations.

Product Planning/Positioning

Industrial goods producers often face basic decisions regarding where in the supply chain they want to position themselves and their products. Do they want to function as a raw material supplier, a supplier of components or semifinished products (e.g., masterbatches), an end-product supplier, or all three? Pulp and paper companies, for example, often function as suppliers of pulp and timber, paper and wood products, and converted products. The manufacturer who operates at more than one level in the supply chain is often said to be "competing with its customers." Although this is not entirely an undesirable position, and in some cases can lead to faster market penetration, it does introduce certain conflicts of interest in strategic planning between one market level and another. Efforts to strengthen a position in one sector can sometimes adversely affect marketing efforts in another sector.

Pricing

Pricing conventions used in industrial marketing also distinguish this field from consumer goods marketing. For example, competitive bidding is widely used in industrial marketing on large equipment and raw material supply orders. Paper companies often will bundle their purchasing requirements from several plant locations to maximize their purchasing leverage. Bids often are based on specifications issued by the purchaser, and, in a strict situation (often with government agencies), may be opened publicly and awarded to the lowest qualified bidder. More often the initial bid may serve only to narrow the field of potential suppliers, and negotiations between competing sellers and prospective buyers may proceed from there.

It follows that many contracts for industrial goods are priced individually. Except for commodity products (e.g., chemical raw materials), which are relatively undifferentiated among different suppliers, orders for industrial goods have unique specifications, delivery terms, and quality requirements, with pricing on an order-by-order

basis. This poses some problems for the marketing of the industrial products in both cost calculations and the value to the end user, and also in the determination of competitors' prices.

On many standard items, list prices are a starting point, with discounts offered for the size of the order and class of customer (e.g., distributor, end user) and with extras or markups for special packaging and freight options. Price negotiation is an important part of the industrial buying and selling process. In each case, the relative skill and purchasing power of large and small industrial customers are taken into account when dealing in the free market environment.

Distribution

Characteristically, conflicts may arise when industrial goods manufacturers have to sell to both a few very large customers and many relatively small accounts. This is particularly true in market segments such as the paint and plastics industries. It is typically more economical for a supplier to sell directly to a large buyer. In addition, most companies have key account programs that focus on selling to large buyers both for strategic reasons and to build strong customer relationships. Small buyers are served more efficiently through agents or distributors that carry a larger mix of smaller volumes to supply these customers with less-than-truckload (LTL) quantities and offer faster delivery as necessary. Because some small accounts eventually become large accounts, and because legal issues prevent most suppliers from exercising domain over all the accounts a distributor solicits, suppliers and distributors often find themselves competing with one another at various times for the larger accounts.

The basic problem (or opportunity, depending on one's perspective) stems from the fact that most markets are in a constant state of flux with growth likely to occur. A distribution system for one stage of market development may not be appropriate at another stage. In addition, the system planned for one market segment may not be effective in another, say, where the buying practices and the size and number of customer accounts are different. Company-owned and -operated distribution systems can be effective in certain sectors but often require large, fixed cost or capital commitments (e.g., warehousing, transportation, inventory) that cannot be changed easily or adapted to shifting market conditions.

Advertising and Promotion

Although media or print advertising plays a smaller role in industrial marketing than in consumer goods marketing, it can contribute in the development of a new product or market when it creates a favorable image with potential buyers and the general public. In addition, the right use of advertising can create a favorable environment for the company's field sales representatives, in their direct dealings with potential buyers and customers, and at industry conferences and trade shows. Industrial marketers increasingly use advertising to create product "pull through" by directing their message at the end user to whom the product ultimately is sold. Building stone manufacturers, for example, have long promoted the beauty and durability of their product through architectural publications, encouraging architects to specify these products in their building designs. The purpose of this approach often is to develop brand recognition with the end user (in this case, the architect or commercial real estate developer) to influence them in the choice of materials that contractors will use. One of the most prominent campaigns developed by an industrial marketer to promote its material to the end user was by BASF, which popularized the slogan, "We don't make a lot of the things you buy, we make a lot of the things you buy better." This campaign successfully created end-user

recognition for its functional polymers. Similar advertising strategies ultimately aim to build stronger competitive positions and stronger relations with key customer accounts.

Customer Relations and Sales

In industrial marketing, buyer/seller relationships tend to be both continuous and complex. They often go well beyond sales transactions and very often involve technical assistance to customers, joint product development efforts, and product service. Advertising on behalf of customers, financing their purchases, and entertaining key managers in customer companies are tactics intended to put sellers in a favorable competitive position. Alliances or customer partnerships also may be formed as part of the buyer/seller relationship. This often involves mutual supply and purchase agreements where either party benefits from a product that the other produces or in some cases where one's by-product can be used by the other party. An example of this type of relationship is in the fumed silica (a reinforcing material used in silicone rubber compounds) industry, where the fumed silica operator supplies a by-product acid such as hydrochloric acid to a neighboring silicone rubber producer, who in turn supplies the fumed silica producer with a chlorosilane feedstock (a critical raw material) from the latter's production process. In general, developing such a strong mutual working relationship with one's customer is pivotal to industrial marketing success.

MARKET SEGMENTATION SCHEMES

Market segmentation schemes are an important part of a market plan designed to sort customers into homogeneous groups according to their purchasing practices and product applications. This type of approach provides the essential framework within which marketing strategies focus on the needs of different market segments.

There are at least four ways of segmenting industrial markets like industrial minerals. The first is by product. A kaolin manufacturer might group his customers in terms of the products they buy—filler, delaminated, engineered, calcined. Market segmentation by product is especially helpful if products are highly differentiated technically and where conveying product knowledge to customers is a critical dimension of selling.

The second scheme is by end-use application. Again, using the kaolin manufacturer example, this type of supplier might segment its markets into groupings such as ceramic, paper, and specialty (e.g., paint, rubber, plastics). This segmentation distinguishes customers by the way each uses kaolin and the type of delivery system that each typically requires. This approach can vary greatly from one customer grouping to another. The most critical aspect of selling is to understand the customer's business and the way the product (in this case, kaolin) serves the customer's needs. The set types of classification schemes also are important in promoting manufacturing facilities in an efficient manner to meet various grade requirements of end-use industries and customers.

The third segmentation scheme is to classify by geography. This scheme recognizes the broadly diverse character of market environments worldwide. Marketing industrial minerals to food and healthcare markets in Europe, for example, requires adhering to different standards than those promulgated in the United States or elsewhere in the world. The differences may arise from government controls, monetary conditions, and the wide variations in marketing and supply infrastructures (agents, distribution terminals, etc.). Under these circumstances, coping effectively with the local market environment may be the critical dimension of successful market development.

Finally, markets can be segmented by the way its customers buy. Government agencies buy products and services differently

than commercial enterprises do. As mentioned, government agencies typically require that suppliers submit bids and, depending on the product, a number of different people may be involved in the buying decision. Large companies buy differently than small companies do: large companies often employ more structured purchasing procedures than do smaller companies and are characteristically more price sensitive.

Which scheme for classifying industrial customers is appropriate for each business enterprise will vary from one industrial market to another. Moreover, the scheme that may be appropriate at one stage of market development may be outmoded at another. In general, segmenting the market by product is useful in the early stages when customers need product education; the most essential factor in competitive effectiveness is technical product knowledge and the ability to communicate it to one's customers. In the later stages of market development, a segmentation scheme by product tends to evolve into segmentation by end-use application, when product uses have been identified and product knowledge has advanced to the point that much can be systematized by type of application. At this stage, competitive strength in the market is based on understanding the technical aspects of the customer's business and of the use of their product in its production system. In the more mature stages of market development, when customer education in product and application knowledge are no longer primary concerns, and when major competitors are equals in the services that they provide, buyer segmentation schemes tend to

predominate. The critical element in marketing success at this stage, therefore, is knowing the customer's purchasing procedures and the emphasis placed on factors such as price, availability of supply, product consistency, and quality.

Although the timing and appropriateness of geographic segmentation schemes vary by product and supplier, the conventional application of this method tends to be earlier rather than later in market development. This assumption is based on recognizing that markets in different parts of the world become more alike with time for any given product. Common patterns of product use and of government influences on product forms, pricing, and promotion begin to emerge along with the marketing infrastructure. Most suppliers tend to subordinate geographic distinctions in developing a market strategy and employ a framework for strategy based on end-use application and buyer criteria. The purpose in considering market segmentation schemes is primarily to help understand the many possible approaches along which market information may be gathered, customers classified, and strategies developed. For each particular market served, suppliers should have subordinate strategies for individual customers.

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Due Diligence and Financial Valuation of Industrial Mineral Assets

Ken Santini, James M. Barker, and Edwin H. Bentzen III

INTRODUCTION

A due diligence investigation of an industrial mineral asset may be requested for multiple reasons. For example, the buyer will require it before taking title or a lender will require it before providing financing. There are also different levels of due diligence. A due diligence investigation of an asset could cover all aspects including reserves, mine, processing plant, environmental issues, markets and sales, and financials, among others. Another investigation could focus on a single issue such as reserves. Due diligence investigations of industrial mineral assets identify risks (failure and impact) and assess the facts and factors related to those risks. The due diligence investigation provides competent backup data for a business decision and must be completed before upper management makes a commitment (Santini and Hammond 2000).

Financial valuation may also be part of the due diligence process. One of the commonly used standards of value is *fair market value*, defined as the cash or cash equivalent price at which property would change hands between a willing buyer and a willing seller, both being adequately informed of the relevant facts and neither being compelled to buy or sell. In assessing an asset's fair market value, the three generally accepted approaches to value—market, income, and cost—can be employed. These approaches are based, respectively, on market exchanges for comparable business interest or assets, the capitalization of income, and the cost to reproduce assets (Santini and Hammond 2000).

No set standard on how to design and complete a due diligence investigation exists (O'Driscoll 1999). Each due diligence team should know the key issues from their perspective and focus on those and perhaps exclude others. The discussion in this chapter, although not all-inclusive, does highlight the complex nature of a due diligence investigation.

Industrial minerals are wide ranging, comprising at least 50 major commodities and thousands of products. Classification of industrial minerals is difficult (Austin 1999), so time should be spent developing an understanding of the industry before venturing forth.

This chapter is presented as an outline because a narrative would be extremely long; each section could be a book on its own. It is not the authors' intention to describe *how* to conduct an investigation, but rather to demonstrate *what* could be investigated for each due diligence case. The outline will aid the due diligence team in ensuring complete coverage. It will also aid management in gauging the specific knowledge needed by the due diligence team.

DUE DILIGENCE INVESTIGATION

A due diligence investigation ranges from the very specific, such as a reserve audit, to a complete audit of all phases of an asset (Santini 1999a, 1999b; Toll 1999).

Due Diligence—What Is It?

- It is a process of evaluating a company or asset from a buyer's perspective and preparing to transition it to new ownership.
- It is a process of preparing a company or asset for sale from the seller's perspective and identifying how and when data should be provided to potential purchasers.

Due Diligence—Why Do It?

- Addresses the basic law of business: caveat emptor
- Risks of the business rest on the buyer
- Representations and warranties in the selling documents can address only a limited number of risks
- Identifies risks and assesses facts and factors related to those risks
- Confirms value and investigates upside potential and synergies
- Provides competent backup data for business decisions
- Required by a lender before funds are released

Due Diligence—Who Does It?

- Company management/employees
- Financial advisors
- Consultants/attorneys/accountants/other specialists
- Type and number of people depend on size of the deal, complexity of the asset, and time available for conducting the investigation

Due Diligence—When Is It Done?

- Typically within a specified time period designated by the seller
- Often in a very limited time period
- After signing of a confidentiality/nondisclosure agreement
- Could involve initial phase before submission of an indicative or qualifying bid
- Should always include a detailed investigative phase prior to closing of the transaction

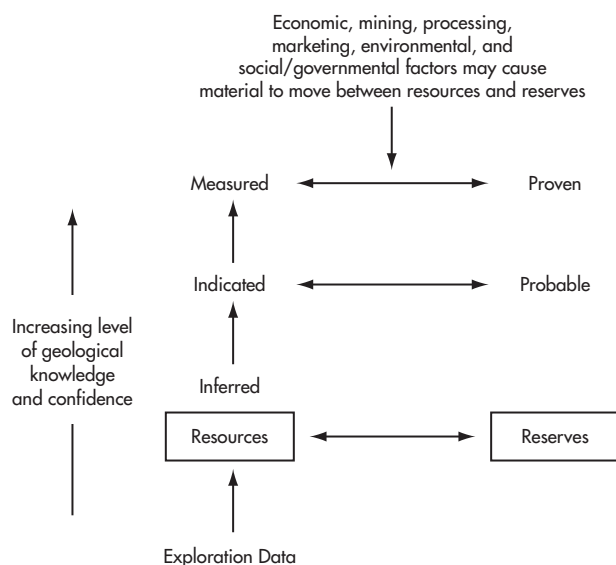


Figure 1. Hierarchy of resource and reserve terms showing relationship among geological knowledge, economics, and other factors. The key point is that resources move into reserves and back to resources depending on nongeologic forces that allow a profit to be made (reserve) or not (resource).

Due Diligence—How Is It Done?

- Visits to data room/seller's office
- Mine/plant/warehouse/terminal site inspections
- Inquiries with regulatory agencies
- Check of court records
- Discussions with suppliers, customers, distributors, agents, seller staff, etc. (if allowed)
- Formal report of findings that includes the following:
 - Proof that assets exist as represented by seller who has the right (title) to sell
 - Identification, description, and assessment of any risks
 - Discussion of strengths and weaknesses of the operation
 - Confirmation of value

Seller's Due Diligence Process—Do's and Don'ts

- Use a financial advisor with expertise in industrial minerals to divest of the asset.
- Have no direct contact with potential purchasers.
- Inform selected company personnel of impending sale.
- Arrange for key personnel to be available during management presentations and data room and site visits.
- Prepare an information memorandum and get a confidentiality/nondisclosure agreement signed.
- Control the process by setting dates and limiting visits:
 - Typically one day each at data room and at operation (travel time additional)
 - Additional site visits as necessary
 - Typically one due diligence team per week
- Ensure that data room is well organized with extra copies of important documents available for potential purchasers.

- Record any documents given to potential purchasers for return if they are not the successful bidder.
- Only allow one company at a time in the data room or at the operation.
- Make sure that all units of an operation are up and running.

Buyer's Due Diligence Process—Do's and Don'ts

- Determine what is for sale, what the time constraints are for data room and site visits, when offers need to be submitted, and what constitutes the bidding process.
- Sign a confidentiality/nondisclosure agreement, and obtain an information memorandum.
- Select members of the due diligence team; use consultants when necessary.
- Have a defined scope of work in hand at the start.
- Distribute the information memorandum to the due diligence team; develop a list of questions to ask during management presentations and data room and site visits.
- Never have direct contact with seller if a financial advisor has been retained.
- Request conversations with customers, distributors, and others, if required.
- Consider a preemptive offer.
- Be prepared to make a counteroffer.

TECHNICAL DUE DILIGENCE

Technical due diligence is focused on the reserve, its extraction, and its processing to products.

- Geology and reserves (Santini 1999c)
- Mine plans and operation (Scriven 1999)
- Process plants and facilities (Bentzen 1999)
- Waste management
- Research and development programs

Geology and Reserves

The reserve audit ensures a potential buyer that the reserves, as presented, are a reasonable and accurate approximation of the tonnage or volume and grade/quality of the reserves present (Figure 1). The reserve audit verifies that the reserves may be used for mine planning or economic analysis.

Geology

- Development of a thorough understanding of deposit geology
- Mandatory field inspection
- Examination of drill core/cuttings/bulk samples and review of analytical data
- Review of geologic reports and reserve studies

Reserve Audit

- It is extremely prudent to reestimate a portion of the reserves:
 - Reestimation area(s) must represent deposit and constitute a minimum of 10% to 30% of reserves.
 - Check reserve audit should be at least 90% of the reserve study.
 - If deviations are found in the reserve check, a total reestimation must be done.
 - It is important to determine reserve expansion potential.

- If the reserve audit is within target range ($\geq 90\%$), accept it as being properly compiled.
- If audited reserve is outside target range, indicate where errors exist and the probable impact on overall stated reserve.
- The audit report should provide independent third-party assurance to the buyer.
- Reserves that pass an audit may be used with confidence in preparing cash-flow projections and in deriving net-present value or internal rate of return.
- In performing an audit, there are four general areas of concern that must be checked:
 - Definitions
 - Parameters
 - Data
 - Procedures
- For each of the four general areas, the auditor must be convinced that the reserve study complies with professional standards and industry practices.

MINING DUE DILIGENCE

The due diligence process at a mine or deposit is best done by an engineer with specific knowledge of ore-body/deposit geology (Scriven 1999). For an undeveloped prospect, the investigation may include feasibility of open-pit, underground, or solution mining.

Mine Data

- Feasibility studies, independent engineering reports, and R&D reports
- Mine plans (1-year, 5-year, 10-year, life-of-mine, etc.)
- Movable reserves:
 - Recovery rate
 - Dilution factors
- Geotechnical issues:
 - Rock mechanics (underground)
 - Slope stability (open pit)
 - Subsidence (solution)
- Production schedule:
 - Ore production and grade/quality
 - Waste production and management
 - Stripping ratios
 - Production schedule related to movable reserves (is life of mine accurate?)
- Ore and waste haulage and transport:
 - Capacity of loaders, trucks, belts, hoists, and so forth
 - Haul distance and cycle times
 - Equipment schedule; age and condition of fleet
 - Adequacy to meet production schedules
- Maintenance schedule, procedures, and policies:
 - Written policy
 - History and schedule
 - Equipment needing frequent repairs or total replacement
 - Spare parts inventory, inventory control, storage, and parts flow from suppliers
- Manning schedule:
 - Crew size, shift schedule, tons per man-shift, and unit productivities
 - Age of workforce
- Utility plan (adequate water, power, air, etc.)
- Ventilation plan (new ventilation shafts, fans, etc.)
- Safety and training:
 - Routine training schedule
 - Policy for obtaining and maintaining certifications
 - Policy for attending classes or technical meetings

Mine Costs

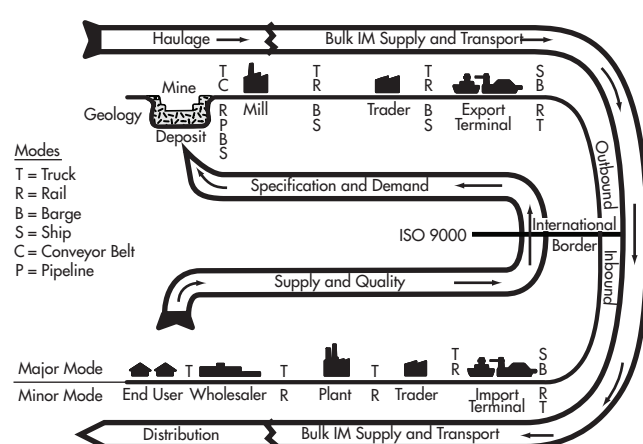
- Fixed and variable operating costs per ton:
 - Labor
 - Equipment
 - Fuel and lubricants
 - Power and water
 - General and administrative
- Capital costs:
 - Replacement
 - Expansion

PROCESSING DUE DILIGENCE

Processing due diligence (Bentzen 1999) involves examining the plant flowsheet, bottlenecks, equipment condition, and replacement costs. This information helps assess how cost competitive the existing plant is compared to similar plants.

Processing Plant

- Flowsheet:
 - Compare original with the actual flowsheet
 - Understand the rationale for recent changes to the flowsheet
 - Describe plant expansion potential and needed changes
- Production capacity:
 - Designed versus actual
 - Availability (percent operating time)
- Production schedule:
 - Production and grade/quality/specifications
 - Waste handling and quantity
 - Matching plant capacity to future production
- Consumption of reagents and other materials
- Review of research proposals and project reports on the process or products
- Manning schedule:
 - Shift size and schedule
 - Age of workforce
- Maintenance schedule, procedures, and policies:
 - Written policy
 - History and schedule
 - Equipment needing frequent repairs or total replacement
 - Spare parts inventory, inventory control, storage, and parts flow from suppliers
- Utility plan:
 - Sources
 - Short- or long-term contracts and renewal costs
- Safety and training:
 - Routine training schedule
 - Policy for obtaining and maintaining certifications
 - Policy for attending classes or technical meetings



Adapted from Barker 1997.

Figure 2. Domestic and export/import transport diagram showing the relationship of the end user to the mine/plant. The various transport modes commonly used at each stage of mineral supply are shown as major (above the line) or minor (below the line). Haulage (off highway) and distribution to end users (delivery) is not usually considered in mineral flow.

Processing Plant Costs

- Fixed and variable operating costs per ton:
 - Labor
 - Equipment
 - Fuel and lubricants
 - Power and water
 - General and administrative
- Capital costs:
 - Replacement
 - Expansion

TRANSPORTATION DUE DILIGENCE

Literature reviews and focus on industrial minerals transport is in Barker and Harben (2004), Barker (1997, 2004), and Barker and Austin (1995). Industrial minerals (IM) transport is complex, often covering multiple modes of transport and frequently crossing international borders (Figure 2). Transport due diligence is not often considered when evaluating other due diligence areas (Barker 1999). An important aspect of due diligence is to see if logistics could be more efficient for incoming raw materials, or outgoing products, or for both. This may be a critical part of the acquisition if increasing transport efficiency helps profitability.

- Cost factors include
 - Type and duration of shipping contracts, if any
 - Mineral or rock produced and form
 - Availability, scheduling, and transit times of desired transport equipment
 - Distance from plant to port, trans-shipper, distributor, or customer
 - Shipment form
 - Handling, docking, warehousing and service companies at each transport change
 - Demurrage exposure

- Insurance and bonding or other risk-avoidance activities
- Government and environmental regulation
- Import and export tariffs and customs
- Cultural or regional differences

• Major transport modes (Table 1):

- Truck (highest cost, most flexible, and most used)
- Rail
- Barge
- Ship (lowest cost, least flexible, least used, but very effective if available)
- Multimodal (use of several modes in one cargo movement)

• Minor transport modes:

- Backpack and pack animal (common in less-developed areas)
- Pipeline
- Postal (small amounts of value-added products)
- Airfreight
- Shipment form:
 - Bulk or packaged (bags, supersacks, cartons, barrels, etc.)
 - Dry or wet (liquid, molten, slurry)
 - Containers

Transportation is more than simply putting products on one mode or another:

- Use of containers and multimodal transport is becoming standard.
- As shipment size or complexity rises, greater care needs to be exercised and use of brokers may be required to lessen risk.
- The buyer must be convinced that the current logistics framework is acceptable or must have a clear idea of the changes needed before acquisition.

MARKETING DUE DILIGENCE

Above all, industrial minerals are market driven, so marketing due diligence is critical (Santini 1999d). Most industrial minerals are sold as raw materials to industry, construction, and agricultural markets. Few (salt, cat litter) are sold directly to consumers. Many individual industrial minerals, through processing differences, yield a variety of products with very different specifications that are sold into very different markets, even when produced from the same deposit with the same mineralogy. For example, glass sand, specialty optical silica, and silica flour for rubber tire manufacture may all come from the same source (Holmes and Santini 1985, 1987 unpublished). Some marketing factors are summarized in Table 2 and in Barker, Austin, and Santini (1999), which includes a detailed outline of an advanced marketing study.

Marketing Categories

- Captive production for use by owner to make a finished product (think internal use)
- Commodity minerals produced in bulk to general specifications (think quantity and low price)
- Specialty minerals produced to meet rigid specifications unique to each customer (think quality)
- Many product lines encompassing both commodity and specialty minerals
- Awareness of where the seller sits in relation to market trends

Table 1. Selected characteristics of transport modes

Characteristics	Truck	Rail	Barge	Ship
Typical U.S. cents/ton-mile	10–25 (high)	2–4 (moderate)	0.75–1 (low)	0.1–0.5 (very low)
Rates and regulation	Negotiated (partly regulated)	Negotiated (partly regulated)	Negotiated (low regulation)	Negotiated (free market)
Flexibility	Very high	Moderate	Low	Very low
Capacity, typical (U.S.)	25 t	100 t	1,200 t	60,000 dwt*
Capacity, typical (Europe)	Varies	Varies	1,500 t	150,000 dwt
Subsidy type	Roadway	Track; land (past)	Locks, waterway	Ports, navigation
Haul containers	Yes	Yes	Yes	Yes
Negotiations (mostly confidential)	Easy; often via regional dispatcher or owner/driver	Hard; railroad often not responsive	Easier with broker, harder without	Less hard with broker, very hard without

Adapted from Barker 1999.

* dwt = dead weight tons.

Table 2. Selected characteristics of marketing commodity versus specialty industrial minerals

Market Characteristics	Commodity Minerals	Specialty Minerals
Place value	High (transport sensitive)	Low (transport insensitive)
Volume	Large	Small
Specifications	Industry standard	End-user customized
Sample evaluation	Short	Long
Properties and uniformity	General	Highly controlled
Testing	Standard	Specific or customized
Substitution	Easy	Hard
Marketing and management style	Business	Technical
Main sales basis	Price (undifferentiated)	Performance (differentiated)
Time to first sale	Short	Medium to long
Rate of market change	Slow to moderate	Rapid to moderate
Need for in-house labs and R&D	Low	High

Adapted from Barker, Austin, and Santini 1999.

Marketing

- Market areas served and market share
- Market studies (company and consultant generated)
- Marketing promotion:
 - Planned and active; results of past efforts
 - Product brochures
 - Trade shows
 - Membership in professional organizations
- Technical sales support:
 - Research and development
 - Technical support offered compared to competitors
- Marketing strengths and weaknesses for each product or line
- Marketing/sales costs

Customers and Distributors

- List of customers
- List of distributors/agents and terms of agreements
- Direct contact with selected customers, distributors, and agents (get approval of seller)
- Volume of sales for company sales staff versus distributors/agents

- Customer service organization and “style”
- Assessment of the company as engineering- or customer-oriented (and whether it should stay that way?)
- Customers satisfaction with products and delivery
- Customers who require ISO (International Organization for Standardization) certification (retain or gain certification?)

Products and Product Lines

- Product types, names, and descriptions
 - Most industrial minerals are marketed by trade name (e.g., Topcoat 90 rather than talc).
 - Consistency and reliable delivery are key success factors.
 - Value-added products have upgraded quality or functionality and thus a higher price.
 - Competitiveness against other producers must be evaluated.
- Quality specifications
- Volume of actual versus budgeted sales
- Annual growth rate (historical/projected)
- Bulk or packaged
- Potential for product substitution

Product Pricing

- Actual versus budgeted
- Pricing structure (contract, spot, list)
- Discounts
- Pricing basis (i.e., f.o.b. or CIF [free on board or cost, insurance, and freight])
- Historical trends
- Forecasts

Sales and Supply Contracts

- Term
- Volume
- Price
- Specifications
- Penalties
- Payment schedule
- Sales revenue

LEGAL AND REGULATORY DUE DILIGENCE

Laws affect every area of an industrial minerals operation, making legal and regulatory due diligence wide ranging (Hayes 1999). These laws affect corporate, tax, environmental, land status, contractual, and a myriad of other functions and factors associated with the asset in question. The various agreements and contractual or regulatory documents uncovered during other portions of the due diligence process will be reviewed by the legal team. Due diligence is seldom purely legal, so consultation is normally done with various appropriate experts.

Legal and Regulatory Due Diligence

- Does the seller own the asset, and have the right to sell it?
- Will the buyer be able to occupy and operate the asset as desired?
- Will the buyer be able to comply with all regulatory constraints to which the asset is subject?
- What current or potential claims exist against the asset?
- Are there guarantees from the seller?

Investigation Effort Required Depends on Nature of Transaction

- Stock acquisition:
 - Buyer acquires the entire entity with all of its assets and liabilities.
 - “Corporate liabilities” include all contract, tort, and statutory claims, even if only remotely related to the desired assets.
 - Such acquisitions typically trigger securities law/regulation issues.
- Asset purchase:
 - It may be possible to separate many of the corporate liabilities from the asset.
 - It is critical to identify those that are attached to asset.

Key Legal Due Diligence Concepts

- Title/limitations on transfer or use:
 - Mining claims, leases, concessions, mining rights, severed rights, water rights, surface access, mill site claims, and so forth.

- Business, personal, and operating property
- Partner/shareholder/foreign entity limitations on change of ownership
- Confidentiality agreements, intellectual property
- Permits, payments, and contracts related to asset operation:
 - Prospecting and mining plans/ permits (including local jurisdiction), permit compliance, and performance bonds
 - Ore/waste haulage contracts
 - Supply/maintenance agreements, equipment leases
 - Royalties; production and property taxes
 - Product sales contracts
 - Distribution/agent agreements
 - Management and union contracts, health and safety plans, retirement obligations
- Corporate affairs:
 - Corporate governance
 - Securities issues (shareholder interactions)
 - Finance
 - Taxes
- Environmental
 - Plans and permits
 - Violations and compliance
 - Bonds
- Litigation
 - Pending lawsuits and threatened actions
 - Judgments, fines, and liens; other regulatory compliance actions
- Seller's representations and warranties

ENVIRONMENTAL SITE ASSESSMENT

An environmental site assessment (Hammond 1999a) is a cost-effective, preliminary, qualitative, environmental investigation conducted to disclose environmental concerns, usually relating to the buyer's risk and liability exposure, prior to the transfer of a property:

- Why: So that environmental hazards or past environmental practices can be identified and disclosed and both the buyer and the seller have a clear understanding of the environmental risks associated with the property transfer
- Where: Any mining or mineral processing property where potential environmental hazards may exist from past or present practices on or adjacent to the site

Reasons for Conducting Environmental Site Assessments in an Acquisition

- To find problems dictating reduction in purchase price or additional indemnification
- To initiate operating practices review
- To identify impediments to permitting/development/production
- To avoid being named the Potentially Responsible Party (PRP)

Phase I Environmental Site Assessments

- Conducted to determine the presence of hazardous or toxic substance contamination at a given site
- Provides sufficient technical information so that a decision regarding the cost/benefit of the transfer can be qualified

- May reveal substances or waste as a result of current or past site activities, unauthorized dumping or disposal, or migration of contaminants from adjacent or nearby properties
- At a minimum include:
 - A review of historical records related to site usage
 - An examination of regulatory agency files and databases
- Includes field reconnaissance of site and adjacent properties
- Characterizes the geological, hydrologic, topographic, and population exposure setting as needed to evaluate potential migration for any contaminants identified
- Normally excludes invasive investigative techniques such as soil sampling, drilling, or groundwater chemical analysis
- Follow formal conduct guidance now provided by ASTM standards E1528-00 and E1527-00

Environmental Site Assessments: The U.S. Regulatory Basis

- Comprehensive Environmental Response Compensation and Liability Act (CERCLA)
- Superfund Amendments and Reauthorization Act (SARA)
- Resource Conservation and Recovery Act (RCRA)
- Clean Air Act
- Clean Air Act Amendments
- Federal Water Pollution Control Act
- Surface Mining Control and Reclamation Act (SMCRA)
- Toxic Substances Control Act
- Occupational Safety and Health Act
- Safe Drinking Water Act
- Hazardous Materials Transportation Act
- Atomic Energy Act
- Endangered Species Act and wildlife regulations

The Phase I Process

- Examination of seller's records and files
- Assembly of maps and geologic/hydrologic information
- State/federal agency interviews and file/database examination
- Air photo examination
- Site inspections and/or overflights
- Operator interviews and document examination
- Interviews with local agencies, residents, and employees
- Documentation
- Conclusions and recommendations
- Business decisions

Contact Agencies in a U.S. Phase I Assessment

- U.S. Environmental Protection Agency
- U.S. Forest Service, U.S. Bureau of Land Management
- U.S. Office of Surface Mining
- State Department of Natural Resources
- State Department of Health
- State Department of Environmental Protection
- Public Utility Commission
- County health department
- Local fire district
- County zoning and planning authorities
- State Conservation Commission

- Department of Public Safety
- State Department of Cultural and Historic Preservation
- Local libraries and historical societies

Regulatory Agency Files and Databases

- Comprehensive Environmental Response, Compensation, and Liability Information System (CERCLIS) registration, assessment, and reports (site location list, event list, National Priorities List [NPL])
- Anthropological, cultural, and historic sites
- Water discharge permits and violations (National Pollutant Discharge Elimination System [NPDES])
- Groundwater and aquifer geology
- Air quality permits and violations
- Solid and hazardous waste disposal (RCRA notifiers, SARA Title III, state permits)
- Mine/operator permits and violations
- Abandoned Mine Land (AML) sites and remediation reports
- Underground storage tank (UST) and leaking underground storage tank (LUST) inventories

Phase I Site Document Review in the United States

- Mine permit or operation plan
- Reclamation plan
- Waste oil management plan
- Regulated waste management plan
- Spill prevention and control plan
- Inert waste disposal permit
- NPDES discharge permit
- Underground injection control permit
- Groundwater discharge permit
- Air emissions permit
- Polychlorinated biphenyls (PCBs) inventory
- RCRA reports
- SARA Title III reports
- Hazardous waste disposal contracts and manifests

Phase I Site Inspections

- Fuel oil storage tanks
- Lubricant/antifreeze storage and distribution
- Maintenance buildings
- Equipment wash facilities
- Hazardous waste collection and storage facilities
- Hazardous materials storage (i.e., solvents, explosives, chemicals, etc.)
- Sewage collection and treatment facilities
- Waste oil collection and storage locations
- Reclamation practices (including what can be disposed of in backfill)
- Underground/surface runoff water control, sediment settling and treatment facilities
- Tailings transport, impoundment, and control
- Laboratories
- Wells and drill holes
- Solid waste disposal sites
- Ore storage sites

- Surplus electrical equipment
- “Bone yards”
- Pits, sinkholes, collapse features, depressions, ground staining, stressed vegetation, refuse piles, discarded containers, barrels, and so on.
- Condition and surface use of surrounding property

FINANCIAL DUE DILIGENCE

Financial due diligence, similar to legal due diligence, affects all areas of an operation and hence requires frequent consultation between team members and other experts. Financial due diligence consists of accounting (Measom 1999), tax (Swearngin 1999), and finance due diligence reviews.

Accounting Due Diligence

- Often overlooked area
- Identification of issues for future financial reporting
- Primary objectives:
 - To verify the completeness, accuracy, and reasonableness of balance sheets
 - To verify that items are not recorded or improperly recorded
- Cash (who keeps it when deal closes)
- Accounts receivable (may need revision language in deal for noncollection)
- Accounts payable (check for unrecorded liabilities)
- Royalties (prepaid or accrued; transferable?)
- Inventories (agree on valuation date)
- Contracts (renewal; transferable?)
- Property plant & equipment (including development and other capitalized costs)
- Mineral reserves (revalue if needed)
- Debt (confirm with creditors; assumable?)
- Equity (stock options, ownership dilution)

Tax Due Diligence

- Tax due diligence involves both the transaction proposed today and projected profit and loss (P&L).
- It focuses on three key areas:
 - Structure of the proposed transaction (taxable or tax free reorganization)
 - Identification and mitigation of hidden tax liabilities
 - Identification and realization of hidden tax benefits

Structure of the Transaction

- Tax-free transactions reduce exposure to hidden tax liabilities and hidden tax benefits:
 - Reduce or eliminate taxes for seller
 - Pass tax attributes to buyer
 - Limitations on future use of tax attributes can be imposed by tax authorities; in the United States, for example, through
 - a. Internal Revenue Code Section 382
 - b. Separate return limitation year (SRLY) provisions
 - c. New regulation creating an “overlap rule” to prevent both Section 382 and SRLY applying to transactions closing after 6/25/99

- Taxable transactions increase exposure to hidden tax liabilities as well as benefits:
 - Consideration should be given to impacts of
 - Income taxes (federal, state, provincial)
 - Sales and use taxes
 - Property taxes
 - Loss of preferred tax status or benefits (i.e., California Proposition 13 grandfather status)
 - Benefits can be associated with step-up in tax basis

Assumption of Hidden Tax Liabilities

- Incomplete tax filings:
 - Verification for all types of taxes related to business activities
 - Verification filings for all jurisdictions in which seller may have conducted business
- Inconsistency in tax filings between buyer and seller:
 - Additional audit exposures
 - Limitation on future filing positions
- Deferred tax liabilities recorded for buyer:
 - Benefits assigned to tax attributes acquired (i.e., net operating loss carry-forwards, capital losses, tax credits)
 - Increase the book value of the acquired assets, therefore impacting future P&L, amortization rates, and so on.

Finance Due Diligence

- Understand current financial structure of the asset (assets, actual and contingent liabilities, shareholder equity, options, etc.).
- Understand deal structure (may trigger audit and other regulatory requirements).
- Identify policies and practices that could have an effect on valuation.
- Perform cash-flow analysis
 - Ability to meet short- and long-term obligations
 - Potential for impairment of assets
 - Reasonableness of pricing and cost structure assumptions

HUMAN RESOURCES DUE DILIGENCE

Human resources (HR) due diligence (Humphries 1999) is a critical area for long-term success of a merger or acquisition. Keeping key personnel on board, on target, and happy greatly eases the almost unavoidable frictions of a successful acquisition.

The Ultimate Scapegoat for a Merger or Acquisition Failure

- Differences in operating style are the most frequently reported post-deal difficulties.
- Cultural incompatibility is blamed for many failures.
- Misconceptions abound:
 - Culture is an intractable force.
 - Culture can be blended gradually.
 - Culture can be changed by preaching.

The Transition Challenge

- Identify the organizational and cultural impediments to an accelerated transition.
- Identify the organizational and cultural constraints on post-transition business performance.

Two Areas of Focus for HR Due Diligence

- Big “HR”—the human resources function:
 - Traditionally, HR is looked at only from standpoint of compliance, risk, and potential negative impact on balance sheet, P&L, or cash flows.
 - It is often an afterthought
- Small “hr”—the human capital of the business:
 - People are generally the “asset” in which significant money is invested.
 - It is essential to look at culture, structure, performance management, and intellectual capital.
 - What is the return on investment (ROI) on people?

Typical HR Due Diligence Areas

- General HR
- General compensation
- Pensions—actuarial
- Compliance
- Postemployment/retirement issues
- Health and welfare
- Executive arrangements
- Organizational and cultural concerns

General HR

- Organizational effectiveness and transition issues
 - HR strategy and structure
 - Efficiency of plan administration
 - Appropriateness of systems; need for new systems
 - Opportunities for outsourcing
- Work force reductions, severance, and payroll tax issues
- Employment compliance, HR policies and procedures
- Labor relations and employee communication
- Cultural factors
- Collective bargaining and unions
- Global work force issues, compensation, and benefits

General Compensation

- Compensation strategy
- Bonus policy and accruals
- Broader stock ownership
- Competitiveness of package

Pensions—Actuarial

- Are all plans identified?
- Are sheltered employees retirement plans (SERPs) active?
- What is plan structure? Whole plan or carve out?
- Are actuarial assumptions okay?
- What are stand-alone expense and buyout/severance impacts?
- Are there unfunded or underfunded international plans?

Compliance

- Are plans compliant with state/national regulations?
- Have filings been made on timely basis?
- Will Pension Benefit Guaranty Corporation (PBGC) be interested?
- Have discrimination tests been satisfied?

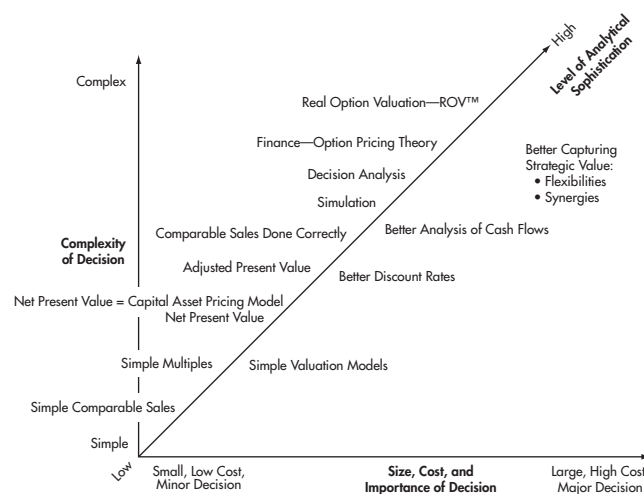


Figure 3. Hierarchy of common methods of asset valuation

- Do stated plan assets actually exist?
- In the United States, are there any Occupational Safety and Health Administration (OSHA) or Equal Employment Opportunity Commission (EEOC) violations?

Postretirement and Postemployment

- If retiree medical/dental and life coverage exist, are there similar issues to pension actuarial?
- Is there reserve for long-term disability (LTD)?
- Is there recurrent severance exposure under FAS 43, particularly for international?
- What is the impact of severance intentions generally?

Health and Welfare

- Current cost of medical and trend—opportunity to reduce cost by managed care or plan design/cost sharing
- Cost of workers' compensation
- Reserve for workers' compensation
- Incurred-but-not-reported (IBNR) reserve for medical and dental
- Cost of insurance coverage

Executive Arrangements

- Employment contracts
- Change in control payments and triggers
- Loss of corporate deductibility and excise tax under Federal Statute 280G
- Accelerated vesting of restricted stock and stock options
- Transition retention and ongoing “incentivization”

VALUATION OF INDUSTRIAL MINERAL ASSETS

No due diligence investigation is complete until the asset has undergone valuation (Hammond 1999b; Hammond and Santini 1999). Figure 3 shows a comparison of some of the common valuation methods.

Valuation Is Part of the Due Diligence Process

- Confirmation of value
- Assessment of risks uncovered during due diligence

- Input for purchase price adjustments (price or deal structure)
- Provision of support for lender appraisals
- Allocation of purchase price for tax and/or accounting purposes

Valuation Defined

- *Webster's*:
 - The act or process of valuing; specifically, an appraisal of property
 - Estimated or determined market value of a thing
 - Judgment or appreciation of worth or character
- Informal:
 - Performed internally or by third party
 - Satisfies business objective
- Formal:
 - Performed by independent third party
 - Often called an “appraisal”
 - Increasingly subject to regulation

Why Do We “Value” Mineral Assets?

- To make decisions (A):
 - Exploration programs
 - Project development
 - Operating strategies
 - Capital budgeting
 - Mergers and acquisitions
- To establish a price (B):
 - Exploration lease/concession bids
 - Asset selling prices
 - Acquisition offers
 - Litigation settlements
 - Financial collateral
 - Purchase price allocation for tax or accounting basis
 - Securities reporting

For A objectives, there may be time to mitigate the impacts of a “bad” valuation; for B objectives, time is often not available.

Standards of Value

- Investment value
- Intrinsic value
- Fair market value
- Fair value

Approaches to Value

- Cost approach
 - Cost to reproduce assets
 - Rarely applicable to mineral reserves
- Market approach (comparable sales)
 - Difficult to identify enough comparable transactions
 - Adjustments usually required to place on truly comparable basis
 - Often best approach for undeveloped resources
- Income approach (cash-flow analysis)

Income-Based Valuation of Industrial Minerals Assets— Developing the Assumptions

Most industrial mineral valuations must be based on a solid market study.

- Market geography:
 - Local
 - Regional
 - Global
 - Current product prices and historical trends
 - Product specifications
 - Impact of competitor capabilities and strategies
 - Potential for product substitution
 - Form in which product is sold
 - Impacts of health, safety, and environmental regulation
- Product pricing projections are usually the most critical model component.
- Different prices for different product forms:
 - Technical specifications
 - Packaging
 - Terms of sale:
 - Existence of a spot or cash market
 - Forward contracts
 - Penalties for out-of-spec material
 - Delivered price and mine netback
 - Transfer pricing when mineral is used as internal feedstock (value-added processing)
 - Export/import tariffs
 - Production capacity sized to the market
- Transportation costs often exceed cost of product:
- Availability
 - Local (e.g., trucking to a railhead)
 - Access to the market (truck, rail, ocean)
 - Transloading and storage
 - Retail distribution
- Marketing costs are often significant for industrial minerals:
- Staff
 - Testing and evaluation (T&E) expense
 - Product quality assurance and control
 - Advertising
 - Inventory

Income-Based Valuation of Industrial Minerals Assets— Building the Model

- Set effective date of the valuation.
- Evaluate lead time for market development that may drive production schedule.
- Escalate/deflate key inputs separately:
 - Product prices
 - Transportation
 - Energy
 - Labor
 - Mine and processing equipment (size to market)

- Include replacement capital.
- Include working capital changes and recovery.
- Include all tax obligations and benefits:
 - Federal, state/province, local
 - Property and use
 - Depreciation, depletion, and amortization shields
 - Tax credits
- Analyze packaging costs:
 - Bags and supersacks
 - Palletizing or containers
 - Quality control
 - Packaging operations
- Assess distribution costs:
 - Warehousing
 - Selling through agents/distributors
- Discount cash flows with appropriate rate for time-value of money.

Income-Based Valuation of Industrial Minerals Assets— Analyzing the Results

- Sensitivity analysis may be useful but often hard to interpret:
 - Production rate
 - Product prices
 - Transportation costs
 - Operating expense
 - Capital expenditures
- As an alternative, build base, upside, and downside cases.
- Probability weight cases to generate expected value.
- Test using comparable sales if data is available.
- “Residual values” can be very important, especially when a low discount rate is assumed.
- Depletion allowances for industrial minerals vary widely for federal taxes in the United States:
 - 5% (sand and gravel) to 22% (fluorspar)
 - Sometimes depends on product form
- Incorporation of financing provisions should reflect “purpose” of the valuation.
- Choose corporate or “stand-alone” analysis.
- Make adjustments to the spreadsheet discounting formula:
 - Mid- or end-of-period
 - Continuous versus discrete

SUSTAINABLE DEVELOPMENT

Sustainable development (SD) is a complex, poorly understood group of social concepts gaining worldwide acceptance as a new way to organize interactions with society. It is discussed in more detail in another chapter in this book. Benefits to mining include gaining and maintaining the critical social license to operate. SD is much more than performing legally required reclamation and calling it sufficient. True SD involves engaging all stakeholders in a given mining venture early, often, and continuously through the entire life of the project with the goal of leaving them with positive benefits after the postclosure activities have been completed. Mining SD is discussed in IIED and WBCSD (2002), Barker (2004), Langer (2005), and Barker and McLemore (2005), among many others. As

Markley (2005) stated relative to the aggregate industry “[SD] activities will move beyond something necessary for success to something necessary for survival.”

A convenient way to quickly evaluate SD is to get answers to the seven questions (IIED and WBCSD 2002; *E&MJ* 2005) commonly used to evaluate an SD program:

- Are engagement processes in place and working effectively?
- Will people’s well-being be maintained or improved during and after the project or operation?
- Will the integrity of the environment be taken care of in the long term?
- Is the economic viability of the company ensured; is the community and regional economy better off not only during operation but into postclosure?
- Is the viability of traditional and nonmarketing activities in the community and surrounding area maintained or improved with the project or operation?
- Are the rules, incentives, and capacities currently in place and will they remain as long as required to address project or operational consequences?
- Does the evaluation show the project to be net positive or negative for people and ecosystems; is a system in place to repeat the assessment from time to time?

SUMMARY

A thorough due diligence investigation before purchasing an asset is necessary to identify both risks and rewards and to determine value. Due diligence applies to both the buyer and seller and has legal ramifications. “Buyer beware” is somewhat tempered by the requirement of the seller to be forthcoming. The buyer has an obligation to understand the asset, so due diligence is required. In addition, for a successful transaction to take place, the buyer must be willing to pay a price for the asset that is acceptable to the seller, under terms and conditions acceptable to both parties.

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Rail Transportation of Industrial Minerals

Charles N. Speltz

BACKGROUND

The history of railroading began in England, in 1797, with the invention of the steam locomotive. U. S. railroading followed shortly thereafter, in 1827, when the first railroad was constructed in the United States—the Baltimore and Ohio. In 1869 the United States was connected coast-to-coast by the first transcontinental railroad. Others followed until, in the zenith of U.S. railroading in 1916—the United States could boast of 254,000 miles of rail (Association of American Railroads 2004b).

By 1980, however, U.S. railroads were in trouble. Excessive regulation by the Interstate Commerce Commission (ICC), coupled with onerous work rules promulgated during the period of regulation, had driven the railroad industry to the brink of insolvency. Twenty-one percent of the nation's track mileage was operating under the protection of bankruptcy courts. Infrastructure maintenance and improvement had been deferred or ignored. The railroad's rate of return on investment was less than 3% (Ekelund and Hebert 1988).

Furthermore, the response of the railroad industry to business sectors that did not generate adequate rates of return was to decrease service, or raise prices, until they became unprofitable or were overtaken by another industry. Witness the loss of passenger service to the airlines, the loss of small-package delivery to intercity buses and parcel delivery services, and the loss of less-than-carload shipments to interstate truckers.

In 1980, the U.S. government passed the Staggers Rail Act. This act eliminated most of the regulatory authority held by the ICC. The act recognized that the railroads no longer had a monopoly on surface transportation and that truck and river transport could and did compete with rail. It also recognized that two-thirds of intercity freight was being moved by non-rail carriers and that if the railroads were unable to increase their rate of return on investment, then the rail system of the country would continue to deteriorate (Ekelund and Hebert 1988).

Although Staggers did not totally deregulate U.S. railroads, the act gave the railroads the opportunity to eliminate inefficient revenue-producing track; enabled the railroads to more easily merge; and most importantly, freed the railroads to confidentially contract freight rates without governmental review or approval. Deregulation has improved the rate of return for railroads, has financed deferred maintenance, and in general terms, has allowed the railroads of the United States to return to health.

Problems still exist, but they are now largely caused by the monopolistic structure of the nation's rail network, which has concentrated itself through merger from 40 Class I railroads in 1980 into 6 Class I railroads today. Some believe that this concentration has resulted in monopolistic behavior by the railroads resulting in problems for customers as well as operating inefficiencies for the rail system itself.

Most complaints involve poor service, high costs for services rendered, or both, and these directly affect the industrial minerals industry. Incorrectly routed, lost, or delayed railcars seem to be the most prevalent complaint; however, the seemingly complete inability to reliably deliver railcars on schedule is a close second.

Most significant is the so-called practice of "differential pricing" wherein the railroads are perceived to "price gouge" customers served by a single railroad to make up revenue that is lost to customers served by more than one railroad (Baker 2003).

Many critics of the existing rail system feel that the best solution for the nation's railroads is to create unbridled competition by permitting "open access" or "competitive access," wherein any customer served by a single carrier could receive competitive rail service by other rail carriers. Needless to say, U.S. railroad operators deny that they price gouge some customers in favor of others and argue that any system of open or competitive access would be confiscatory and not serve the public good.

Regardless of the problems facing the rail industry today, when shippers have many transportation options, the railroad is, far and above, the most significant and economically viable transportation means for the U.S. minerals industry.

In 2003, U.S. railroads transported 958 billion metric tons (1,055 billion short tons) of mineral commodities including coal, metallic minerals, finished products, industrial minerals, and sand and gravel. In the same year, the minerals industry earned U.S. railroads revenues of \$11.8 billion, approximately 31% of the total revenues earned by the entire U.S. rail industry.

In 2004, U.S. railroads delivered 1,509 billion metric-ton miles (1,663 billion short-ton miles) of freight service at an average cost of 2.59¢ per metric-ton mile (2.354¢ per short-ton mile) (Association of American Railroads 2004a).

This average cost of 2.354¢ per short-ton mile demonstrates the importance of rail transportation to the minerals industries. Relative to other commodities, many minerals or mineral products (especially industrial minerals) are low-value commodities. Freight

charges are often several times greater than the cost of the mineral. Because of this generally low value of industrial minerals, low-cost, economical surface transportation is critical to the well-being of the minerals industry and the nation.

THE RAILROAD AS TRANSPORTATION

Rail transportation is one of four domestic methods for long-distance surface transportation of mineral commodities, the others being over-the-road trucks and navigable river and coastal shipping.

Rail movement of goods, like water transportation, is an inflexible method of transportation. Water transportation can serve only those locations with access to navigable water. Rail delivery can only serve those locations that have rail access. Regardless of economics, or desirability of rail service, if a location is not served by a rail system, it cannot avail itself of the generally lower prices provided by rail transport. Construction of new rail service is frequently not practical because it is expensive and must be paid for by the customer. The rail companies no longer pay for new rail construction.

The inflexibility of the rail system affects the shipper in two ways. First, a truck can generally load and discharge at any source or destination—rail cannot. Second, truck shipments can be scheduled; train delivery dates can only be approximated.

Further, rail service is not time sensitive. An average train consists of 48 cars, most carrying differing commodities, shipped from different origins, and consigned to different destinations. This heterogeneity demands that the train be assembled at some central point of origin, perhaps disassembled, sometimes more than once, at some intermediate station, and finally classified for local delivery to the final destination. A truck can be driven directly from one point to another and a very precise schedule can be maintained. The additional handling required by rail shipments creates a situation in which schedules are approximate at best and completely fallacious at worst.

RAILROADS IN THE UNITED STATES

Three classes of common carrier and one class of noncommon carrier railroads operate in the United States as defined by the Surface Transportation Board (STB); the three classes are defined by annual gross revenues for purposes of accounting and reporting (Bureau of Transportation Statistics 2004):

- Class I. Rail companies with annual operating revenues of \$277.7 million or more are usually termed “mainline” railroads.
- Class II. Rail companies with annual operating revenues of more than \$40 million but less than \$277.7 million are usually referred to as “regional” railroads.
- Class III. Rail companies with annual operating revenues of less than \$40 million are generally called “short-line,” “local line-haul,” or “terminal” railroads.
- Private. Rail companies that are privately owned and not common carriers are private railroads.

Class I—Mainline Railroads

There are six Class I (mainline) railroads operating in the United States (Baker 2003):

1. Burlington Northern Santa Fe (BNSF)
2. Norfolk Southern (NS)
3. Union Pacific (UPRR)
4. Canadian National (CN)/Illinois Central (IC)
5. CSX Transportation (CSXT)
6. Kansas City Southern (KCS)

Additionally, the Canadian Pacific Railroad, which owns the Soo Line and two Mexican railroads, Ferrocarril Mexicano and Transportacion Ferroviaria Mexicana, would be considered Class I railroads if they operated in the United States.

Class I railroads are common carriers. They are interstate railroads, with BNSF and UPRR dominating the region of the United States west of the Mississippi River; the NS and CSXT monopolizing the region east of the Mississippi; and KCS and CN Railways being principal players in the vital north-south corridor, more or less paralleling the Mississippi River.

Each of the Class I railroads is a monopoly. Each owns its rights-of-way and its tracks and equipment, and each maintains the exclusive right to operate over its system. Each railroad has complete freedom to raise or lower freight rates, accept or refuse new business, and deny customers competitive rail service from other carriers. Only when it is not advantageous to exercise their monopolistic power, specifically in the area of “reciprocal switching,” will railroads choose not to exercise their monopolies.

Monopolistic power was diluted by the STB as a condition of merger under the terms of the Staggers Act. If a customer was served by more than one rail carrier before a merger and the result of the merger would deny that customer access to multiple carriers, mergers were structured by the federal government so that those customers having prior service from multiple rail carriers would still have that multiple service after the merger. “Switching rights” were extended to competing rail carriers so that those customers deprived of multiple rail carrier service as a result of the merger would regain that multiple service.

Furthermore, many mainline systems granted to other competing carriers, as additional conditions of merger, operating rights over parts of their systems. Such grants are termed “trackage rights” and give the competing carrier the right to use tracks it does not own for a fee. Such rights usually prohibit the owner of those rights from serving any existing customers that did not have multiple rail system service before the merger.

For example, in 1995, when the Union Pacific merged with the Southern Pacific, the BNSF was granted trackage rights from Denver to the San Francisco Bay area and specifically, in conjunction with the Utah Railroad, was granted rights to the eastern Utah coal fields and other Utah industries that previously enjoyed multiple rail carrier service.

Mainline systems generally cooperate well with one another when cooperation suits their purposes, but the shipper cannot expect that cooperation to be extended to their private requirements.

In general terms, mainline systems will compete with one another when competition is direct, but no system, mainline or regional, will reduce its rates unless it finds that rate reduction in its own best interests.

Developing a totally new mine or processing facility is the only way to gain service using trackage rights held by an alternate carrier who does not own the track. The new mine or processing facility must install new rail access. Use of previously existing rail access is sufficient reason for the track's owner to deny use of the alternative carrier's trackage rights. Alternatively, trackage rights can be used by an existing facility if that existing facility did not previously use rail transportation and if new rail access is constructed.

Managerial Tip 1

Railroad marketing does not accept hypothetical or possible competition as reality. A threat, written or verbal, to change transportation schemes is ineffective. Competitive pricing is spurred only by the actual commencement of shipping by an alternative method, by truck or rail, or through the construction and use of a trans-loading terminal.

Managerial Tip 2

The most economical scheme of rail shipping is via a single line. Single-line shipments are referred to as a “single-line haul” or “direct haul.” On occasion, single-line hauls are termed “local,” even when the delivery is interstate. When a direct haul is not possible, railroads will attempt to maximize the distance a shipment moves on its lines, even if an alternative route is more advantageous to the shipper.

Rail movements using two separate carriers, end to end, will cost the same as if the movement were made on two separate, unrelated, unconnected, and independent systems. Exceptions exist; if one of the rail systems is attempting to increase traffic on the rail segment to be used, better pricing may be available. Alternatively, if competition exists, perhaps an alternate route using another carrier, most carriers will accept some level of revenue over nothing, assuming that the carrier has any desire for the business.

Class II—Regional Railroads

Regional railroads, which can best be described as small mainline railroads, are common carriers. They are indistinguishable from Class I railroads except for geographic extent and total gross revenue. Regional railroads serve smaller geographical areas but are subject to the same operating rules as Class I railroads.

Class III—Short-Line Railroads (Local Line-Haul, Switching, and Terminal Railroads)

Short-line railroads, including local line-haul and terminal railroads, are those small rail systems that cannot be economically operated by the mainline or regional carriers. They frequently consist of sections of mainline railroad that would have been abandoned by the Class I or II railroads if not acquired by an independent operator.

Most short-line railroads were created because the rail segment had too few customers or low traffic volume and was unable to generate sufficient revenue to justify continued operation under the ownership and work rules of a mainline or regional carrier.

Switching railroads are created to provide switching services to a specific area in which the Class I railroad is unable to offer cost-effective service. If a switching railroad services a port, it can be termed a terminal railroad. The terms switching and terminal railroads are frequently interchanged.

As an example, Rail Link, Inc., operates a switching, or terminal, railroad at the Port of Greater Baton Rouge in Louisiana. Originally the port was switched by the Union Pacific, but the Union Pacific was unable to economically provide the level of service demanded by the port authority (the Greater Baton Rouge Port Commission).

Other short-line railroads were created when mergers between two mainline or regional railroads provided parallel service to common destinations. One of the two parallel routes became redundant and was slated for sale or abandonment.

As an example, the Atchison, Topeka and Santa Fe Railroad had tracks from Fort Worth, Texas, to Brownwood and Temple, Texas, with a line between the latter two towns. The westernmost route, from Fort Worth to Brownwood, was deemed surplus and was sold to the South Orient Railroad.

Most short-line railroads are captive to the Class I railroad that permitted their creation. This captivity to the Class I, which created the short line, is termed a “paper barrier.” A captive short line is “closed” to interchange with other carriers. For example, the San Luis and Rio Grande Railroad operating from Walsenberg to Antonito, Colorado, is a short line created from Union Pacific assets. Although the San Luis and Rio Grande terminates at Walsenberg, an interchange point with the BNSF, it is captive to and interchanges only with the Union Pacific. It is closed to the BNSF.

Exceptions do exist. If the rail line converting to a short line interchanged with multiple carriers before becoming a short line, it will continue to interchange with multiple mainline systems. For example, the Montana Rail Link, originally belonging to the Burlington Northern system, operates from Billings, Montana, to Spokane, Washington, and interchanges with the BNSF at four separate points; with the Montana Western at Garrison, Montana; and with the Union Pacific at Sandpoint, Idaho.

Short lines are smaller, less bureaucratic, have fewer work-rule provisions, and are often more flexible than mainline systems. In most cases, a short-line railroad is capable of offering more personalized problem-solving service than the larger railroads.

Private Railroads

Private railroads are not common carriers, are generally dedicated to serving a single customer, and have been purchased or constructed specifically to serve that customer.

A mainline system may want to abandon a short, underperforming, inadequate-revenue-producing branch line, perhaps a line serving a single customer. But the line is too short or economically incapable of supporting a short-line railroad. Any customer situated on such a branch line may be forced to acquire the track or be denied future rail service.

Alternatively, a customer captive to a single carrier may find it advantageous to construct a private railroad to connect with a second carrier. Construction of the branch line creates instant competition and should serve to reduce freight rates.

PRACTICAL CONSIDERATIONS OF THE FOUR CLASSES OF RAILROADS

Mine operators cannot choose their rail service providers because mines are located where the mineral to be mined is found. Most mines are remote and are indeed fortunate to have any rail service at all.

If a mill or processing plant is planned and precise location is not an issue, that facility should be constructed with direct access to two rail systems. As an alternative, the facility should be sited on a short-line railroad that provides access to multiple carriers. Competition between two carriers will keep transportation costs lower than if the facility is captive to any single carrier.

Competing railroads work well together when given no other choice. The originating railroad defines the route, and will attempt to maximize the distance that a shipment travels on its system and minimize the distance traveled on a competitive system. If the destination is open to reciprocal switching, the shipper will likely suffer no harm. If the destination is not open to reciprocal switching, however, the receiving carrier will define its portion as a line haul

and likely charge a disproportionately higher tariff for completing the shipment.

In such a case, the shipper may be able to negotiate some other intermediate interchange point so that both carriers will receive a more proportionate share of the transportation charge. The originating carrier has little or no incentive to shorten its share of the route because its division of the total revenue is proportional to its share of the route. When confronted with the choice to cooperate with another rail carrier or lose the business, railroads are likely to decide that a little less revenue is better than no revenue at all.

RAILROADS AND THE INTERNET

The Internet has radically changed the relationship between railroads and their customers. Before the Internet, all business between the railroads and their customers was conducted by telephone, fax, or surface mail. Surface mail was slow, faxed instructions proved to be unsatisfactory, and telephone instructions were often misinterpreted. The computer, modem, and Internet changed everything, making instantaneous communication possible and creating a permanent record of instructions sent and received. No longer can a verbal miscommunication serve as an excuse for mistaken instructions.

All six Class I rail systems, as well as the two Canadian systems, Canadian Pacific and the Canadian National, have Web sites. The two Mexican railroads do not. All Class I and II railroads are rapidly converting exclusively to Internet instructions and orders. A customer using verbal or written orders or instructions, for whatever reason, can expect to pay a fee for such usage.

Web sites of the various railroads and their capabilities are given in the Establish Business Relationship section of this chapter.

RAILROAD EQUIPMENT (ROLLING STOCK)

Railroad equipment or “rolling stock” exists to provide virtually any service that the mineral industry requires. Operators use open-top cars when the cargo is not weather-sensitive, covered cars for weather-sensitive materials, tank cars for liquids, low-volume cars for dense materials, high-volume cars for low-density products, and specialized cars for unusual situations.

Crude mineral transportation is most commonly accomplished with open-top cars, either gondolas or hoppers. Gondolas are either “low” or “high” sided. Hoppers are open for transport of crude, non-weather-sensitive products or covered for transport of processed, dry, or finely divided mineral products.

Gondolas

All gondolas are open-topped and subject to weather, wind erosion, and contamination from thrown objects. There are no restrictions to cargo type, except that the shipment of hazardous wastes or materials requires special permission.

Low-side gondolas are referred to as “scrap cars” because one of their primary uses is to transport scrap metal. Low-sides are available in two lengths, 52 ft and 65 ft, and have an overall height of less than 9 ft. Low-sides are often delivered contaminated or dirty from previous service. Although railroad regulations require that cars be returned sufficiently clean to reload with another commodity, reality dictates—particularly when the car has been in scrap service—that corners, dimples, and structural irregularities sometimes trap contaminants.

Low-side gondolas are most frequently used to ship oversize materials, such as riprap or dimension stone, and difficult-to-unload materials such as bauxite, clay, iron ore fines, and nonferrous metal concentrates.

Low-side gondolas are frequently in poor structural condition with moderate to severe damage to the sides and bottom of the



Courtesy of Charles Speltz.

Figure 1. Low-side gondolas loaded with bauxite

cargo box from loading and unloading of scrap metals, steel, pipe, and other heavy materials. The side walls of the car are often bent outward, a condition referred to as “bowed out.” Although not specifically harmful to the commodity being loaded, a bowed-out car provides an opportunity to load cargo off-center. Off-center loading is discussed in the Receive and Load Cars section in this chapter.

Low-side gondolas must be loaded and unloaded from the top. Common machinery for unloading gondolas are crane-mounted clamshell buckets, hydraulic excavators operating from the side or above the car, and specially equipped backhoe tractors or excavators mounted on top of the car (Figure 1).

Hydraulic excavators can operate from the top of the cargo if the cars are loaded to full, visible capacity. If not loaded in this way, the excavator must operate from movable decks set on top of the car. Either technique is a low-to-medium-unloading system capable of unloading 10 to 20 cars in a single 8-hr shift.

Specially equipped backhoe tractors, riding along the side rails of gondolas, furnish a very safe, economical method of unloading gondolas. Because of the maximum size of the bucket on backhoes, however, daily output is less than that achieved by hydraulic excavators.

Because of their inability to reclaim material from the ends and corners of the cars, clamshell buckets or hydraulic excavators working over the side of the car require additional labor, or a small skid-steer loader, to thoroughly clean the cars. Neither technique is a high-volume unloading method and neither is recommended for sustained operations.

High-side gondolas, sometimes referred to as “bathtubs,” are 11 ft tall or higher and are normally used to transport lower density materials such as coal or coke (Figure 2).

High-side gondolas are frequently unloaded by rotary dump wherein the entire car is turned upside down and the cargo is discharged through the top of the car. Top-mounted backhoes or hydraulic excavators operating from the top of the car are also used.

Hydraulic excavators operating from alongside the car are not acceptable for unloading high-side gondolas because the boom of the excavator cannot reach the bottom of the car.

Open-Top Hoppers

Open-top hoppers are the most common railcar used to transport crude mineral commodities (Figure 3). Frequently referred to as “coal cars,” open-top hoppers are mainly used to ship coal, sand and gravel, and crude minerals and ores. Open-tops have a volume between 3,610 and 4,000 cu ft and carry between 93 and 115 net



Courtesy of Charles Speltz.

Figure 2. High-side gondola equipped with rotary couplers



Courtesy of Charles Speltz.

Figure 3. Open-top, cross-dump hopper

short tons. Open-tops, like gondolas, are subject to weather, contamination from thrown objects, and wind erosion of contained cargo.

Open-top hoppers are not acceptable for oversize products such as riprap, mine-run, uncrushed rock or ore; non-free-flowing materials such as bauxite; or wet, mineral concentrates.

Open-top hoppers are equipped with doors on the bottom of the car. Hoppers with doors mounted perpendicular to the axis of the car are termed "cross-dump hoppers," and those with doors parallel to the axis of the car are called "side-dump hoppers." Side-dump hoppers are primarily used for ballast distribution and are not usually available for commercial applications.

Some open-top hoppers are equipped with rotary couplers that allow the car to be completely overturned and emptied without uncoupling the cars. Rotary dump cars are usually identified by a solid color band on each end of the car (Figure 4).

Open-top hoppers are constructed with 33- or 45-degree end plates. The shallower end plates are applicable to the shipment of gravel; clean, crushed stone; and other free-flowing materials. The steeper end plates should be used for coal, coke, sand, soil, and other non-free-flowing materials. Railroad managers have created mainline systems with a mixture of open-top hoppers. Carriers are unwilling to guarantee delivery of cars with a specified end-plate slope; the customer must use what is delivered.



Courtesy of Charles Speltz.

Figure 4. Bottom-dump hopper with rotary couplers (note that one end of the car is painted white, signifying that the car is equipped with rotary couplers)

Open-top hoppers require supervision when unloading is complete. Railroad regulations require that all doors be closed and locked before release of empties. Although hopper doors are often difficult to close and lock, level of difficulty is no excuse for leaving doors open or unlocked. Open doors can swing violently, snag the rail, or break loose from the car. They are a recognized safety hazard and have even caused derailments.

Switching crews have instructions not to move cars with open doors. Demurrage (see Accessorial Charges section) incurred as a result of open doors is difficult to protest. Further, rail tariffs allow for extra charges if the railroad must close doors.

When confronted by doors that cannot be closed and locked, the car should be reported as "bad order" because of defective doors. The railroad is then responsible and has no recourse to the customer.

Managerial Tip 3

Covered Hoppers

Covered hoppers are completely enclosed, sealed, weatherproof, windproof, and secure from thrown objects (Figure 5). Covered hoppers are loaded from the top through longitudinal or circular doors aligned on both sides of the top of the car. Cargo is discharged from sliding gate doors arrayed along the bottom of the car.

Covered hoppers range in volume from 2,000 to 5,000 cu ft and have capacities up to 110 net tons. They are most applicable for transportation of dry, fine mineral such as cement, lime, bentonite, phosphate, perlite, or soda ash.

Pressure Differential (Discharge) Cars

On first glance, pressure differential cars (pneumatic or "PD" cars) look like covered hoppers except for the plumbing found on the bottom of the cars (Figure 6). In effect, PD cars are large "pressure pots" from which the contents of the car are removed pneumatically. Low-pressure air, usually between 7 and 10 psi, forces the contents of the car downward through a metering device, either a



Courtesy of Charles Speltz.

Figure 5. Covered hopper

gate or a rotary valve, into a high-volume stream of low-pressure air that delivers the product to storage, either truck or silo.

Low-pressure air is provided either from a stationary source, usually a high-horsepower root blower, or from the delivering truck using a transmission-mounted “power-take-off.” In most cases, because of its higher power and higher air volumes, a stationary source of air delivers faster, more economical delivery of product.

PD cars are most often used for delivery of portland cement, fly ash, hydrated lime, and any other dry, finely divided products. Although materials as coarse as $\frac{3}{4}$ in. may be unloaded pneumatically, the efficiency of the operation is indirectly proportional to the size of the product. A given stream of low-pressure air will move more finely divided than coarse material.

Pneumatic transportation should not be used when product degradation is an issue. For example, oil-well proppant (frac) sand, even though delivered and used pneumatically at the job site, should not be transported in PD cars because the unloading process will degrade particle size and generate undesirable fines.

Rail companies rarely, if ever, have pneumatic cars available as part of their car fleet. In most cases, PD cars are owned or leased by the shipper and they are almost always dedicated to shipping a single product. Exceptions to this rule exist when the empty railcar can be completely cleaned (usually water washed), before reloading with a different product or where the products are mutually compatible, such as portland cement and fly ash.

Tank Cars

Tank cars are tanks on railway wheels and are used to transport liquids (Figure 7). Most commonly used to carry oil, asphalt, liquid chemicals, and other petroleum products, tank cars are also used by the industrial minerals industry to transport brines.

Specialized Cars

Bottom-Dump Gondolas

This type of gondola (Type E-equipped gondola) is rare, almost extinct. If any still exist, they are almost certainly in private fleets.

Drop-End Gondolas

These are available in both low- and high-sided configurations, and are equipped with a lockable door on each end of the car. Drop-ends allow a small tractor to enter the car from the end and unload cargo.

Like open-top hoppers, all doors on covered-top hoppers must be closed and locked prior to shipment. Unlike open-top hoppers, covered hoppers have doors on both the top and bottom; both sets must be closed and locked. Open doors on the top have blown off. Because of their cantilevered construction, open doors on the bottom have become warped, bent, and unclosable. Warped bottom doors permit leakage and loss of product. Shippers are responsible for accepting cars tendered by a railroad for loading. When a car is loaded and billed, the shipper acknowledges that the car was suitable for use, and any leakage or loss of product is the shipper's responsibility.

Managerial Tip 4



Courtesy of Charles Speltz.

Figure 6. Pressure differential car



Courtesy of Charles Speltz.

Figure 7. Tank car



Courtesy of Charles Speltz.

Figure 8. Side-dump gondola

Drop-end gondolas are most commonly used to carry wood products such as wood chips or sawdust, but they are also used to transport mineral products.

Side-Dump Gondolas

Sometimes referred to as “riprap cars,” these gondolas are used to carry and discharge oversized materials, most commonly mine-run ore or riprap (Figure 8). Side-dumps are equipped with pneumatic cylinders that rotate the entire car body while simultaneously lowering the side walls. Cars can only be discharged where high-pressure (100–125 psi) compressed air is available, either from a locomotive or from an external supply.

Side-dumps allow cargo to be discharged alongside the track at any location served by rail. They are most frequently used to deliver riprap or ballast to the point of use without unloading and transshipment from an intermediate location.

Railroad companies have a limited supply of side-dump gondolas and are reluctant to allow their use for any nonrailroad application. Most side-dumps are privately owned, available from rail-served open-pit mines, and generally in poor physical condition. In addition, side-dumps are heavy with substantially higher tare weights than either gondolas or hopper cars.

Iron Ore Cars

Iron ore cars (“taconite” or “T1” cars) are manufactured to handle dense materials such as iron ore, taconite pellets, or metal concentrates. They are short, usually about 33 ft long (versus 55 ft for a standard hopper or gondola), are more heavily constructed than other cars, and are equipped with heavy-duty doors to withstand dense materials.

Taconite cars are generally not available for commercial use outside the iron ore industry.

Molten Sulfur Cars

Molten sulfur cars are used to transport sulfur in a molten state. The cars are equipped with internal steam pipes to re-melt the contents of the car. The melting temperature of sulfur is 245°F, and it will remain molten for a considerable period after loading. The exact duration depends on outside temperatures.

THE RAIL SHIPPING PROCESS

The shipping process consists of 11 steps:

1. Establish business relationship.
2. Determine car type.

3. Determine freight rates.
4. Order cars.
5. Receive and load cars.
6. Release loads and bill.
7. Monitor and trace cars.
8. Receive loads.
9. Unload cars.
10. Release empty cars.
11. Pay freight bill.

Establish Business Relationship

The initial step in dealing with any railroad is to establish a business relationship that includes credit arrangements. The initial portal into a railroad system is via the customer service department or the World Wide Web site for each railroad.

Although the customer service departments will not actually provide such entry, they will refer the new shipper to the appropriate departments to discuss shipping needs, arrange credit, provide instructions for entry into the appropriate electronic commerce programs, and generally facilitate the creation of the business relationship.

The customer service phone number and Web home page for each mainline railroad follow

UPRR	(800) 272-8777, www.up.com
BNSF	(888) 428-2673, www.bnsf.com
CN/IC	(800) 601-7630, www.cn.ca
NS	(800) 635-5768, www.nscorp.com
CSXT	(577) 744-7279, www.csx.com
KCS	(800) 282-8700, www.kcsi.com

A knowledgeable sales representative will be assigned depending on the size of the customer and the railroad system to be used. The representative will assist the customer in all steps involved in building a business relationship with the railroad.

Determine Car Type

The type of railcar to be used is based on the product to be shipped and the method of loading and unloading. Once the car type and capacity is selected, determine if the originating railroad can supply the cars. If another railroad is involved, can the other railroad furnish the cars? Are private cars available? Should they be purchased or leased? What is their monthly cost? What are the lease terms?

Railroad companies will not construct or pay for new access to projects. In the past, the customer desiring new access paid for the construction of that access, and the rail carrier offered an allowance based on traffic actually shipped to pay for the construction. Such an allowance no longer exists. There is no reference to such an allowance in any railroad publication.

Such an allowance is available, however, as part and parcel of any negotiations involved in negotiating rail service for a new project. Any allowance would be given as a freight rate reduction, not as a construction allowance.

Sales personnel for the railroads will not voluntarily offer such an allowance, but if the railroad wants the business, particularly if there is competition with another carrier, such an allowance is available and negotiable.

Managerial Tip 5

Table 1. Types of freight pricing documents

Class of Document	Type of Document	Characteristics of Document
Public	Public tariffs	Available on Internet
	Open quotes	Group rates
	Price lists	Point-to-point
		Mileage rates
Private	Contracts	Confidential
	Letter quotes	Single-party
		Single-commodity
		One origin
		One destination

Does the railroad provide any price relief if private cars are used? A full-service lease (triple net) includes lease cost, car maintenance, property insurance, and taxes; leases are available in any combination. Does the movement or contract justify purchase or lease?

Determine Freight Rates

There are two types of pricing agreements for determining freight rates: public and private (Table 1).

Public pricing documents—whether published as tariffs, price lists, or open quotes—are available to any rail shipper. They are not confidential, are open to the public, and are available either in hard copy (although hard copies are being phased out) or via the Internet. Today, shippers requiring hard copies can print them directly from the Web pages of the publishing railroad. Public rates are most applicable to the occasional or low-volume shipper. Whenever a public price is used to make a shipment, reference to the source document should be made on shipping documents.

U.S. railroads quote prices by commodity in three formats. They are

1. Point-to-point is the most specific format and is preferred over other formats. The origin and destination are specified.
2. Group-to-group rates define origins and destinations as geographic groups. If available, point-to-point rates supersede group-to-group rates.
3. Mileage rates are determined by distance, which is found in a railroad publication or on the Internet. Both point-to-point and group-to-group supersede mileage rates.

All railroad price quotations are commodity specific. Transporting higher-value commodities costs more than transporting lower-value commodities.

Shipments must be properly identified for purposes of determining freight rates. If a carrier determines that a commodity is being shipped under an improper tariff (i.e., it is being shipped as a lower-value commodity to gain a lower transportation charge), the carrier may adjust the freight bill to reflect the proper commodity and tariff charge. Also, if a shipment is lost or damaged and was tendered on an improper rate, the railroad may refuse to honor any claim to recover the loss because the shipment was improperly tendered. In any case, the claim would be settled for the value of the lower-priced commodity, not the actual value of the improperly tendered commodity.

Public freight rates can be found on the Internet or in the specific pricing publications of the rail service provider.

If a specific rate cannot be found, requests for freight rates can be made to the customer service departments of each railroad. In most cases, requests must be made via the Internet or via e-mail to the appropriate customer representative. At a minimum, a request

Determination of a proper STCC is subjective. In many cases, a given commodity may fit into more than one STCC group. There is no prohibition against shipping on the most advantageous STCC number as long as that STCC number fairly identifies the commodity being shipped and is not simply a subterfuge for obtaining a lower transportation rate.

Managerial Tip 6

must include the name of the shipper and receiver, the location of each, the commodity and its Standard Transportation Commodity Code (STCC), the size of shipments to be made, the anticipated annual volume, the type and owner of the cars, the name of a contact person, and the phone number and e-mail address of the contact person. The customer service representative will request any other requirements.

STCCs are available through most of the Web pages of the Class I railroads. If the railroad provides computerized freight rates, there is a way to look up the commodity code.

If a public rate quote precludes a shipment, perhaps the price quoted is too high; private quotes might be available if the shipment is sufficiently large or long term. Private quotes are negotiated with the appropriate customer service representative or commodity specialist for the specific commodity being shipped. Private rate quotes are not available for single-car or intermittent shipments.

Letter quotes are short-form contractual freight quotes. Like full contracts, they are confidential and usually apply to a freight rate for a single commodity being transported between a single origin and a single destination. Contractual freight rates are available if a potential rail movement is sufficiently large, long term, or both. Contracts are confidential and are distributed only to parties to the movement. There is no set rule for the contents of contracts; however, railroads are reluctant to enter into contracts unless the volume of the movement is substantial or the duration is 1 year or more. Rail contracts are available only through the customer service representative.

In some instances, the contract may specify a certain minimum annual volume or a percentage of total shipments to be made under the terms of the agreement. If so, the agreement will require the shipper to certify that the terms of the agreement were fulfilled and the railroad will reserve the right to audit the shipper's documents to verify that the certificate is correct.

Order Cars

The next step in making a rail shipment is to order cars. Six pieces of information are required: the company making the order and its address, the type of car, the commodity to be loaded, the number of cars required, the date or dates when the cars are needed, and the location for empty car delivery.

The easiest way to place car orders is via the railroad Web site; each carrier has an online process for ordering equipment. Car orders can also be placed through customer service departments.

If a shipper is a volume customer, most rail systems will encourage the customer to contact the appropriate car distributor. Car distributors are usually assigned by car type, geographic region, commodity, or all three. The names and phone numbers for car distributors are available from customer service departments or in some cases from the Web sites.

If an empty car has been ordered and delivered and the car is not loaded but returned to the carrier empty, a switching charge will be assessed and collected from the party ordering the cars.

Empty car delivery for loading is not time specific. Railroads make no guarantee of delivery time or quantity of cars. Even when multiple cars are ordered for shipment at the same time on the same bill of lading, there is no guarantee that all cars will arrive at the same time.

One exception exists—the Loading Origin Guarantee (LOGS) program from the BNSF. This program provides a method to guarantee delivery of a specific number of certain types of empty cars on a weekly basis. The program is reciprocal, meaning that a failure to perform on the part of the shipper or the BNSF results in penalties due the other party. Other railroads are implementing equivalent programs.

Receive and Load Cars

After empty cars are delivered, the shipper has 24 hr, beginning at the first midnight after delivery of the cars, to load and release the cars. If multiple cars have been ordered for delivery at the same time, for shipment at one time, and all cars are listed on a single bill of lading, the free time for loading begins at the first midnight after delivery of the final car or on the date for which the multiple cars were ordered. If cars are held beyond the free time allowed, demurrage (see the Demurrage and Furtherance section in this chapter) is chargeable (BNSF 2004a, 2004b, CSXT 2001, KCS 2000, NS 2000, UPRC 2004a).

If multiple cars for loading have been ordered for delivery and shipment at one time, all cars are on the same bill of lading, and the cars arrive piecemeal (i.e., one at a time) before the order date, the shipper may load those cars and hold them until the final car arrives. There is no penalty for holding cars delivered before the order date. If the loaded cars are released and not billed, however, furtherance charges would accrue (see the Demurrage and Furtherance section in this chapter).

Privately owned or leased cars delivered to private tracks can be held for an indefinite period with no demurrage accrual. But if private cars are delivered to railroad-owned tracks or held in storage on railroad-owned tracks, storage charges do accrue.

The consignee, or shipper, is responsible for inspecting empty railcars and for determining their cleanliness and mechanical condition. Railroads will attempt to deliver clean and mechanically sound equipment for loading but will not guarantee or offer a warranty that any equipment delivered is acceptable for loading. The acceptability or lack thereof is the responsibility of the shipper. When a car is loaded and billed, that act is *prima facie* evidence that the car was acceptable for loading. Any damages or loss of lading resulting from leaking doors or holes in the car body are the shipper's responsibility. Any contamination resulting from dirty cars is, likewise, the responsibility of the shipper, not the railroad.

Railcars cannot be loaded to exceed their load limit, which is posted on the side of all railcars along with the maximum gross weight and the tare weight of the car. The maximum gross weight of a car is determined by car construction, specifically its undercarriage. Cars appearing visually identical may have different maximum gross weights and consequently different load limits.

Railroads quote freight rates in two ways: by the carload and by actual weight. If the rate is quoted by the carload, the railroad has no responsibility for weighing except to check for overloaded cars. When the rate is based on actual weight, the shipper may specify that weight if the shipper has a certifiable method of determining actual weight and if the shipper has created a weight agreement with the railroad. If the rate is quoted by actual weight, the weight is determined by the railroad, and the railroad is responsible for weighing the car and determining the actual weight.

Although there is no regulation or requirement that air hoses be reconnected and cars coupled, a shipper is well advised to do so. Connecting air hoses and coupling cars requires time, and if the switching crew is unable to provide this service and complete their assigned work, a shipper may not receive the level of service anticipated.

Managerial Tip 7

When shipping open-topped cars, gondolas, or hoppers, rainfall can cause overloading. Railroads consider only the fact that the car is overloaded, not the reason for the overloading. Consequently, shippers should load cars lighter than their marked capacity to allow for increased weight resulting from possible rainfall. However, if a shipper is certain that an overweight condition is due to rainfall, a sensible source of action is to call for a re-weigh, assuming that the water will drain or evaporate and the weight of the car will return to an acceptable range. An accessorial charge will be made for the re-weigh unless the new weight is within the load limits of the car.

Managerial Tip 8

All freight rate tariffs based on actual weight will specify a minimum weight. Should the railroad be unable to weigh a car, for whatever reason, and cannot determine the actual weight, the minimum weight quoted in the tariff will be the weight for billing purposes.

If a shipper wishes to weigh a car moving under a carload tariff, the railroad will assess a scale charge. More details are given in the Accessorial Charges section in this chapter.

Railcars must not be overloaded. Should the railroad determine from a scale weight that a car is overloaded (i.e., that the car is determined by scale weight to be heavier than the load limit of the car or the gross weight is heavier than the load limits of the track at any point along the route of movement), the car will be stopped and reduced in weight (regardless of location) by the shipper or the shipper's independent agent and reweighed before movement can continue. Penalties accrue for overweight cars (see the Accessorial Charges section in this chapter).

Railcars must be loaded along their centerline with weight distributed evenly along the entire length of the car. Off-center loading is not permitted. Weight should be distributed evenly over each set of wheels. Visual inspection can determine off-center loading; the cars lean to the overloaded side. Off-center cars will derail on curves. When a railroad switching crew notices an improperly loaded car, they will not switch it. Instead they will reject it, and the railroad will notify the shipper that the car is improperly loaded and demurrage will accrue until the off-center condition is corrected. If cargo shifts in a car, even if the car was initially properly loaded, the shipper is responsible for correcting the loading, regardless of the location of the problem. The shipper will incur demurrage charges while the load is being corrected.

Once loading is completed, if the cars have been moved or uncoupled during the loading process, they should be recoupled, their air hoses reconnected, and their hand brakes set on every single car or on at least two cars of a multiple string of cars. Even when cars are parked on an apparently level track, hand brakes should be set.

Loaded cars should not be released without billing. If a railroad pulls cars that have been released but for which billing has not been submitted, the cars will be declared "no bills" and penalties and furtherance charges can be levied.

Regardless of which rail system is used, all acknowledgments and copies of bills of lading and way bills that are created by the railroad and generally available from the Web site should be printed. The person submitting the bill of lading should date and initial all paperwork as documentation in the event of any dispute or improper invoice.

Managerial Tip 9

Release Loads and Bill

Two actions are required after the railcars are loaded: the railcar is released and the transaction is billed.

The following terms relate to releasing and billing of railcars:

- **Consignee:** The party designated on the bill of lading as the entity entitled to receive delivery of the goods (KCS 2004)
- **Consignor:** The party in whose name a railcar is ordered for loading and/or the party furnishing forwarding instructions (CSXT 2003)
- **Commodity:** STCC number or the description of the goods being consigned (UPRC 2004a)

Car release consists of notifying the railroad that the car is loaded and ready to be shipped (pulled). The car can be released verbally, by fax to customer service, or via the Internet. In the immediate future, all releases must be made on the Internet; no verbal or faxed releases will be accepted without an additional charge.

Car release is not the same as billing; car billing, the bill of lading, is the documentation required to ship and route the car. The bill of lading provides the identification numbers for each car being shipped, contains the name of the shipper and the receiver, identifies the commodity being shipped, provides for payment of freight charges, and outlines other pertinent information about the shipment.

Internet filing is either required or soon will be required. It is more secure and the shipper can receive instant confirmation that the bill has been properly completed and accepted. Bills of lading cannot be verbal, but they can be faxed to customer service for an additional fee.

Car release can be included with the bill of lading. Alternatively, the bills of lading may be filed pending release of cars, or filed with a future effective date and time.

Bills of lading should be checked for errors. Any changes made after acceptance of a bill of lading can result in additional charges to the shipper (see the Accessorial Charges section in this chapter).

Monitor and Trace Cars

After the railroad accepts the bill of lading, the shipper should download and print a way bill from the railroad's Web site. The way bill officially documents the shipment. Any changes or modifications of the way bill can incur charges to the shipper, even if changes are minor or insignificant.

All mainline railroads are able to trace shipments on their Web site. There are two forms of shipment tracing available: public and private. A public trace allows the public to trace railcars but gives only the current location of that car. A private trace permits only those party to the shipment to conduct a detailed trace that includes

the history; the current location; the estimated time of arrival (ETA); and, in some cases, the future routing and schedule of the shipment.

The ETA shown on a trace report is, as stated, "estimated." The variables involved in a rail shipment can frequently cause delays of up to several days beyond the scheduled ETA. From time to time, cars get lost, break down, or are bad ordered. Variability in delivery schedules can put the shipment receiver in a difficult situation. For example, should the receiver order unloading equipment in anticipation of delivery and incur extra expense if the delivery might not arrive on schedule, or should the receiver wait until the cars arrive to order equipment and personnel and risk incurring demurrage if that equipment and personnel arrive later than anticipated?

Alternatively, cars may be traced using www.Steelroads.com, a Web site sponsored jointly by a number of U.S. and Canadian railroads. The site can be used to conduct both public and private traces as well as a number of other activities. Users must register with Steelroads and be sponsored by one of the supporting carriers.

Receive Loads

Four options for delivery of incoming railcars are available to the customer receiving loaded cars: *order-in*, *spot-on-arrival*, *keep-full*, and *constructive placement*.

1. **Order-in.** Cars arriving at the switching yard of the delivery carrier will be held there until the customer orders the cars to be delivered. All such orders must be in writing (fax or Internet).
2. **Spot-on-arrival.** Cars arriving for delivery will be placed immediately on arrival, providing there is capacity on the receiving track. No order is required by the consignee; no notice is provided by the delivering railroad.
3. **Keep-full.** When more cars have arrived for delivery than can be accommodated by the capacity on the receiving track, cars will be held in constructive placement by the railroad and delivered as space is available. No order is required by the consignee unless consignee wishes to order-in a specific car.
4. **Constructive placement.** When a railcar cannot be actually delivered because of any condition attributable to the consignor or consignee, the cars will be held on the tracks of the delivering carrier, notice will be sent to the party entitled to be notified, and demurrage will be charged pending instructions.

Immediately after the loaded cars are received, the cars and cargo should be inspected for damage and for integrity of seals on doors and locks if sealed. If damage is found, the delivering railroad should be notified before unloading.

Initial notification may be verbal but should be followed by written communication asking the railroad to inspect the shipment. The railroad should either agree to inspect the shipment or waive rights to inspection. If rights are waived, they should be waived in writing.

If the railroad agrees to inspect the damage, any demurrage incurred while waiting for the inspector is not chargeable to the consignee.

Any notification by the inspecting party of inability or failure to inspect should be recorded along with time of notification and names of the individuals giving and receiving notice. If inspection has not been conducted within a reasonable period, the railroad should be notified again.

If the railroad waives inspection, a neutral third party should inspect the car and its contents, and any report resulting from the inspection should be made part of any claim filed against the railroad. Photos should be taken of any visible damage.

Railcars should be traced daily, not only to find diversions of cars, but to maintain control of the shipment. Cars can be incorrectly routed, lost, bad or derailed, or simply delayed for an excessive period of time. Problems can be addressed by creating a problem log with the customer service department.

Managerial Tip 10

If goods are lost from a bulk shipment in a hopper car and one of the doors is defective, broken, or open, the loss of goods is subject to claim against the railroad for loss of lading. But if the door simply leaks because it is warped or fails to make a tight seal, any claim for loss of goods is credited against the shipper and not the railroad. The shipper, not the railroad, is responsible for ascertaining whether a car is suitable for loading. Determining suitability includes both mechanical condition of the equipment and cleanliness. The act of billing and releasing a railcar is *prima facie* evidence that the car is clean and in acceptable mechanical condition for use (UPRC 2004b).

Lading escaping from an unsound gondola—one with holes or cracks in the bottom or side walls—is credited against the shipper, not the railroad, as previously described for hopper cars.

Loss incurred from a covered hopper with open or leaking “loading doors” might be claimed against the shipper or the railroad, depending on whether the door was properly closed and locked or the locking mechanism was defective. Inspecting the car after arrival can usually determine culpability.

Unload Cars

After the cars arrive at their destination, the consignee has 48 hr of free time to unload the car, with time beginning at the first midnight after the car is received. See the discussion of demurrage for further details about free time and charges for holding cars.

Cars should be completely unloaded and cleaned if they are not scheduled for reloading with identical cargo from the same origin as the shipment being unloaded. Railroad rules require that cars be emptied and cleaned sufficiently so that the next cargo can be loaded without contamination. In practice, however, car distributors generally ask (or the shipper should specify) if clean cars are required. If clean cars are needed and if there is any danger of cross-contamination, the railroad usually cleans the cars before delivery for loading.

Cleaning requires time—time to deliver the car to the cleaning facility, time to clean the car, and time to return the car to the shipper. If empty cars are needed for loading and delivery time is a factor, the shipper should consider cleaning the cars.

Release Empty Cars

After unloading the railcar, the car must be “released empty” to the switching railroad. Although most railroads still accept car releases verbally, the trend, as in the case of releasing loaded cars and billing cars, is toward electronic release using the Internet. Extra fees may be incurred for verbal or faxed releases. The switching railroad will not remove an empty car until it has been released. The exact date and time of the release, not the date and time that the car is actually removed, is the time of record for purposes of demurrage.

Normal operating procedure for U. S. railroads is to give a switch crew written orders based on customer requests and releases

The imposition of demurrage charges on cars being unloaded is one of the most expensive and contentious accessorial charges imposed by railroads. Complete and detailed records are required to contest demurrage charges. A log book in which detailed records of car deliveries and switches is demanded. That log book should record the exact date and time of all switches performed by the railroad and the exact order in which cars are spotted upon delivery.

If newly delivered cars are spotted in front of cars previously delivered, whether or not the new cars impede unloading of the previously spotted cars or not, the cars delivered previously may be declared “off spot,” and demurrage on those previously delivered cars will not begin until the first midnight after the cars have been rearranged in proper chronological order. Declaration of an off-spot condition must be made to customer service and should be followed with written confirmation.

Alternatively, if a switch order specifying a delivery sequence for the cars has been properly given to the railroad and the cars are delivered and spotted incorrectly, all cars spotted incorrectly may be declared, in writing, off spot and demurrage will not begin until the cars are rearranged in the proper order as specified in the switch order.

Managerial Tip 11

received before creating written orders. Normally these orders must be received by midnight, or in some cases by 6:00 AM. In most instances, a switch crew will not remove an empty car unless it has written orders to do so.

If the railroad removes a loaded car in error, the railroad will return the car at no additional expense to the car’s consignee. Carriers will not be responsible for any incidental expenses (for example, expenses incurred when a plant ran out of raw materials) resulting from the accidental removal.

Pay Freight Bill

A freight bill is created by the shipping railroad on the date of shipment. Payment can be made by check, wire transfer, or, in some cases, by credit card. Most Class I and II railroads in voice and accept payment via the Internet.

Payment terms vary slightly among the different carriers, but all demand payment regardless of whether the shipment has been delivered. Most railroad systems charge interest on overdue payments. An unpleasant reality of the railroad collection system is that the payment for services rendered is frequently due before those services have been performed.

The due date for freight bills for cars that have not yet been delivered can be postponed until the date on which delivery is actually accomplished. A railroad may still levy interest for late payment of freight bills, but any such payment of interest can be protested, usually successfully.

Incidental errors on freight bills such as erroneous weights, improper charges per ton, or billing based on a carload rate when a tonnage weight should apply can be corrected on the freight bill. An explanation should be attached and the proper payment rendered in accordance with railroad payment terms. Railroad error is not acceptable grounds for nonpayment of freight bills.

ACCESSORIAL CHARGES

Since deregulation, railroads charge for services rendered in addition to the actual charges of freight from point to point. These charges are called accessorial charges or chargeable services. "Actual placement," for example, means the actual physical delivery of a railcar to an accessible position for loading or unloading or to some other point designated by the consignor or consignee (UPRC 2004c) is an accessorial charge.

Accessorial charges most applicable to the mining industry are

- General rules and charges
- Demurrage and furtherance
- Storage
- Weighing and reweighing
- Overloaded or overweight cars
- Reconsignment and diversion
- Switching

The monetary charges levied for various accessorial services vary between railroad systems and tend to escalate with time. The appropriate tariff for each system should be consulted to determine the effective charge.

General Rules and Charges

Each railroad maintains a set of general rules and charges (BNSF 2001c, CSXT 2002, KCS 2002, CN Railways 2004, UPRC 2004c) relating to those rules. In the past, rule books were available in bound form. Today, rule books are available only on the Internet. The shipper, or railroad customer, who needs a hard copy may print a copy directly from the Web site.

The following Web page addresses include the general rules and charges published by the U.S. Class I railroads:

- BNSF: <http://domino.bnsf.com/website/prices.nsf/PriceRpt?Open&mp>
- CN Railways: www.cn.ca/productservices/chargeableservices/en_KFCchargeableservices.shtml
- CSXT: www.csx.com/index.cfm?fuseaction=assessorialactive
- KCS: www.kcsi.com/pdf/kcs9011.pdf
- NS: www.nscorp.com/nscorphtml/pdf/nsle.pdf
- UPRR: www.uprr.com/customers/ind-prod/pdf/6600cBook.pdf

Of the hundreds of rules included in the above general rules and charges, several of the rules more specifically apply to the minerals industry and are discussed in detail in the following sections.

Demurrage and Furtherance

Demurrage is charged on empty cars being loaded or awaiting loading; on loaded cars being or a waiting unloading; and on any cars being stored, held, or kept out of revenue service by actions of a customer. Demurrage is also charged on any cars "constructively placed" (i.e., cars being held on railroad property awaiting delivery to the customer's facilities).

Demurrage, furtherance, and storage charges apply to railroad-owned equipment on railroad or private property and private equipment when stored on railroad property. Demurrage charges do not accrue on private equipment held on private or leased tracks. A track leased from the railroad is treated as a private track.

Railroads do not compensate owners or lessees of private equipment held or delayed by the railroad. Because railroads do not guarantee any route or delivery date, any expenses incurred by owners or lessees of private equipment are not reimbursed.

Web page addresses for demurrage and furtherance rules and charges follow:

- BNSF: <http://domino.bnsf.com/website/prices.nsf/PriceRpt?Open&mp>
- CN Railways: www.cn.ca/productservices/chargeableservices/en_KFCchargeableservices.shtml
- CSXT: www.csx.com/share/csx/assessorial/forms/docs/CSXT_8100_Demurrage_Provisions_Section_VIII_as_of_122002_REF10286.pdf
also www.csx.com/share/csx/assessorial/forms/docs/A_quick_guide_for-managing_demurrage-REF10310.pdf
- KCS: www.kcsi.com/pdf/kcs6000.pdf
- NS: www.nscorp.com/nscorphtml/pdf/demurrage_faq.pdf
- UPRR: www.uprr.com/customers/demurrage.pdf

Loading Demurrage

Loading demurrage is charged when a customer receives empty cars destined for loading. Time starts at the first midnight after the cars are placed or the midnight of the date for which the cars were ordered, whichever is later. Most U.S. railroads allow 1 day for loading. KCS and CN Railways allow 2 days. Demurrage does not accrue for Sundays and listed national holidays unless demurrage was chargeable for the day preceding.

Table 2 presents demurrage charges for empty cars held for loading or constructively placed awaiting delivery for 1 day where 1 day is allowed for loading.

Unloading Demurrage

Unloading demurrage is charged when a customer receives loaded cars destined for unloading. Time starts at the first midnight after the cars are actually delivered or when notice of constructive placement has been given, whichever is earlier. All U.S. railroads allow 2 days of free time for complete unloading of cars.

Table 3 presents demurrage charges for loaded cars held for unloading or constructively placed awaiting delivery for unloading.

Sundays and holidays are excluded from demurrage unless demurrage is being charged on the preceding day. A list of holidays exempt from demurrage charges is contained in the demurrage rules of each individual railroad.

Furtherance

Furtherance is charged when a car is released without billing by a customer or received by the railroad from another railroad without forwarding instructions. Time starts at the first midnight after the car is received. No free time is allowed for furtherance.

Furtherance charges are levied at the same rate as demurrage charges.

Furtherance is not levied if billing has been properly submitted but the railroad fails to remove the cars. Likewise, furtherance is not levied if the shipper has prepared proper billing and the originating railroad fails to provide the connecting carrier with correct documentation. Either situation is defined as railroad error.

Storage

Storage is a fee charged when either the consignor or consignee requests that an assigned car be stored for an extended period either on or off railroad property. Storage also applies when private cars are held on railroad property.

The primary application of storage is using railcars for mobile warehousing. Storage is common within the plastics or chemical industries but rare in the minerals industry.

Table 2. Demurrage charges for empty cars held for loading where one free day is allowed

Spot Date	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Monday	Tuesday
Monday	Spot	Free	Debit	Debit	Debit	Debit	Debit	Debit	Debit
Tuesday		Spot	Free	Debit	Debit	Debit	Debit	Debit	Debit
Wednesday			Spot	Free	Debit	Debit	Debit	Debit	Debit
Thursday				Spot	Free	Debit	Debit	Debit	Debit
Friday					Spot	Free	Free	Debit	Debit
Saturday						Spot	Free	Free	Debit
Sunday							Spot	Free	Debit

Notes:

- “Spot” means the car was delivered before midnight.
- “Free” means no demurrage time is charged.
- “Debit” means demurrage is charged.
- No offsetting credits are allowed for cars delivered for loading.

Examples:

- Cars delivered on Monday, Tuesday, Wednesday, or Thursday are allowed 1 day of free time. All additional days are charged demurrage.
- Cars delivered on Friday receive Saturday and Sunday as free days. Monday would be a day of demurrage.
- Cars delivered on Saturday receive Sunday and Monday as free days. Demurrage does not accrue for Sunday, and Monday is the free day.

Table 3. Demurrage charges for loaded cars held for unloading where one free day is allowed

Spot Date	Monday	Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Monday	Tuesday
Monday	Spot	Free	Free	Debit	Debit	Debit	Debit	Debit	Debit
Tuesday		Spot	Free	Free	Debit	Debit	Debit	Debit	Debit
Wednesday			Spot	Free	Free	Debit	Debit	Debit	Debit
Thursday				Spot	Free	Free	Free	Debit	Debit
Friday					Spot	Free	Free	Free	Debit
Saturday						Spot	Free	Free	Free
Sunday							Spot	Free	Free

Notes:

- “Spot” means the car was delivered before midnight.
- “Free” means no demurrage was charged.
- “Debit” means demurrage was charged.
- If a car is released on the day it is delivered or on the first free day, one day of credit is given against chargeable demurrage.
- Credits are not transferable between months.

Storage is not demurrage. Cars are stored, and released from storage, by written order from the party to whom the cars have been assigned, or in the case of private cars, the car owner or lessee.

Storage is charged per diem. Additionally, switching is charged for putting cars into and taking cars out of storage.

Storage charges are not levied on private cars stored on private tracks although switching charges are applicable for moving cars into and out of storage.

Storage charges are usually less than demurrage charges.

Weighing and Reweighing

Loaded railcars are weighed for two reasons. First, the tariff is based on actual weight and the railroad must determine the actual weight using certified scales. Second, the cars are weighed to see if they are overloaded.

If the freight rate is based on actual weight contained in the car, the carrier is responsible for determining weight.

If the shipper disagrees with the weight determined by the carrier, the shipper may request a reweigh. If the reweigh shows that the original weight was within a certain specified tolerance, the shipper will be assessed a reweigh charge.

If a reweigh reveals that the original weight determined by the carrier was incorrect by the specified tolerance, the documentation and billing on the car will be corrected to reflect the newly determined weight and the shipper will not be assessed a reweigh charge.

Overloaded or Overweight Cars

Overloading railcars is inherently unsafe. With the encouragement of the STB, railroads are assessing high monetary charges for overloads or overweights.

An overloaded car is defined as a car loaded in excess of its load limit, which is stenciled on the side of the car.

An overweight car exceeds the load limits placed on a route that the car is scheduled to take.

When an overloaded or overweight car is identified, the action taken by the carrier will depend on the weight of the car. If the car is less than 2,000 lb overweight, in most cases it will be allowed to continue in transit and a minimum penalty will be assessed. If the car is more than 2,000 lb overweight, the car will be stopped, an overweight penalty will be assessed, and the consignor will be ordered to take corrective action, which entails removing excess

The excessive penalties levied by the rail carriers for overloads and overweights justify whatever action is required to avoid them. Open-top cars should be loaded to account for potential rainfall. Consideration should be given to loading cars lighter than their stenciled net weight to provide a safety factor against overloads.

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lading. That excess lading may be loaded onto another railcar or carried to a proper disposal site.

The railroad's overload department can supply the names of local contractors qualified to remove the excess lading. Contractors exist in virtually every large city and metropolitan area. Charges levied by contractors to lighten an overweight car are frequently exorbitant because local contractors recognize the vulnerability of the shipper and the high cost of mobilizing a crew from a distant location.

If the excess lading is placed in a second railcar, that second car may be billed at the price from the point of origin where the excess lading is loaded and may be billed as a fully loaded car.

In addition to the overweight penalty, switching charges to and from the point of corrective action may be levied, along with demurrage charges for time required to remove the excess lading. Finally, the railroad may levy a reweigh charge for weighing the car a second time.

Reconsignment and Diversion

A diversion is any change in any billing or shipping document that changes the route or destination of a previously billed railcar.

Typical diversions are changes in destination, route, or location of consignee. A diversion requires that physical action be performed on the railcar to alter its route or destination. A reconsignment is a change in any billing or shipping document that does not change the route or destination of the railcar.

Typical reconsignments are changes in the

- Name of consignor
- Name of consignee
- Commodity code (STCC)
- Party paying the freight bill
- Payment method from "prepaid" to "collect" or reverse

Typical diversions are

- change of origin
- change of destination
- change of route

Reconsignments or diversions must be accomplished in writing on company letterhead and will not be accepted if any of the following are true:

- The railcar has reached its destination.
- The railcar has been delivered to another carrier.
- The railcar has been blocked (connected) into a train that will carry it to its final destination or interchange point with another carrier.

Although railroads will usually make a best-effort attempt to execute a diversion, they will not guarantee, nor be responsible for, executing the diversion at a specified time or place.

The party requesting the diversion or reconsignment is responsible for paying charges levied by the railroad. Normally a

diversion charge is substantially more expensive than a reconsignment charge, because the diversion requires physical action on behalf of the railroad.

Multiple car shipments tendered on a single bill of lading from a single shipper at a single origin to a single consignee may not be separated by diversion.

If a reconsignment or diversion order has more than a single change, all changes will be executed and only one charge will be levied—the highest applicable charge.

Empty cars returning from a destination may be diverted at no charge if no alteration of route is required.

Switching

Switching is moving a railcar from one location to another. Line-haul or cross-country movements are excluded from the definition.

Five types of switching are defined in railroad rules and regulations: reciprocal, intraplant, intraterminal, interterminal, and intermediate (see, for example, UPRC 2004d).

Reciprocal Switching

A reciprocal switch is the delivery of railcars by a carrier that does not participate in the line haul and for which the switching carrier has agreed to provide services for a fixed price. When a carrier delivers a railcar to its destination but another carrier serves the customer to which the car is to be delivered, the switch performed by the second carrier is a reciprocal switch. A reciprocal switch charge includes the empty delivery and the removal of the load, or the reverse.

A reciprocal switch charge is normally included in the rate quote. Public tariffs issued by each carrier specify the total sum, which can apply to reciprocal switching. The specified switching allowance is the total allowed for the entire movement, including switching at both ends of the movement.

Reciprocal switching is not available for all customers at every station. Each station will have switching limits defined by the carrier at that station. A reciprocal switch is not available to customers located outside the switching limits. A switch to that customer will require a line-haul charge.

Some industries located within the switching limits defined by a carrier may be closed to reciprocal switching. A carrier uses closure when it can perform both the line haul and the local switch and wishes to deny the line haul to any other carrier that could perform the line haul but not the local switch.

Switching beyond the switching limits of a carrier will entail payment of additional switching charges. These additional charges can be found in the switching charges for each carrier.

Intraplant Switching

An intraplant switch is moving empty or loaded cars from one track to another, or from one point to another on the same track, within the confines of the same plant or mine site, without leaving the tracks of the plant or mine site.

As an example, if a mine site had multiple tracks and needed cars switched from one track to another, or needed the cars on a certain track rearranged, an intraplant switch would be required.

Charges are assessed for each car moved with an intraplant switch.

Intraterminal Switching

The term intraterminal switching means switching from one location to another, other than intraplant switching, within the switching limits of one station of the same railroad.

Continuing the above example, if the mine site and preparation plant were located on the same railroad, at the same station, but

at different locations, a switch between the two locations would be an intraterminal switch.

Interterminal Switching

Interterminal switching means switching between one railroad and another within the switching limits of the same station or industrial district.

Again, as in the previous example, if the mine site and preparation plant were located on two separate railroads but within the switching limits of the same station or industrial district, a switch between the two locations would be an interterminal switch.

Interterminal switch charges are normally more expensive than intraplant or intraterminal switch charges and are assessed for each car switched.

Interterminal switch charges will be assessed by both railroads participating in the switch.

Intermediate Switching

Intermediate switching means a switch made by a railroad between the interchange tracks of one carrier and the interchange tracks of another carrier within a station's switching limits. The intermediate switching railroad neither originates or terminates the shipment nor receives a line haul for the shipment.

If a line-haul shipment was being made using two separate carriers and the two carriers did not directly connect at the interchange station, an intermediate switch by a third carrier would be required.

For example, at Baton Rouge, Louisiana, if a line haul were made on the KCS for a UPRR switch, the IC (CN Railways) railroad would be required to make an intermediate switch because the KCS and the UPRR do not directly interchange.

Interchange switch charges are normally included in the reciprocal switch charge, which is included in the line-haul charge.

CONCLUSION

The importance of railroading to the industrial minerals industry cannot be minimized. Interstate railroads transport a significant percentage of the mineral commodities moved in the United States.

During the past era of regulation, railroad transport was a simple matter. The simplicity demanded by governmental regulation, however, almost destroyed the railroad industry in the United States. Bankruptcy and insolvency were immediate threats to the entire industry.

Passage of the Staggers Act in 1980 freed the railroads from most governmental regulation, permitted multiple mergers of rail systems, and resulted in six mainline carriers in the United States. Each of the six holds monopolistic hegemony over certain regions of the country.

Antiquated work rules and inflexible management, both vestiges of the era of governmental regulation, continue to hinder effective operation of the railroads.

Railroads have been unable or unwilling to expand their infrastructure to meet a continuing expansion of business resulting from the general growth of the economy of the United States. Specifically, this failure to improve infrastructure has created significant difficulties for the railroads and for the customers they serve as the United States recovered from the recession of 2001–2002. Many attribute this failure to an insufficient rate of return on investment, but an equal number of railroad critics claim that the failure is one of management and that return on investment for railroads could be at an all-time high.

Unless U.S. railroads can improve their performance and control costs, government re-regulation is an eventuality. Some critics of

the railroads believe that the rights-of-way, now owned by the operating carriers, should be separated from the carriers and turned into common carriers, open to any and all operators capable of meeting safety and operational rules and regulations. Needless to say, the U.S. railroad industry vehemently opposes any such re-regulation.

Recent price increases that exceed the price increases of industrial or consumer goods, however, would lead the independent observer to conclude that the railroad industry has recognized its monopolistic status and that it is starting to take advantage of that position. The future of U.S. railroads will depend largely on their response to the realization that they are a monopoly.

What course the industry will take is uncertain. Will the railroads of the United States grow and recapture much of the business lost to interstate trucking or will the railroads continue to transport a smaller percentage of general freight until they become noncompetitive and lose the general freight business completely? Abandoning passenger service, small-parcel delivery, and less-than-carload shipments to competitors is history. Now, railroads telegraph their disinterest in single-car or occasional shipments, or both, by denying a supply of railcars or by simply providing such poor service that the shipper is forced to use an alternative mode of transportation, regardless of cost.

In any case, railroad transportation will continue to be overwhelmingly important to the industrial minerals industry. Except in those areas where water transport is available, rail transport is the only competitively priced transportation available. Whether this situation continues into the future will depend solely on the reaction of the railroads to the new economics created by their monopolistic status.

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Road Transportation of Industrial Minerals

Paul Moore

Hauling bulk industrial minerals by rail and ship is unmatched for moving large volumes over long distances. Road transport, however, remains an equally important transportation mode for mineral movements throughout the world. Trucking offers convenience, flexibility, low cost, and versatility, giving it distinct advantages over rail or water transport in many situations, despite the fact that it lags behind in terms of fuel efficiency and emissions.

In a 2003 report, the American Association of State Highway and Transportation Officials (AASHTO) stated that in 2000, trucks moved 78% of U.S. domestic freight tonnage (st), generated 60% of its short ton mileage, and accounted for 88% of its dollar value, the highest percentage in each category. Trucks moved 11 billion st, valued at \$9.5 trillion, over 2.6 trillion short ton-miles in 2000. Trucking movements are expected to grow to 17,296 million st by 2020, an increase of 62%. Short ton-miles by truck are predicted to grow to 4,174 billion in 2020, an increase of 58%.

Rail moved 16% of total domestic freight tonnage in 2000, second to transportation by truck. Rail movements tended to be longer in distance than truck movements and therefore accounted for a proportionately higher share (28%) of short ton-miles. Rail movements also tended to involve lower-value commodities than truck movements, so rail represented a proportionately lower share (6%) of total domestic freight value. Rail moved 2 billion st valued at \$600 billion over 1.2 trillion short ton-miles in 2000. Water (river barges and coastal and lake steamers) moved 6% of tonnage, 15% of short ton-miles, and 1% of value.

This truck dominance is also seen in more specific statistics for industrial minerals shipments. According to the U.S. Geological Survey (USGS), of the total industrial sand and gravel produced in the United States in 2003, 64% was transported by truck from the plant to the site of first sale or use, with only 35% transported by rail and 1% by other methods. These figures reflect the fact that, specialty ground silicas aside, the vast majority of the sand and gravel produced in the United States is used domestically at consumption sites located relatively close to the producer. Certain commodities, particularly those shipped in large bulk volumes for international export, such as borates, soda ash, and potash, are largely moved by rail to ports, but trucks may still form part of the logistical chain.

Trucking comes into its own when shorter distances and smaller volumes are involved. Indeed, most industrial minerals delivery routes from a mine or plant to the final customer involve some kind of road transport. This covers everything from the entire

route to the final leg to the customer from a port or warehouse storage area or the initial journey to a port or rail-siding stockpile. Intermodal movements are also common, such as the transport of steel ocean containers by a mixture of road and rail.

This is not to say that trucking is restricted to short-distance haulage. Some industrial minerals are trucked long distances, particularly in developing countries and where an efficient, regular rail freight service does not exist. The scarcity of the occurrence of a particular mineral worldwide may also mean that a 500-km or even 1,000-km truck haul is still economic.

The challenge for the producer and consumer is finding out what works best economically for their particular logistical path, taking into account issues such as practicalities of volume, location, required flexibility of supply, in-place infrastructure, distance, and the environment.

This chapter reviews the main reasons why trucking is still the mainstay of the industrial minerals industry, and gives examples of global trucking scenarios for a variety of industrial mineral types.

PRACTICALITIES OF VOLUME

The largest volumes of minerals over the longest distances move by ship and rail, simply because it is almost always far more efficient and cost-effective (particularly in terms of fuel consumption) to do so. A single railcar may carry 90 or 100 t and a unit train may consist of 100 railcars in some cases, such as the railing of soda ash by Union Pacific from Green River in Wyoming to Portland, Oregon, and more recently to Longview, Washington, for export to Asia. This type of volume movement—up to 10,000 t in one train—across such a long distance is simply impractical when it comes to truck transport.

Many of the world's key industrial minerals are produced in small mining operations, however, with low-cost trucking the main form of transport. China is the key example of this, where for minerals such as barite, fluorspar, magnesite, bauxite, and talc, most of the actual mines are very small, and their production is trucked to a regional stockpiling area such as a railhead for onward transport to a port for export. For example, much of the production of white filler barite is near Guiyang City in Guizhou Province. From there, white barite from numerous small mines is trucked to railheads in Nanning, Guangxi Province, where the material is railed to southern Chinese ports for export. Similar logistical routes are used in other Chinese provinces for other minerals.

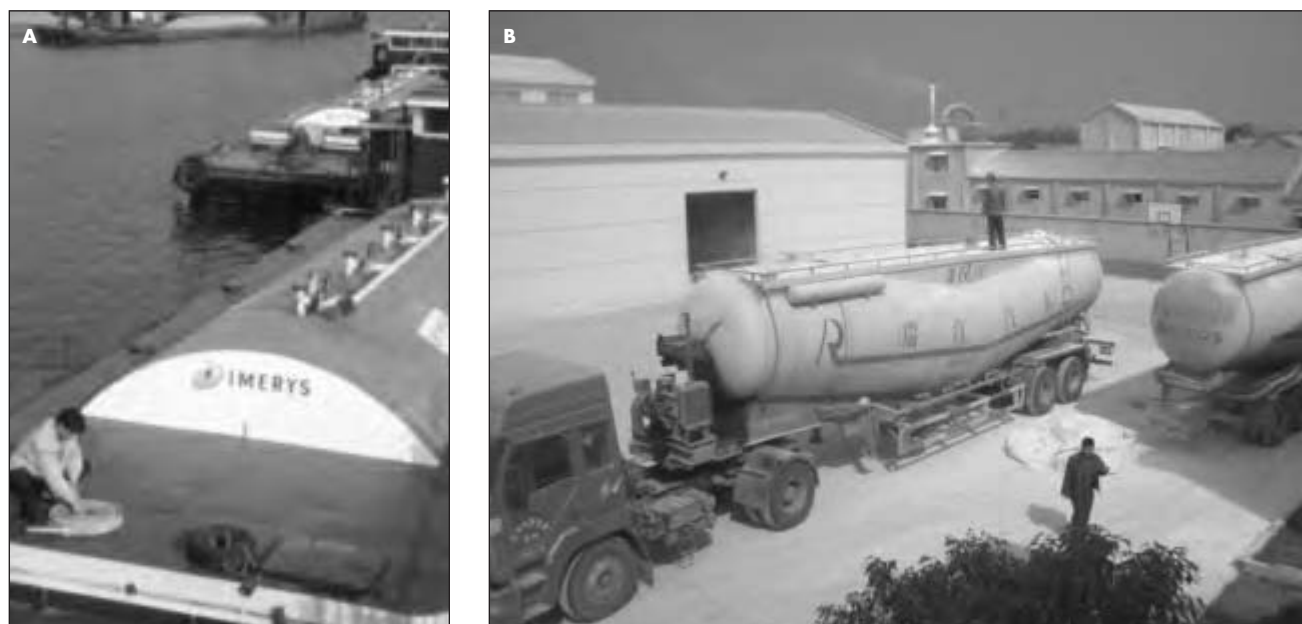


Figure 1. Two transportation options for GCC in China—(A) Imerys uses 300-t barges for some shipments from its Nanling operation (courtesy of Tom Grow for Imerys); and (B) the truck tankers are loading GCC at the operations of Sunny Stone Industry Co. Ltd., also in Anhui Province. Sunny Stone produces a range of lump, chippings, and powders for various customers, including Asia Pulp and Paper's Dagang mill (courtesy of Sunny Stone).

Although trucking in China is cheap, it is not without its obstacles. In May 2004, the Chinese government implemented new highway laws strictly enforcing restrictions on truck gross weight. Through the country's massive drive for infrastructure improvements, China has discovered that the rapid deterioration of its roads has been partly caused by years of wear from overloaded trucks. To keep freight costs down, and swiftly move large volumes, it has been standard practice in China for suppliers of materials and goods to exceed the designed load specifications of the trucks they use. Typically, a 25-t truck would receive a load of 45 t, for a freight rate of, for example, \$25/t from mid-China to Xingang port. The new load-limit law meant that such loads had to be reduced, thereby increasing freight costs and sometimes delaying transport of the material to port. If a truck is detected as overloaded, it is confiscated and the driver is briefly jailed. This, together with railcars being tied up in iron ore and coke transport, has caused severe shortages of mineral stockpiles at ports that are already seeing major delays and demurrage fees because of ocean shipping congestion.

LOCATION

Location means everything to the economics of industrial minerals. Many of the world's industrial minerals operations are in remote parts of the world, far from any rail siding or port and often in hilly terrain. Trucking is the first and only option, whether all the way to the point of consumption or to the nearest available rail or water transport point.

Many examples exist of very long distance shipments of minerals by truck. In Brazil, Mineracao de Amianto SA (SAMA), one of the world's largest chrysotile producers, trucks its product some 1,600 km from the Cana Brava mine to the port of Santos. New vermiculite producer IBI Corp. trucks flake vermiculite some 800 km from the Mbalé District in Uganda to the port of Mombasa in Kenya.

For wide spread, lower-value minerals shipped in moderate volumes to local consumers, trucking is the most practical option. Good examples are regional lime and limestone operations trucking product to consumers in the same area such as carpet manufacturers, glass plants, and sugar factories.

Other areas are simply too remote for trucking to be feasible. The potential for the extensive lithium, barium, strontium, potash, and magnesia reserves of the Qaidam Basin in China's Qinghai Province has been talked about for years, but their remoteness has limited development until now. The construction of the 1,142-km Qinghai-Tibet Railway is scheduled for completion in 2007, and the Chinese government hopes it will open up the area and its mineral resources.

On the other hand, if a consumer is in a relatively built-up area, often no room exists for a new rail spur, even if the capital exists to build it. Sometimes inland waterways can be used, as in the case of Imerys's Nanling operation in Anhui Province, China (see Figure 1A), where barging is used to transport ground calcium carbonate (GCC) slurry, but generally truck is the only option in more congested regions (Figure 1B). Likewise, barging is used extensively to transport minerals down the Rhine from the ports of Rotterdam, Antwerp, and Amsterdam to reach consumers in western Germany.

INFRASTRUCTURE

Although it overlaps, to some extent, with "location is important," infrastructure is concerned more with available capital and the economic worth of making major investments when considering the return on mineral sales. If the mine or processing plant is not located close to a mainline rail siding, the costs involved in constructing a rail spur are considerable. Similarly, smaller producers and consumers of minerals may not have the loading and unloading infrastructure in place to handle large, bulk shipments. The available silo or



Courtesy of Industrial Minerals.

Figure 2. Trucking is widely used to transport industrial minerals in Turkey. The Calmag truck (left) is being loaded with caustic calcined magnesite big bags for export. This is trucked to a nearby rail siding at Tavsanlı where it is transferred to railcars. The photograph on the right shows a truck delivering sodium feldspar to Kaltun's bulk storage and homogenization site near Gulluk port, in southwest Turkey.

warehouse space will also determine the nature of transport used. Truck transport still requires investments such as overhead bulk silos and a weighbridge, but the cost involved pales compared to the cost of a rail set-up.

Rail systems also vary in extent, quality, and efficiency throughout the world. In France, which has limited inland waterways and what some companies consider an "inconvenient" rail freight system, trucks dominate mineral transport. For example, leading world GCC producer Omya AG conducts virtually 100% of its GCC freight by truck in France. In the United Kingdom, kaolin shipments for key domestic accounts are made by rail, such as kaolin slurry railed to UPM's Caledonian paper mill in Irvine, Scotland. The bulk of the kaolin is exported from the Cornwall ports of Fowey and Par, however, so dry bulk kaolin is trucked there from Irvine for stockpiling at the docks and loading onto ships. Imerys operates a fleet of 50-t articulated tipper trucks for this purpose.

Inefficiencies in national rail systems may also mean rail cannot be used to its potential despite the existence of the basic infrastructure. An example of this is Turkey, now one of the world's most important industrial minerals producers and a global player in sodium feldspar, borates, and magnesite supply. The Turkish rail system, developed under Atatürk's rule, is extensive. A lack of investment over the years, however, together with a powerful domestic trucking lobby, has meant that much of the country's mineral production now uses truck despite the existing rail network. Figure 2 shows delivery of sodium feldspar from a mining operation to the Kaltun processing, storage, and blending site near Gulluk port, where the finished material is trucked again a short distance for loading onto bulk vessels for shipment to the Spanish and Italian tile industries.

CONSUMER SIZE

Just as the size of the mineral producer affects whether trucking is used, so too does the size of the consumer. Large mineral operations will often ship material by both truck and rail, with some of the larger accounts served by rail and the more numerous smaller accounts served by truck. For example, key accounts for large, bulk lime operations supplying the steel and flue-gas desulfurization (FGD) industries may be served by multiple 100-t railcars, with the smaller accounts served by trucked 1-t big bags or 25-kg sacks wrapped in plastic on pallets. In the industrial sands market, large

shipments to foundry and glass consumers may be made by rail, with materials for smaller accounts such as filtration and sports/leisure shipped by truck.

ENVIRONMENT

Where a choice exists between road and rail, the impetus has increasingly been to move minerals traffic to rail because of the savings gained in terms of emissions, and noise, safety, and traffic levels on public roads. Moving to rail has the additional positive effect of improving the public image of a mining or processing operation, because the movements become far less obvious to the public if made off the roads. Equally, in terms of planning applications for new mineral operations, getting permission to allow heavy mineral truck traffic on a well-used public road is often the most difficult hurdle to overcome.

In an article in a Vermont newspaper (*The Rutland Herald*, August 23, 2004), Bruce Edwards reported that progress has been made for a rail spur to Omya's marble-mining operation in Middlebury, Vermont. The proposed rail spur would eliminate the marble trucks that currently use Route 7 between Middlebury and Florence, where Omya's huge GCC plant is situated. This single, \$20 million, 3-mile rail spur between the Middlebury marble quarry and the main rail line would take 75,000 truck trips per year off the road.

COST AND OWNERSHIP

Large companies dominate rail and shipping freight services. In the United States, the so-called Class 1 carriers such as Union Pacific, CSX Transportation, BNSF Railway, and Norfolk Southern dominate. In Europe, a few rail freight carriers tend to dominate trade in each country, such as Railion in Germany, Société Nationale des Chemins de Fer (SNCF) Fret in France, and English Welsh & Scottish Railway Ltd. (EWS) in the United Kingdom. This situation is less marked in ocean shipping, where of ten numerous brokers and options are available, but it depends on the particular route concerned.

By contrast, trucking tends to suit much smaller companies with a small truck fleet. Mineral producers, particularly in developing countries, often use individual private-owner operators. In the United States, small haulage companies that combine a group of owner-operators are the most commonly used. For example, the Alabama-based lime company Cheney Lime & Cement lists no

fewer than 12 trucking companies that handle lime from its plant in Shelby County. By contrast, it is served by only one rail carrier—CSX Transportation—which owns and operates the track rights in that region.

In many cases, the industrial minerals supplier dominates the business of the trucking company—in contrast to rail, where industrial minerals often form only a fraction of the overall rail company revenues. For example, the Association of American Railroads (AAR) lists nonmetallic minerals at 7.4% of its Class 1 tonnage traffic in 2003, well behind coal at 43.6%. This means that the industrial minerals companies are farther down the list in the priorities for the railroads, which may have only a few people responsible for minerals marketing in the whole group. The situation becomes even more complex on rail when a relatively small volume is being moved across an area covered by several different rail companies—ultimately this all adds to costs for the mineral supplier.

Rail service and railcar reliability have become major issues in the U.S. industrial minerals industry in 2004–2005, particularly on the West Coast, where routes have been affected by heavy rain and floods. In these types of situations, the versatility of the truck is apparent. By contrast, often a particular minerals operation may represent the main business for one or several trucking companies. U.K. barite producer M-I Drilling Fluids UK uses Barhaul, a local haulage company, to transport its drilling-grade barite products from the underground mine in Aberfeldy, Scotland, to the grinding facility near Aberdeen. This is a symbiotic partnership in which the M-I contract accounts for the majority of Barhaul's business, and it is useful for M-I to have a local company focused on delivering the best service to its main client.

This is not to say that large trucking companies do not exist. For more specialized movements such as volatile and reactive materials or fine-grained powdered materials, special vehicles are often needed. Examples include Norbert Dentressangle, which ships large quantities of soda ash and other mineral powders in Western Europe using more than 900 tanker trucks.

Larger minerals producers may also own or long-term-lease their trucking fleet. Ameri-Co Carriers is a wholly owned subsidiary of Amcol International Corp., and the majority of its business is the transport of Amcol's natural sodium bentonite-based products such as cat litter and environmental liners. The company, however, also has a growing base of outside customers. In Europe, silica sand specialist SCR Sibelco and its partner companies throughout Europe operate large tanker truck fleets. Larger contracts may be handled by the customer, such as the railing of dolomite from Lhoist's operations in Belgium to consumer Nedmag in Veendam, the Netherlands.

TRUCK TYPES

The range of vehicle types used to transport industrial minerals varies by volume and the nature of the material. Simple bulk tipper trucks are often used for nonreactive, free-flowing materials such as silica sands and limestone for basic industrial uses. Slurries such as GCC and kaolin are transported in special tank trucks into which the material is pumped at a tank farm and unloaded in a similar way at the consumer point such as a paper mill.



Courtesy of Triple Crown Services Company.

Figure 3. The Triple Crown RoadRailer is one type of intermodal solution. The RoadRailer's unique air-ride system lifts the trailer gently as it is backed over the bogie for attachment. Once the bogie is in place, the air system lowers the trailer and lifts the tires off the tracks.

Other volatile materials such as lime or finely powdered materials are shipped in pneumatic silo trucks equipped with a blower to blow the material into the consumer storage silo (e.g., at a precipitated calcium carbonate plant). Bagged minerals, including pallets of small bags and larger bulk bags, are also trucked, but generally on flatbed trucks or inside an ocean container.

One trend in recent years has been combining truck and rail transport in so-called intermodal routes. This more commonly involves transferring ocean containers from rail to truck or vice versa, but can also involve transferring loose bulk or big bags. This is common in situations where the mine and plant of a small producer are not served by rail and the rail volumes are insufficient to justify investment in a rail spur, even though there is a rail siding relatively close by. Instead, material is loaded onto trucks and transferred to the railcars at the siding.

Larger players have invested in intermodal hubs along the most heavily used parts of the logistical network (Figure 3). In the U.S. market, Solvay serves customers requiring less than railcar volumes using 12 bulk rail-to-truck terminals. These provide a reliable source for customers and a nearby supply position to deal with urgent product requests.

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Ship and Barge Transportation of Industrial Minerals

Barry Parker and MID-Ship Marine Inc.

INTRODUCTION

This chapter summarizes the waterway and marine transport logistics of industrial minerals. Transportation is a critical element of the minerals business because deposits of raw materials may be in locations that are widely separated from where they are processed (Barker and Austin 1995; Barker 1997; Barker 2004; Barker and Harben 2004). Processing facilities may in turn, be oceans away, or perhaps miles away along a river, from industrial consumers further down the logistics chain. Transportation costs are often the single most crucial element in determining the ultimate profit or loss—the basic feasibility—of a specific mineral operation and associated transportation movement.

Ocean transportation in deep-sea vessels is discussed in the same chapter with barge transportation along U.S. inland-river and intracoastal-waterway systems because they are interrelated.

Topic Definition

This chapter covers the waterborne transportation of industrial minerals in bulk (see the glossary at the end of this chapter for definitions). The focus is on international deep-sea shipping as well as on U.S. domestic movements of industrial minerals by barge. The chapter also discusses fungible industrial minerals that move in dry-bulk carriers, sometimes as full cargo and sometimes as parcels. *Parcels* are multiple consignments transported on the same vessel, albeit with integral physical or suitable artificial segregations to prevent commingling of the shipments.

History

The industrial minerals business has evolved along with advances in transportation capabilities. The availability of economical ocean and barge transportation has enabled more distant sources of industrial minerals supply to be exploited and economically transported to processing or consuming locations. Industrial minerals are often found hundreds or even thousands of miles away from facilities where they are processed, and water transportation often binds the individual links in industrial minerals supply chains.

Economies of scale are possible where supply chains can handle larger vessel sizes such as *Capesize* behemoths capable of hauling 180,000 or even 300,000 t of coal or iron ore. Few industrial minerals, however, move in vessels larger than *Panamax* size. For this reason, the emphasis in this chapter is on smaller vessels, known as *Handysize* or *Handymax* size, capable of transporting 25,000 to 50,000 t of material.

Classification and Industry Structure

Maritime transportation can be segmented very broadly according to trades and types of vessels:

- *Dry bulk*: These vessels transport industrial or agricultural raw materials and semiprocessed materials primarily in bulk. They range widely in size from barge (transporting typically 1,500 t of materials) up to the huge *Capesize* ships that are too big for most ports. Industrial minerals typically move on dry-bulk vessels, often as parcel shipments. The service speeds of self-propelled deep-sea vessels typically range from 10 to 15 knots.

Within the dry-bulk category, certain vessel types and sizes predominate, as shown in Table 1.

- *Container/liner*: Goods packed in ISO standard cargo containers, typically 20 ft (6.058 m) or 40 ft (12.192 m) long, are transported by vessels specifically configured for carrying containers. Industrial minerals are sometimes containerized. Container vessels generally operate in “liner trades,” with widely published regular schedules known well in advance. Rates are also negotiated in advance and would be included within a confidential service package.
- *Liquid bulk (tanker)*: Tankers carry bulk crude oil, refined or intermediate petroleum products, industrial chemicals, and oils derived from agricultural processing. Such vessels are not suitable for industrial minerals, except where grain is shipped in tankers (and the cargo is loaded and discharged by spout or pneumatic equipment).
- *Specialized industrial*: These are highly specialized vessels, built specifically for transporting particular commodities. Examples include liquid-gas carriers, livestock carriers, and refrigerated cargo carriers (for meats, fruits, and vegetables). An overlap occurs with industrial minerals, where vessels are designed to transport ores or materials in self-unloading bulk carriers or in slurry form.
- *Cruise/passenger*: The passenger shipping segment is a highly visible sector of the market but is not relevant to the transportation of industrial materials.

Within dry-bulk shipping, a deep-sea (ocean-going) component exists along with a domestic barging component. The deep-sea shipping industry is mainly an international business, whereas the U.S. inland-river-barging industry is domestic. Both are subject to technical regulation by their respective *Flag State*, which is the

Table 1. Bulk vessel types and characteristics with typical Mississippi River barge dimensions shown for comparison purposes

Common Vessel Types	Typical Deadweight, tons and meters of draft	Typical Dimensions, length by beam	Typical Cargo Handling Gear
Barge	1,500 t on 9 m	59.44 m × 10.67 m	None, gearless
Handysize	26,000–33,000 t on 9.5–11 m	165–185 m × 23–29 m	4 or 5 cranes at 25 t each
Handymax	45,000 t on 11.6 m	186 m × 30.5 m	5 cranes at 25 t each
Super Handymax	55,000 t on 12.26 m	190 m × 32.26 m	5 cranes at 30 t each
Panamax	75,000 t on 14 m	225 m × 32.26 m	Usually gearless
Capesize	172,000 t on 17.75 m	289 m × 45 m	None, gearless

country where the ship is registered and which is therefore responsible for enforcing the applicable international conventions or domestic laws and regulations as they affect vessel operations.

Most countries maintain “national flag” vessels to handle their domestic- and government-sponsored movements as well as any military requirements. Deep-sea manned vessels must meet requirements of the SOLAS (Safety of Life at Sea) Conventions. Vessels must be inspected annually by their Flag States. Often, authority for such inspections is delegated to *classification societies*, which are international organizations that employ networks of surveyors and inspectors throughout the world who examine vessels. Vessels are also subject to detailed physical surveys, which are required every 5 years and usually coincide with out-of-the-water dry dockings.

For barges in the U.S. domestic trades, the American Bureau of Shipping handles technical regulation, enforcing regulations promulgated by the U.S. Coast Guard.

After the terrorist attacks on the United States on September 11, 2001, a new set of regulations concerning security of vessels and ports or shore facilities were added to requirements facing both shipowners and terminals.

Despite the array of technical, safety—and now security—regulations facing the industry, the bulk-shipping segment is not subject to economic regulation. Freight levels rise and fall depending on the interaction of cargo demand and vessel supply and are freely negotiated. Bulk shipping is sometimes described as the last bastion of the free market.

The shippers of cargo, who charter vessels (and are thus known as *charterers*), rely heavily on the free market for their supply of vessels. The supplier of the shipping tonnage may be the actual owner, or the supplier may be an operator who takes a vessel on charter from the primary owner and then resells space on the vessel to cargo owners.

Statistics

Freighting of industrial minerals is a subset of a much larger marketplace in dry-bulk shipping. The dry-bulk marketplace comprises dozens of subsectors representing the market in each commodity. The vessels in the marketplace are flexible and able to handle many cargo types, and thus they can respond to market opportunities among multiple subsectors and evaluate the most attractive daily returns. The industrial minerals trades form a small subset, estimated to be less than 20% of the total tonnage.

Table 2 shows the growth of the major commodity trades (in millions of metric tons). Major bulks are iron ore, coal, grains, bauxite and alumina, and phosphate rock. These major bulks move on dry-bulk carriers, but the total tonnage includes commodities that may move on specialized vessels. Tables 3 and 4 show the growth of the dry-bulk shipping fleet.

The balance of overall supply and demand over a multiyear time horizon determines the overall levels of freight rates in the marketplace. Vessel demand is also subject to short-term economic

influences, weather, seasonality, and market timing. In addition, technical, structural, and physical disturbances—mechanical breakdowns, inefficiencies, or plant production problems—are factors. Supply chain influences to or from the plant (such as rail, truck, or barge shortages) can and will cause delays and congestion—which, in turn, will affect overall vessel supply. Demand can be very volatile, especially where a number of charterers may be competing for available vessels. Even in the industrial trades, scheduling considerations can heighten this volatility. For example, where commodities are sold under yearly contracts, there may be a rush to move material just before the end of an expiring contract. Because of the many raw materials moved in bulk carrier vessels, shippers of industrial minerals may face rates that are determined exogenously.

Vessel supply is less flexible, involving capital investments in long-lived assets. The economic life of bulk carriers is typically 20 to 25 years. In poor freight markets, the owner may decide to scrap the vessel before the end of its economic life. In strong freight markets, owners may decide to invest in extra maintenance and repair that will enable the vessel to continue trading beyond the 20-year mark.

The interaction of semi-fixed supply and rapidly shifting demand brings about volatile freight markets. Strength in the sector from 2003 to 2004 resulted from a sharp increase in demand in the face of little new tonnage on order for vessel supply. Strong demand from countries such as China and India (with their huge populations) has been and will be a major factor that makes demand forecasting difficult, if not impossible. The strong freight market did lead to reduced scrapping and more vessel orders, but new tonnage is typically not delivered until 18 to 24 months after an order is placed.

TECHNOLOGY

Vessel Configurations

Most of the vessels involved in the industrial minerals trades have the generic term of *bulk carriers* and are Handysize and Handymax- or Super Handymax-size vessels, with Panamax-size vessels used as the demand increases (the latter depend on port infrastructure and restrictions). Unlike general cargo vessels with multiple decks and obstructions, bulk carriers have cavernous holds and large hatches that provide loading and discharging equipment substantial access throughout the holds. Bulk carriers can also be strengthened so that they can take full loads of dense or heavy cargo in alternate holds without placing undue stresses on the vessel's structure. As a matter of economic practicality, vessel owners will build versatile vessels that can handle a wide variety of cargoes. A few may build a vessel for a particular user on a particular multiyear contract.

Many configurations of vessels exist based on intended purpose and on a variety of designs. For example, certain vessels intended to be used for international trade into the Great Lakes will be designed to lift maximum tonnages of cargo on the draft and beam constraints imposed by the Saint Lawrence Seaway. The seaway restrictions are currently about 7.925 m (26 ft) freshwater draft, 23.8 m (78.1 ft) beam, and about 225 m (738 ft) length overall.

Table 2. Movement of major and minor dry-bulk materials in deep-sea trades, Mt

Dry-Bulk Materials	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004
Major Bulks*										
Iron ore	402	392	428	428	405	450	453	482	524	587
Coal subtotal	403	425	451	453	464	514	546	568	613	658
Steam	242	261	282	284	302	340	377	399	441	474
Coking	160	165	170	169	162	174	168	169	171	184
Grains subtotal	216	219	229	226	247	264	260	271	264	265
Wheat/coarse	184	185	190	187	205	214	207	214	205	206
Soybeans	32	34	39	40	42	50	54	58	59	59
Bauxite/alumina	52	54	55	55	54	54	54	54	57	66
Phosphate rock	30	31	32	31	31	28	27	26	26	27
Major bulks subtotal†	1,103	1,121	1,195	1,193	1,201	1,310	1,340	1,402	1,484	1,604
Minor Bulks										
Sugar	34	36	37	38	40	36	41	44	46	46
Agribulks	80	81	82	92	95	87	87	91	90	94
Fertilizer	61	60	63	64	67	68	69	71	73	76
Scrap	46	46	49	46	45	46	44	45	48	53
Cement	53	55	56	45	45	46	46	45	47	48
Coke	15	13	13	11	15	19	18	14	17	24
Pig iron	14	12	14	13	12	12	12	12	13	14
Forest products	167	163	166	156	158	161	164	160	163	166
Steel products	198	200	195	189	174	187	181	186	197	206
Others	31	33	33	33	34	36	37	37	391	40
Minor bulks subtotal	699	699	708	687	685	698	699	705	733	767
Major and minor bulks total	1,802	1,820	1,903	1,880	1,886	2,008	2,038	2,106	2,215	2,372

Adapted from UNCTAD 2004; Clarksons Research Services Limited 2005.

* Major bulks totaled 448 Mt in 1970, 796 Mt in 1980, and 968 Mt in 1990.

† Totals may reflect rounding errors.

(LOA), but the last is usually not a serious restriction—the beam and draft are the most serious.

The vessel description is crucial for all personnel involved in vessel chartering. Fundamentally, the vessel must fit into its intended load and discharge ports and berths; its configuration will also influence how much cargo can be carried and how fast it can be loaded and unloaded.

The vessel description can have legal implications as well, when the vessel is described in the *charter party* between the vessel owner and the charterer. The charterer must exercise extreme diligence to be certain that vessels are capable of meeting the requirements of sales contracts on the underlying commodities.

Numerous vessel designs exist within the bulk carrier category. Four common designs are encountered in the industrial minerals trades: *TESS45* type, *Federal Oshima* type, *Federal Shimanto* type, and *Federal Saint Laurent* type.

The *TESS45* vessels (and their larger and smaller similar designs), as well as similar type vessels, are workhorses trading all over the world. These vessels, many of which are controlled by the Montreal-based shipowner Fednav Ltd., are worth noting because their design configuration allows them to trade into and out of the Great Lakes, and they are able to maximize the cargo intake on the draft and maximum beam restrictions of the Lakes–Seaway System. A number of shipowners and vessels can and do trade into and out of the Great Lakes—where the typical season runs from April through the middle of December. After about December 15–25, the system is closed for the winter; any ships that are late in exiting are sometimes caught until the system reopens at the end of March of the following year.

Numerous minerals parcels are imported through the Great Lakes, most coming from the Far East, Australia, New Zealand, Africa, and South America.

Shoreside Facilities: Terminals and Equipment

Depending on the commercial terms of the commodity sale, the cargo interest may become involved with the loading and discharging of the cargo. There are many terminals and facilities where industrial minerals can be loaded and unloaded, but the terminals are links in a broader supply chain.

The choice of a terminal for use in a particular cargo move will depend on a host of factors, some of which, in turn, will depend on capabilities or requirements in a particular commercial contract. Although there are some exceptions (for instance, in a dedicated run over an extended period of time), the charterer must warrant to the shipowner that the port is a safe port. Shippers (and receivers) of minerals should require a similar warranty from their business partners in the supply chain who are actually responsible for nominating the particular port.

Some of the important factors to be considered in choosing an actual berth for cargo operations are the following:

- Draft: What is the depth of water alongside the loading or discharging berth?
- Airdraft: What is the height above the waterline of the highest point on a vessel?
- Storage: Can cargo be stored without contamination or exposure to elements?

Table 3. The dry-bulk shipping fleet

Year (start)	Existing Fleet	Subtract: Layup	Tons Operating	Add: Combination in Dry	Operating Dry Fleet*
1993	215	1.6	213.4	16.1	229.5
1994	219	1.5	217.5	13.9	231.4
1995	225.5	1.3	224.2	15.2	239.4
1996	242.2	1.1	241.1	11.3	252.4
1997	252.1	0.9	251.2	11.3	262.5
1998	263.3	1.0	262.3	7.0	269.3
1999	263.3	1.5	261.8	5.3	267.1
2000	267.4	1.9	265.5	6.2	271.1
2001	276.3	1.3	275.0	4.3	279.3
2002	288.5	1.8	286.7	3.7	290.4
2003	295.9	0.5	295.4	2.5	297.9
2004	303.3	0.5	302.8	4.0	306.8
2005	320.8	0.6	320.2	5.3	325.5

Source: *The Platou Report 2004*.

* Operating dry fleet is equal to the starting fleet minus tons in layup plus combination carriers in dry-bulk trades. Numbers may contain rounding errors.

Table 4. Breakdown of the dry-bulk fleet into size categories*

Year	10,000–60,000	60,000–79,999	80,000+	Total
1993	103.8	51.9	59.4	215.1
1994	103.4	53.4	62.2	219.0
1995	104.2	56.3	65.0	225.5
1996	108.9	59.8	73.6	242.3
1997	112.5	60.6	79.0	252.1
1998	115.3	64.7	83.3	263.3
1999	116.6	65.7	81.0	263.3
2000	117.5	68.1	81.9	267.4
2001	118.2	71.3	86.8	276.3
2002	121.1	77.5	89.9	288.5
2003	123.7	80.3	89.9	293.9
2004	129.4	74.9	97.3	301.6
2005	134.1	80.2	104.3	318.6

Adapted from *The Platou Report 2004*; Clarksons Research Services Limited 2005.

* The end-2004 fleet of Handysize bulk carriers in the 10,000–40,000-dwt (deadweight ton) range comprised 2,742 vessels. The average vessel deadweight within the category was approximately 26,600 dwt. Within the Handysize fleet, 57% of the tonnage was 20 years old or older, and 25% was less than 10 years of age. At the end of 2004, approximately 66.8 Mdwts of dry-bulk tonnage was on order, including 161 vessels comprising 4.7 Mdwts in the Handysize sector. Size breakdown may reflect rounding practices and discrepancies between sources.

- Rail access: If the cargo comes inbound by rail (or is forwarded on to a receiver with a rail facility), does the terminal have rail access?
- Barge access: If the cargo comes inbound via the river system (or is trans-shipped into a barge after arrival at a port), is the terminal situated so that barges can load or unload alongside the vessel or at adjacent berths? Are barges available?
- Truck access: For very small lot sizes, or where minerals are shipped in containers, can trucks easily service the terminal?

- Handling equipment: Is the type of equipment suitable for the cargo being shipped? Are gantries (on shore) or floating equipment (in the river) suitable for handling of the cargo? What rate of throughput is provided? Is the rate of throughput consistent with underlying commercial terms?
- Physical restrictions: Do the vessel dimensions interfere with quick loading and discharging of the cargo at the particular terminal? Can the cranes (shore cranes or loading equipment) reach into the holds of the ship?
- Waterside: Is the dock long enough to accommodate a particular vessel?
- Hours: Does the terminal support the 24-hour work usually needed for minerals movements?
- Dimensions: Is the water deep enough at the dock, even at low tide, to accommodate the vessel? At high tides, will the vessel dimensions enable it to remain clear of any obstructions?
- Restrictions: Clarify in advance that the terminal will allow normal vessel operations, which may include taking on fuel (by barge), delivery of supplies, or crew changes.
- Regulatory: Confirm that the terminal is in compliance with regulations relating to environmental or maritime security matters.

MARKETING: THE MAJOR TRADES AND THE BROKER NETWORK

The demand for ocean freight represents derived demand, reflecting patterns in the materials markets that underpin the demand for freight. As noted in the Statistics subsection in this chapter, the marketplace for freighting of industrial minerals is a subset of the much broader dry-bulk transportation market.

Shipowners and cargo interests are located all over the world and are often represented by shipping brokers who are compensated by commissions that represent a small portion of the gross freight. The shipowner pays the commission. Shipbrokers are on call 24 hours per day, 7 days per week, throughout the year. *SHINC* means “Sundays and holidays included,” and, because of the global nature of the shipping market and the fact that there may be hundreds of relationships (if not thousands) that need to be managed continuously, SHINC is especially important during periods of high volatility. It is important that the “right” broker be used to suit the individual client’s needs and market coverage. Historically, shipping brokers add value by filtering the enormous amount of market information generated daily and enabling charterers to minimize their freighting costs, subject, of course, to achieving optimal transportation coverage for their raw materials movement program.

In today’s globalized economy, and because of the interconnectivity of the relationship of ocean freight to the other demands of the total supply chain, the broker must understand all facets of the shipment in question. Even in today’s high-technology environment, the broker is more valuable than ever in interpreting market conditions and developments while guiding their client. Brokers are bound by their commitment to integrity and professionalism. Thus, “choose your broker carefully and wisely” is sound advice.

The role of the shipping broker is paramount in arranging transportation of industrial minerals. Historically, brokers have specialized in representing either shipowners or representing charterers of ships; with the vast improvements in communications throughout the 1990s and 2000s, however, the lines have become increasingly blurred. Typically, brokers in London, Oslo, Greece, and Hong Kong have specialized in representing owners. The charterers’ brokers have clustered in business centers tied to the processing of raw materials. Singapore has emerged as a shipping center, particularly

after reversion of control of Hong Kong to the People's Republic of China in 1997. With the ascendancy of Asian economies, Singapore, Seoul, and now Beijing continue to grow in importance.

The Role of Barging in Logistics

The movements of industrial minerals are often part of supply chains encompassing numerous intermediaries and multiple transportation modes. The imported raw materials may not be processed at or near an actual port of importation but rather at a facility on the U.S. inland waterway system (Figure 1).

More than 1 billion st of materials annually move throughout the inland waterway system, as shown in Table 5.

Table 6 shows the breakdown of movements on the inland waterway system by commodity groups and by river systems. Industrial minerals fall within the crude minerals group. As in the deep-sea shipping segment, minerals comprise a very small percentage of the overall totals. Geographically, most of the trade originates on the Mississippi River and the Ohio River branches.

Mineral cargoes transported on the inland waterway system will typically move in covered barges. A towing company will put together a tow consisting of up to 30 barges of various types. The typical covered barge, with a rake shape, has the following dimensions.

Length:	59.44 m (195 ft) to 60.96 m (200 ft)
Beam:	10.67 m (35 ft)
Depth:	2.74 m (9 ft)
Light draft:	0.53 m (1 ft 8 in.)
Cargo:	
On 2.74-m (9-ft) draft	1,360 t
On 3.0-m (10-ft) draft	1,542 t

The 1,360-t cargo capacity of the typical barge compares with the 91-t capacity of a railcar and the 22.7-t size of a cargo truck, enabling greater economies of scale for barge transport over the other transport modes. In evaluating the economics of moving cargo originating at, or destined for, locations not directly contiguous to a navigable waterway, the cost of additional rail or truck transport must be considered.

The overall barge fleet (Table 7) has some 24,530 dry-cargo barges that trade on the Mississippi River system and inland waterways. The dimensions of the barges have been standardized to enable them to meet physical restrictions on the river system, including locks on the Upper Mississippi and tributaries, as well as draft restrictions.

As with deep-sea shipping, bulk commodities moving in barges are not subject to rate regulation, but the barges and towsboats must comply with safety and security regulations promulgated by the U.S. Coast Guard.

Economics

Freight Rates Over Time

The interaction of vessel supply and demand leads to the *time-charter* hire rates (dollars per day) and voyage freight rates (dollars per ton), which are described in this section.

The rates that are paid by shippers of industrial minerals are quoted on voyage terms, in dollars per ton (in worldwide trade, this is generally *per t*). The rates on a given move will depend on many voyage-specific criteria but also on the general levels of the freight market as determined by the supply and demand interaction. These rates reflect conditions for many vessel types capable of hauling dozens of different materials throughout the world.

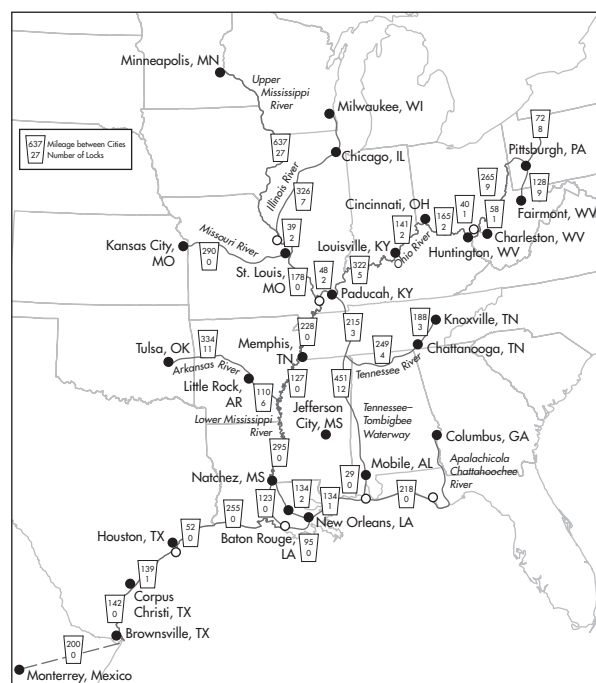


Figure 1. Map of the U.S. inland waterway system

The general market levels are indicated by timecharter rates, which reflect what the charterer will pay, on a dollars-per-day basis, for the use of a vessel. Under the timecharter contract the shipowner must maintain the vessel and supply the crew. These timecharter rates (sometimes called “hire” rates) are converted by the shipowner into the more familiar dollars-per-ton rates quoted to minerals shippers.

Figure 2 shows the trend in hire rates from the mid-1970s through 2003 for two types of Handysize vessels (16,000 and 30,000 dwt). These rates represent period timecharter employment, meaning that they are not sensitive to geography. Six time series are shown; each of the two vessel types has three time series: 6-month charters, 1-year charters, and 3-year charters. The graph shows the 6-month rates to be more volatile than the longer-term rates across both size categories. The market’s upward spike in 2003 is visible on the right side of the graph.

Figure 3 shows daily hire rates for selected Handymax timecharter routes for vessels of approximately 45,000 dwt, including the TESS45 types, from mid-2000 through mid-2004. Unlike the period timecharter rates in Figure 2, these hire rates are sensitive to geography. The rates for trips from the Atlantic Ocean to the Pacific Ocean (U.S. Gulf–Far East and trip out to Far East) are higher than those for trips where vessels remain in the Pacific. As in Figure 2, the market’s sharp upturn in mid-2003, where vessels such as the TESS45 types could earn as much as \$50,000/day, is clearly visible across each of the time series.

Timecharter to Voyage Conversions

Freight rates in the bulk trades are freely negotiated between the charterer and the shipowner or operator. Shipowners base freight rates on prevailing market levels, as reflected in terms of dollars-per-day timecharters. In their conversions, shipowners begin with a timecharter rate that would reflect the prevailing market conditions at the time of the negotiation. The calculations start with a dollars-

Table 5. Materials moving in U.S. domestic waterborne commerce (1994–2003), millions of short tons*

	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003
Internal	618.4	620.3	622.1	630.6	625.0	624.6	628.4	619.8	608.0	609.6
Coastwise	277.0	266.6	267.4	263.2	249.6	228.8	226.9	223.6	216.4	223.5
Lakewise	114.8	116.1	114.9	122.7	122.2	113.9	114.4	100.0	101.5	89.8
Total†	1,099.0	1,093.1	1,100.8	1,112.6	1,094.1	1,061.8	1,069.8	1,042.5	1,021.0	1,016.1

Source: USACE Waterborne Commerce Statistics Center, undated.

* Rounding may result in commodity tonnages that do not add up to the totals for a waterway.

† Total includes minor trades not previously detailed.

Table 6. Domestic U.S. waterborne traffic, annual tonnage, millions of short tons

	Calendar Year 2002	Calendar Year 2003	Change, %
National Internal Commodities			
Coal	174.6	170.7	-2.26
Petroleum	145.6	149.5	2.62
Chemicals	47.6	51.5	8.15
Crude materials	115.1	119.0	3.41
Manufactured goods	27.1	25.9	-4.35
Food and farm	91.0	84.0	-7.70
Manufactured equipment	5.9	7.7	29.92
Other	1.0	1.3	30.25
Waterways			
Allegheny River	2.8	3.3	17.69
Atchafalaya River (Upper)	10.7	9.7	-8.87
Atlantic Intracoastal	1.8	1.8	2.22
Big Sandy	25.1	22.6	-9.86
Black Warrior River	19.0	21.0	10.43
Columbia River*	15.5	16.0	2.87
Cumberland River	22.6	20.6	-8.73
Gulf Intracoastal*	107.7	117.8	9.47
Illinois Waterway	43.0	45.0	4.55
Kanawha River	19.2	19.8	3.12
McClellan-Kerr Waterway	11.9	13.0	9.12
Mississippi River*	316.2	308.2	-2.53
Missouri River	8.3	8.1	-2.61
Monongahela River	38.2	27.6	-27.79
Ohio River	243.1	228.8	-5.91
Snake River	4.3	5.3	24.64
Tennessee River	43.9	49.8	13.41
Tennessee Tombigbee	6.2	6.2	-0.17
National Totals†			
Domestic	1,021.0	1,016.1	-0.48
Lakewise	101.5	89.8	-11.52
Coastwise	216.4	223.5	3.26
Intraport	90.0	86.9	-3.44
Intraterritory	5.1	6.4	25.47
Internal	608.0	609.6	0.26

Source: USACE Waterborne Commerce Statistics Center, undated.

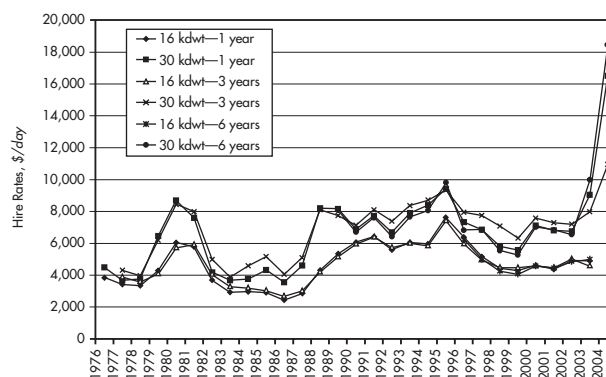
* Includes domestic coastwise tonnage.

† All national totals exclude fish and waterway improvement materials.

Table 7. Nonself-propelled barge and towboat fleet profile

Profile Characteristic	Total, All Regions	Atlantic, Pacific, and Gulf Coasts	Inland Waterways and River System	Great Lakes
Number of dry cargo vessels	27,272	3,686	24,530	218
Cargo capacity, t	39,095,045	6,321,580	32,373,210	373,038
Number of towboats	5,172	1,779	3,265	128
Average horsepower	1,901	2,268	1,757	1,279

Source: USACE Waterborne Commerce Statistics Center, undated.

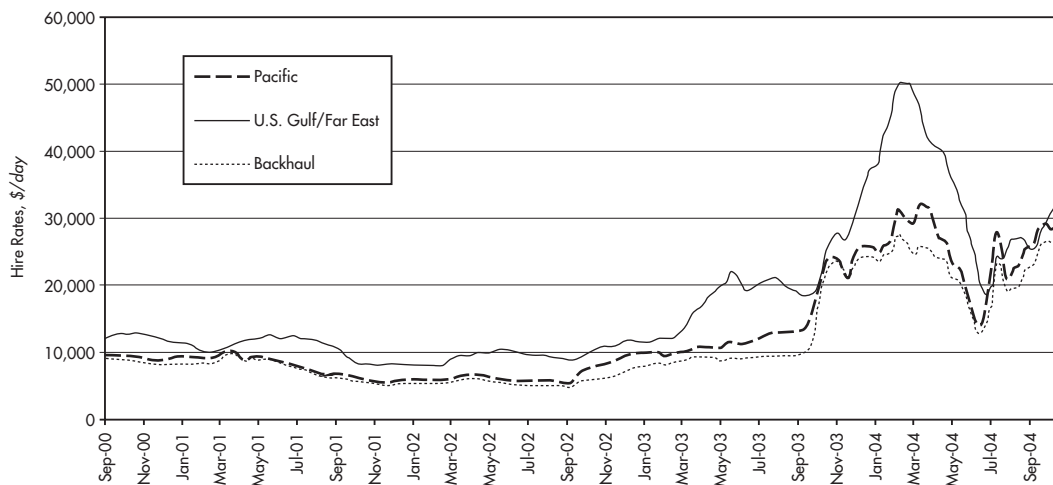


Source: Clarksons Research Services Limited 2005.

Figure 2. Timecharter rates for Handysize vessels (1976–2004), kdw

per-day timecharter value for the vessel, then build in other costs of the voyage (fuel, port-related, and sometimes canal costs) based on the estimated number of days in the voyage, which is then divided by the number of tons carried to arrive at the cost per ton. Depending on the relative negotiating strengths of the owner versus the charterer, the actual voyage rate agreed-on may work back to a timecharter return to the owners that is above (or below) the prevailing levels.

The overriding factor in determining the final freight level paid will be market demand at the time of negotiation. The shipowner will do their calculation, evaluate the market, and determine the desired return, but the minute there is competition (be it between different shipowners or different charterers), all the calculations will become moot and the freight rate will be established according to final negotiations and who wants the business more.



Courtesy of The Baltic Exchange Ltd. © 2005.

Figure 3. Timecharter rates for Handymax trades

The shipowners are quite adept at evaluating different financial results from the thousands of messages received daily advising them of cargo inquiries, port congestion, costs, etc. A good broker representing the charterer becomes invaluable, with the capability to level the playing field and, in most cases, bring competing shipowners to the negotiating table. In some cases, all that may be necessary for the charterer to benefit is for the broker to somehow convincingly create the perception of competition.

The voyage rates in charter calculations are predicated on free in and out (FIO) terms to the shipowner. The cargo shipper or receiver rather than the shipowner will pay for loading and discharging. The dollars-per-ton cost for loading and discharging the cargo will be negotiated separately between the shipper or receiver and the terminals at each end.

Shipowners and cargo shippers have developed standardized ways of estimating the profitability of voyages, based on conversions between the shipowners' timecharter dollars-per-day (timecharter) rates and the cargo shippers' focus on dollars-per-ton (voyage) rates. The calculations will yield unique results for each set of parameters entered regarding the vessel, load and discharge rates, fuel prices, voyage routing, and other factors. These calculations are done on proprietary software.

The actual agreed-on rate will be the result of negotiations between owner and charterer. The shipowner will use computerized calculations run internally and in conjunction with a broker to develop a freight quote. The cargo shipper may use similar analytic tools to estimate the likely economic return that the shipowner is earning, and may use such an analysis in negotiations. Calculations of a freight quote contain estimates such as port costs and fuel consumption as well as miscellaneous costs and extra days to account for weather-related contingencies. Each participant may estimate the voyage costs somewhat differently. In any case, efficient operation is rewarded. If a number of participants are using a particular cost or a standard number of days for a particular activity, that time interval will be reflected in the prevailing dollars-per-ton rates negotiated in the marketplace. If a certain shipowner can perform the activity more cheaply than others, or in a shorter time period, the timecharter (dollars-per-day) equivalent of the dollars-per-ton rate will be enhanced. Note that market conditions that vary weekly, daily, and sometimes hourly determine the ultimate freight rate.

REGULATION

Shipping is an international business, and therefore the regulatory system is international. This section has no discussion of economic regulations such as freight tariffs because the bulk shipping business is economically unregulated.

Most of the regulations governing the safe operation of vessels, the handling of cargo, and the newly important maritime security concerns are coordinated through the auspices of the International Maritime Organization (IMO), a United Nations body based in London. Member countries where vessels are registered and documented are known as Flag States. Flag States enact legislation that implements provisions agreed on in IMO conventions. For example, in the United States, the U.S. Coast Guard promulgated regulations in 2003 that reflected an IMO agreement reached in late 2002. Nations that interface with vessels through cargo loading or discharging operations are called *Port States*, and those vessels may transit the economic zones of coastal states. Table 8 shows leading Flag States as of March 1, 2004. Note that the leading industrial countries, which generate trade, are not the leading Flag States.

IMO membership comprises 160 countries that negotiate and agree on international diplomatic conventions. The ratification procedure gives leading Flag States a greater weighting. The dictates of Flag States are very often delegated to classification societies that examine vessels. As an example, the U.S. Coast Guard performs vessel inspections but also delegates parts of this role to the American Bureau of Shipping, one of the world's leading classification societies.

Some of the more important regulatory conventions, negotiated at the IMO and enforced by flag, port, and coastal states, are as follows:

- SOLAS (Safety of Life at Sea), an international agreement that covers the safe operation of vessels, and also tonnage measurement and certain cargo-stowing practices aboard vessels.
- MARPOL (Maritime Pollution Convention, also known as the International Convention for the Prevention of Pollution of Ships) that covers oil or other pollution matters and compensation for pollution incidents.

Table 8. Leading shipping registries (Flag States)

Flag State	Number of Vessels	Vessels, dwt	Combined Number of Vessels	Combined, dwt	Number of Bulk/Ore Vessels	Bulk/Ore, dwt	Total Number of Vessels	Total, dwt	Percentage
Panama	906	55,786,756	14	1,459,619	1,505	95,365,652	2,425	152,612,027	24.00
Liberia	475	41,293,970	20	1,723,094	297	17,063,609	792	60,080,673	9.50
Greece	281	31,677,832	2	130,782	287	19,149,377	570	50,957,991	8.00
Malta	280	17,423,443	6	476,169	479	20,398,399	765	38,298,011	6.00
Bahamas	212	24,061,782	17	1,318,136	246	12,217,292	475	37,597,210	5.90
Cyprus	144	7,337,497	0	0	438	21,875,867	582	29,213,364	4.60
Hong Kong	73	7,497,537	3	288,604	357	21,310,309	433	29,096,450	4.60
Singapore	307	17,336,827	8	1,166,000	157	9,974,828	472	28,477,655	4.50
Marshall Islands	180	19,015,372	8	696,530	91	5,569,009	279	25,280,911	4.00
Norway	220	11,343,323	29	3,679,646	88	5,418,731	337	20,441,700	3.20
People's Republic of China	184	4,522,716	0	0	337	12,457,276	521	16,979,992	2.70

Source: Clarksons Research Services Limited 2005.

- ISM (International Ship Management) Code that covers shipping company management practices onshore and onboard vessels.
- ISPS (International Ship and Port Security) Code that covers security matters at port facilities, within shipping companies, and aboard vessels.

This is only a partial list; there are approximately 40 international conventions on matters related to maritime trade and shipping. Issues of cargo carriage are considered in both the SOLAS and MARPOL rules as well as the International Maritime Dangerous Goods (IMDG) Code, originally a supplement to the SOLAS rules, which became mandatory on January 1, 2004.

Disputes between shipowners and charterers of the vessels are generally settled by panels of arbitrators following well-established sets of precedents and industry practices. The brokers in most major shipping centers are members of industry associations that unofficially enforce standards of acceptable business conduct in the absence of formal regulation. Arbitration panels are usually convened in either London or New York. Very rarely, when one party is not satisfied after having exhausted the arbitration route, it will bring suit through the court system. Longer-term contracts may stipulate that the initial recourse will be through the courts.

OUTLOOK AND FUTURE TRENDS

The bulk freight markets represent a pure economic marketplace. Rates are determined by the interaction of supply and demand with vessel charters negotiated through the broker network. The industry has been subject to dramatic increases in regulatory scrutiny in recent years concentrating on safety and then on security. Following the advent of the ISPS Code in 2004, no economic regulation exists in bulk shipping.

In the summer of 2003, freight levels across the range of vessel sizes moved sharply higher, peaking in the late winter of 2004 before dropping slightly. After a softening of 2 months' duration, rates moved sharply upward again throughout 2004, in many cases eclipsing the highs set earlier in the year. In the late winter and into the spring of 2005, the market softened, albeit to levels that were very firm by historical standards.

The market strength can be attributed to demand stemming from dramatic increases in the demand for raw materials in China and other Asian countries, especially in the iron and coal trades. Not only were cargo tonnages up substantially, but longer hauls were also the norm. Incremental iron ore demand was sourced from

Brazil rather than from Australia, the conventional source. The existing fleet could deliver fewer cargoes each year because the haul from Brazil was farther, thereby putting extreme upward pressure on the available supply of vessels. The raw material movements first affected the Cape size sector, with the tightness spreading to the Panamax and Handymax sectors as well. As China's steel production increased, exports of finished products brought about a surge in demand for Handymax tonnage.

As has been the case historically, expectations of future levels brightened in the stronger market, leading to a surge in orders for vessels, with deliveries scheduled for 2005 and into 2006. Analysts are evaluating how the interaction of volatile demand with increasing supply would play out. In early 2005, spot market rates were much higher than forward rates as evidenced by period time charters where vessels are taken for 1, 2, or even 3 years, or by increased activity in the nascent forward-freight market, a sector where financial contracts tied to freight indices are traded. The forward discount suggested that most market participants felt that the market would soften.

From the 1980s through 2003, certain ceilings on rates were in evidence. The market surge of 2003 broke through those ceilings. Generally, demand can be very volatile as charterers flood the markets with cargoes and then pull back if rates appear to be moving sharply upward.

According to technical analysts who focus on the patterns of rates, when rates do retrench, they settle at levels above the previous highs. The psychology of the freight markets is no different than other commodity markets, where traders "buy on the dips," having missed a chance to buy earlier. In Figure 3, showing freight rates for Handymax vessels, the previous ceiling was in the region of \$10,000/day. Although it is impossible to provide a precise forecast, a likely pattern for the future is that freight rates will be very volatile, at levels above the market highs of pre-2003. The freight levels will be set through continual testing of previous lows (and highs, when the market surges upward).

Fundamental forecasters, who look at the size of the fleet in relation to demand, point to an increased supply of new vessels as they are delivered from shipyards. Most analysts, however, expect strong demand from China, India, and other Asian economies, which may continue to fuel the market and absorb at least the initial new tonnage.

A shipbroker with expertise in the movements of industrial minerals does far more than merely "fix" ships. The broker can

advise opportune times to charter vessels, in addition to providing clients with a complete picture across the many different trades that comprise the charter market.

INTERNET RESOURCES

- Clarksons Research Services Limited, London; <http://www.clarksons.net>
- Fearnleys, Oslo, Norway; <http://www.fearnleys.com>
- Informa Publications, London; <http://www.informatrade.com>
- Lloyd's Register-Fairplay, Surrey, United Kingdom; <http://www.lrfairplay.com>
- R.S. Platou Group, Oslo, Norway; <http://www.platou.com>
- Maritime-Research Inc., Parlin, New Jersey; <http://www.maritime-research.com> and <http://www.shipping-markets.com>
- Witherby's Publishing, London; <http://www.witherbys.com/homeframe.html>

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GLOSSARY

All details about: All details about.

Bareboat charter: A contractual arrangement in which a vessel owner pays finance costs only, but then charters the vessel out to a bareboat charterer that will be responsible for the actual operation (crewing, maintenance, insurance) of the vessel. The bareboat charterer will then act as an owner with respect to freight transactions in the marketplace.

Barge: Nonself-propelled vessel generally used for transportation in a river and inland waterway system.

Beam: The width of a vessel.

Bill of lading: Document evidencing ownership of the cargo, issued by the vessel's master. The bill of lading weight indicates how much cargo has been loaded aboard the vessel.

Bulk carrier: A vessel dedicated to the transport of solid bulk cargoes.

Bulk shipping: Shipping of materials that are not packaged. Generally refers to industrial raw materials (e.g., coal, iron ore) and agricultural commodities.

Capesize: A vessel that is unable to transit the Panama Canal because of its size. Generally refers to dry-cargo vessels greater than 80,000 dwt and are typically in the size range of 130,000 to 180,000 dwt. Such vessels typically transport iron and coal.

Charter party: The contract between the charterer and the owner (or controlling party) of a vessel that outlines the terms and conditions of carriage. The terms of the contract will vary depending on the trade and market circumstances. Broadly, the charter party will cover voyage freighting or a timecharter of the vessel.

Charterer: The buyer, or user, of freight services. May also be the actual shipper or receiver of the cargo, but may also be an intermediary that, in turn, subcharters the vessel onward or provides parcel transportation.

Class: The major classification societies are Lloyds Register (LR), American Bureau of Shipping (ABS), Det Norske Veritas (DNV), Germanischer Lloyd (GL), and Bureau Veritas (BV). See also Classification society.

Classification society: An inspection company, usually with surveyors stationed in ports around the world, that supervises technical inspections of vessels, often acting in the capacity as the inspection arm of Flag States.

Contract of Affreightment: A timecharter agreement calling for multiple liftings of either full vessel loads, or parcels, usually between the same loadport (or range of ports) and discharge port (or range of ports).

COP/CQD: Custom of the port/customary quick dispatch. These terms, typically used together and in place of fixed loading and discharging speeds, remove a good amount of risk and exposure to the cargo interests, and, conversely, place a greater risk and more exposure on the shipowner.

Deadweight tons (dwt): The carrying capacity of a ship measured in terms of the weight, in tons, of the cargo, fuel, provisions, and passengers that the vessel can carry.

Deep-sea vessel: Vessels that trade between ports on voyages that take the vessels more than 80 km from shore. Generally, this designation refers to manned vessels of at least 500 gross tons that are subject to the SOLAS Convention.

Disponent owner: The owner, in a contractual sense, of a vessel that is chartered in from the actual owner (or another disponent owner).

Draft (or draught): How deep a vessel is submerged below the waterline.

DWAT: Deadweight all told. The total deadweight, including cargo, fuel provisions, etc.

FFA: Forward freight agreement—a contract with a financial settlement, between a buyer and seller of forward freight, tied to levels of a freight index or one or more routes with a freight index, used for hedging purposes.

FIO: Free in and out, from the vessel's viewpoint. The cargo interest(s), who may be the charterer of the vessel (or may be the shipper or receiver), must arrange and pay for loading and discharging of the cargo.

FIOST: Free in and out, stowed and trimmed—where the charterer is also responsible for the stowing of the cargo (typically break-bulk/general cargo), or, in the case of bulk commodities, where the charterer is also responsible for the trimming of the cargo.

Fixing or fixed: The process of freight negotiations that will lead to a binding contract between the shipowner (carrier) and the charterer—that is, “we are now fixed.”

Flag State: The country where a vessel is registered, responsible for enforcement of international safety and technical regulations.

GR/BA: Grain/bale—the cubic capacity of the vessel’s cargo hold, measured in either cubic meters or cubic feet. Grain capacities—measuring capacity for freely flowing cargo—will usually exceed the bale measurement, which refers to baled cargo.

GRT: Gross register tons—a volumetric measurement (each ton = 100 ft³) used to describe a vessel, especially for computing wharfage and port costs.

GRT/NRT: Gross register tons/net register tons—in vessel descriptions, both are used, with the NRT measure referring to the volume in cargo spaces.

Handysize, Handymax, and Super Handymax: Handysize vessels are usually 15,000–35,000 dwt, Handymax vessels are typically 37,000–48,000 dwt, and Super Handymax vessels are 50,000–55,000 dwt. They take a wide range of bulk cargoes, with Handysize, and lately, more Handymax-size vessels, being frequently employed in the parcel trades.

HO/HA: Holds/hatches—the number of cargo holds and the number of hatches, in ship descriptions.

Lakes draft: Allowable draft for vessels transiting the Saint Lawrence Seaway, connecting the Great Lakes with the Saint Lawrence River.

Liner service: A shipping service according to fixed schedules known and widely published in advance. Contrasts with *tramp service*.

Liner terms: A charter contract where the shipowner, or carrier, is responsible for the loading and discharging of the cargo. Contrasts with *FIO* terms.

LOA: Length overall (of a vessel).

Long ton (lt): A unit of weight equal to 2,240 lb.

Metric ton (t): A unit of weight equal to 1,000 kg (typically converted as 2,204.6 lb).

Operator: In the bulk shipping context, a seller of freight services on vessels that are chartered from the actual vessel owner (or from a disponent owner).

Owner: The seller of freight services. May also be the carrier that deals with the charterers, but not in cases where the owner is acting as an intermediary (chartering the vessel outward to another owner who may actually be dealing with cargo owners). Generally the *head* or *registered* owner is the financial and legal owner (and ultimate controlling party) of the vessel.

Panamax: Refers to the largest vessels that can transit the Panama Canal, effectively limited by the maximum breadth (beam) of 32.26 m (just shy of 106 ft). Based on current vessel design criteria, such restrictions typically equate to vessel deadweight

sizes ranging from about 60,000 dwt (usually older vessels) up to a maximum of about 78,000 t (newer vessels). Such vessels carry a wide range of bulk cargoes, including grains, coal, and iron ore. They may also transport industrial minerals parcels.

Parcel shipment: A shipment less than the full carrying capacity of a vessel. Typically, multiple parcels will be handled by shipowners and operators who typically specialize in providing such parcel service.

SHEX: Sundays and holidays excluded—referring to time allowed for vessel loading and discharging.

SHINC: Sundays and holidays included—referring to time allowed for vessel loading and discharging.

Short ton (st): A unit of weight equal to 2,000 lb.

SOLAS Convention: Safety of Life at Sea Convention—the body of international law that governs the safe operation of vessels.

Spot charter: A charter for one lifting, typically loading within several days of concluding the charter (or fixture), as distinguished from a consecutive voyage charter, or a lifting done under a contract for multiple liftings. Usually refers to a voyage arrangement where the charterer pays an agreed-on dollars-per-ton freight rate under voyage terms.

SSW: Summer salt water—the DWAT of a vessel can vary depending on the salinity of the water, and SSW specifies that the deadweight described is measured using salt water, without any restrictions for winter conditions.

Stowage factor: The number of cubic feet per ton that a specific commodity will occupy in the vessel’s holds. Industrial minerals are typically dense cargoes with stowage factors in the range of about 15 to 40 ft³/t (as well as lower and higher).

Timecharter: A charter contract in which the charterer pays a daily hire rate (dollars per day) for the use of the vessels. The charterer directs the movement of the vessel and must pay fuel, port, and canal costs.

TPC: Tons per centimeter immersion—the number of tons of cargo that will cause the vessel to draw an additional centimeter of draft.

Tramp service: A trading pattern in which the vessel is not on a fixed schedule, instead booking “cargoes of opportunity,” that is, at each time of availability and after evaluating the potential profitability as well as projected ongoing employment. This type of service contrasts with *liner service*.

Trimming: Refers to the arranging of bulk material in the vessel hold for optimum stowage and vessel stability characteristics, and to minimize the possibility of cargo shifting (as may happen with some commodities).

Voyage charter: A charter contract where a freight rate is quoted on a dollars-per-ton basis. The owner of the vessel operates the vessel but also must pay for fuel and port costs.



Mine Safety and Health Law

Anne T. Nichting, Laura E. Beverage, and Karen L. Johnston

Federal regulation of workplace health and safety in the mining industry has developed as a consequence of growing national concern over recurring fatal accidents and mining disasters. Today, safety and health in the mining industry is governed by the Federal Mine Safety and Health Act of 1977 (known as the Mine Act). When Congress passed this legislation, it stated, “The first priority and concern of all in the coal or other mining industry must be the health and safety of its most precious resource—the miner” (Mine Act, Section 2[a]). (The Federal Mine Safety and Health Act of 1977 is codified at 30 U.S.C. Section 801, *et. seq.* For ease of reference, however, all subsequent citations to the 1977 Mine Act in this chapter will refer to the specific section of the Mine Act and not the U.S.C. citation.)

The Mine Act is extremely complex with a variety of exceptions and details that are beyond the scope of this chapter. Compliance with the Mine Act, and the regulations adopted pursuant to it, depends on the specific facts and circumstances of a given situation. Therefore, nothing in this chapter should be considered as the rendering of legal advice, and readers are responsible for obtaining legal advice from their legal counsel with respect to any specific situation. The information provided is intended for educational purposes only.

HISTORY AND KEY COMPONENTS OF THE MINE ACT

Mining has a long history in this country, as does the federal government’s efforts to regulate what has been perceived to be a dangerous occupation and workplace. Regulation of the health and safety of miners in the United States began in 1891 with the first federal statute governing mine safety, “An Act for the Protection of the Lives of Miners in the Territories,” Chapter 564, 26 Stat. 1104 (1891) (known as “the 1891 Act”).

This legislation, which applied only to mines in the U.S. territories, established several mandatory safety standards, including minimum ventilation requirements at underground coal mines, the construction of escape shafts, the use of safety catches, and hoisting equipment requirements, and prohibited operators from employing children less than 12 years of age. The 1891 Act authorized the U.S. president to appoint mine inspectors for each U.S. territory. The inspectors were required to check the mines in their territories annually and provide reports to the U.S. secretary of the interior.

It was not until 1952 that Congress passed the first federal statute granting inspectors the authority to cite an operator for violation of a federal safety standard. The Federal Coal Mine Safety

Act Amendments of 1952, Public Law 82-552, 66 Stat. 692 (1952) (known as “the 1952 Act”) was designed to supplement, but not replace, existing state regulations. Applied to all coal mines with more than 14 miners, the 1952 Act set forth mandatory safety standards, established enforcement procedures and review, and mandated annual inspections in certain underground coal mines. However, the penalties authorized by the 1952 Act were minimal and could only be assessed for entering an area closed by a withdrawal order or for refusing to admit an inspector onto mine property. Failure to comply with the mandatory safety standards would not result in a penalty against the operator. The 1952 Act gave inspectors the authority to issue withdrawal orders for (1) situations of imminent danger or (2) where the operator had failed to abate a violation within the stated amount of time. These two types of withdrawal orders remain part of the enforcement scheme today.

In 1966 Congress passed legislation specific to non-coal mines. The Federal Metal and Nonmetallic Mine Safety Act of 1966, Public Law 89-577, 80 Stat. 772 (1966) (known as “the 1966 Metal/Nonmetal Act”) provided for minimal enforcement authority in the nation’s metal and nonmetal mines. The 1966 Metal/Nonmetal Act differed somewhat from existing coal mine legislation in that it promulgated standards, many of which were advisory and not mandatory.

In 1969, Congress passed the Federal Coal Mine Health and Safety Act, Public Law 91-173, 83 Stat. 742 (1969) (known as “the 1969 Coal Act”), which was more comprehensive and stringent than any previous federal legislation governing mine safety. The 1969 Coal Act covered surface and underground coal mines, required two annual inspections of surface operations and four annual inspections of underground operations, and greatly increased federal enforcement powers. Violations of the 1969 Coal Act would result in monetary penalties, and criminal penalties could be imposed for knowing and willful violations. With the 1969 Coal Act, Congress expanded upon and strengthened previously existing safety standards and adopted health standards. The 1969 Coal Act included specific procedures for the development of improved mandatory health and safety standards and provided compensation for miners who were totally and permanently disabled by “black lung” disease.

The legacy of the foregoing safety and health legislation, however, was its ineffectiveness at making the mining industry safer, resulting in passage of the 1977 Mine Act. Basically an enforcement act, it was borne out of congressional frustration with multiple

mine disasters seen as a result of operators' indifference to safety and health. The mine disasters included a 1968 explosion at a coal mine in Farmington, West Virginia, that left 78 miners dead; a 1972 fire at the Sunshine silver mine in Kellogg, Idaho, that claimed the lives of 91 miners; and two explosions in 1976 at the Scotia coal mine near Whitesburg, Kentucky, that left 26 dead.

Congress noted:

The [1976] Scotia disasters demonstrated once again that until Congress finally provides truly effective mine health and safety laws, and insists on responsive administration and enforcement of those laws, this problem will continue to occur. (Senate Committee on Human Resources, Federal Mine Safety and Health Amendments Act of 1977, S. Rep. 95-181, 4-5 [1977])

The Mine Act repealed the 1966 Metal/Nonmetal Act and amended the 1969 Coal Act to make it applicable to all types of mines. Under the Mine Act, many functions and duties that were the responsibility of the secretary of interior under the Coal Act were transferred to the secretary of labor. The Mine Act provides the statutory framework for the Mine Safety and Health Administration's (MSHA's) enforcement authority and sets forth a number of enforcement tools. Some of the major features of the Mine Act are the following:

- Transferred the federal agency charged with enforcement of federal mine safety and health legislation from the Department of the Interior to the Department of Labor (MSHA) on March 9, 1978
- Strengthened the enforcement tools that were available to the government
- Increased emphasis on protecting miners' health
- Allowed for greater involvement of miners or their representatives in processes affecting their health and safety
- Set up procedures for assessing and collecting civil penalties resulting from violations of regulations
- Provided broad mandatory training requirements for miners

FEDERAL MINE SAFETY AND HEALTH REVIEW COMMISSION

The Federal Mine Safety and Health Review Commission (the "Review Commission") was created by the Mine Act to provide for an impartial tribunal to hear contested cases. The Review Commission and its Administrative Law Judges (ALJs), assigned to the Department of Labor, are responsible for reviewing the lawfulness of the labor secretary's enforcement actions. In addition, the Mine Act grants the Review Commission broad authority to formulate national policy pursuant to the Mine Act, issue declaratory orders to ensure compliance with the Mine Act, and consider constitutional questions.

Created by Congress in 1977, the Review Commission is a five-member panel patterned after the Occupational Safety and Health Review Commission. The president, with the advice and consent of the Senate, appoints the commissioners for 6-year terms. The Mine Act requires that commissioners possess the training, education, or experience necessary to carry out the functions of the Review Commission.

Review Commission ALJs have jurisdiction to review: (1) citations and withdrawal orders, (2) the reasonableness of abatement times, and (3) the modification or termination of citations and orders. In addition to hearing enforcement actions, the ALJs hold hearings on Section 105(c) discrimination complaints and Section

111 compensation claims. ALJs are career government officials with lifetime appointments.

Strict Liability

The Mine Act states that the secretary of labor *shall* issue a citation whenever the secretary believes that a mine operator has violated its requirements or any of its mandatory standards (Mine Act, Section 104[a]). In addition, the Mine Act requires that a penalty be assessed against "[t]he operator of a...mine in which a violation occurs" (Mine Act, Section 110[a]). The courts have interpreted these two provisions of the Mine Act to hold that a mine operator is liable for a violation of the act or its regulations, even if the operator did not cause or create the violation. This principle of liability without fault for violations of the Mine Act and its regulations means that an operator can be held responsible for violations committed by either hourly or salaried employees and, under certain circumstances, for violations committed by independent contractors.

Enforcement Provisions and Penalties

Under the Mine Act, MSHA has at its disposal a number of enforcement tools, commonly referred to as *citations* and *withdrawal orders*. As discussed in more detail later, a citation requires corrective action to be taken but does not result in cessation of the activity or equipment at issue. In contrast, a withdrawal order results in halting the activity or the use of a piece of equipment subject to the order. The MSHA inspector has a fair amount of discretion in deciding which type of enforcement action to issue. However, the enforcement action must meet the legal standards, which have been further refined by case law, in order to properly classify a violation under each provision of the Mine Act. In addition, a key issue under the Mine Act's enforcement section is MSHA's determination of special findings, which are discussed in more detail in the Special Findings section of this chapter.

Citations

The most commonly issued enforcement action is Section 104(a) of the Mine Act. If, as a result of an inspection or investigation, an inspector believes that an operator has committed a violation of the Mine Act or any of its implementing rules, regulations, or orders, the inspector must issue a citation to the operator with "reasonable promptness" (Mine Act, Section 104[a]). The citation must describe the particular nature of the violation and must allow a reasonable abatement period.

The description of the violation usually consists of a summary of the condition or practice the inspector believes to be in violation of the standard and the identification of the specific area or piece of equipment involved. The citation must also indicate the MSHA standard or section of the Mine Act that the inspector alleges was violated. The MSHA inspector also notes the date by which the violation must be corrected or abated. Failure to comply may result in a withdrawal order for failure to abate.

Withdrawal Orders

An MSHA inspector may issue a variety of withdrawal orders, depending on the circumstances. The effect of a withdrawal order is to immediately shut down the area, equipment, or practice that is alleged to be in violation of the standards. All personnel associated with the condition or practice must be withdrawn, except those necessary to correct the violation.

Imminent Danger. Under Section 107(a), MSHA can issue a withdrawal order for a condition or practice "which could reasonably be expected to cause death or serious physical harm before such condition or practice can be abated," regardless of whether

the condition or practice violates a standard or rule (Mine Act, Section 3[j], 107[a]). A federal appellate court decision interpreted the Mine Act's imminent danger language to mean that a Section 107(a) order is appropriate when the condition or practice observed could reasonably be expected to cause death or serious physical harm to a miner "if normal mining operations were permitted to proceed in the area before the dangerous condition is eliminated" (*Eastern Associated Coal Corp. v. Interior Board of Mine Operations Appeals*, 491 F.2d 277, 278 [4th Cir. 1974]). A violation of Section 107(a) does not require a finding of violation of a mandatory safety or health standard. However, the imminent danger finding may be coupled with such a finding and result in increased penalty amounts. If a MSHA inspector believes that a condition or practice presents an imminent danger, the inspector must determine the area affected and immediately direct the withdrawal of all persons, except those necessary to abate the condition or practice.

Failure to Abate. A withdrawal order may be issued for the area or equipment affected by the violation for a failure to abate, or correct, the violation within the time prescribed (Mine Act, Section 104[b]). Failure-to-abate orders can result in penalties of up to \$6,500 per day that the condition continues.

As discussed, a MSHA inspector is required to establish a reasonable time for abatement of the conditions cited. On reinspection, the inspector determines whether the citation has been corrected and, if not, whether the circumstances warrant an extension of the abatement period. If no extension is warranted, the inspector will issue a Section 104(b) withdrawal order requiring all persons in the area affected by the violation to leave immediately. A failure-to-abate closure order prohibits all persons from entering an area covered by the order, except those necessary to correct the violation. Once the inspector determines that the violation is fully corrected, the closure order is terminated.

Untrained Miner. Under Section 104(g), a withdrawal order will be issued for failure to provide mandatory training required under the Mine Act. When a Section 104(g) order is issued, it will identify the specific miner(s) lacking the required training and declare that the miner is a hazard to himself and to others. The miner(s) identified must be removed immediately from the mine until the appropriate training is given.

Accident and Recovery. In the event of an accident at a mine, the Mine Act authorizes a MSHA inspector to take all appropriate actions, including the issuance of withdrawal orders during rescue and recovery operations and during accident investigations (Mine Act, Sections 103[j], [k]). Following an accident, the most commonly issued order is Section 103(k), which serves to preserve the accident scene while an investigation into the cause(s) of the accident proceeds. A Section 103(k) withdrawal order is also used to control an operator's recovery operations. This is different from other withdrawal orders in that no penalty is associated with it because it is not issued as the result of a violation.

Pattern of Violations. MSHA has promulgated "pattern of violations" regulations pursuant to Section 104(e) of the Mine Act. This section requires MSHA to give written notice to a mine operator who has a pattern of violations designated as significant and substantial (S&S) (Mine Act, Section 104[e][1]). (The concept of S&S is discussed in more detail later.) The regulations permit the issuance of withdrawal orders to operators that exhibit a pattern of noncompliance with a safety standard, demonstrating the operator's disregard for the health and safety of miners. MSHA's regulations are found at Part 104 of Title 30 to the Code of Federal Regulations (CFR). Fortunately, to date, this onerous enforcement tool has not been commonly used.

Civil Penalties Issued to Operator for Violation of a Standard

A mine operator who receives a citation or withdrawal order is subject to a maximum civil penalty assessment of \$60,000 per violation (Mine Act, Section 110[a]). Typically, the penalty amount is first proposed by MSHA's Office of Assessments, using the six general criteria set forth in Section 105(b)(1)(B) of the Mine Act and the penalty assessment formulas in 30 CFR Section 100.3(a):

1. Appropriateness of the penalty to the size of the business of the operator charged
2. Operator's history of previous violations
3. Whether the operator was negligent
4. Gravity of the violation
5. Demonstrated good faith of the operator in attempting to achieve rapid compliance after notification of a violation
6. Effect of the penalty on the operator's ability to continue in business

MSHA may also assess higher penalties against a mine operator with an excessive history of violations. An operator's overall history of violations is considered every time a violation is assessed. Penalty points are calculated on the basis of the average number of assessed violations per inspection day for the preceding 24-month period. If a mine operator has an excessive history of violations, it will affect the penalty amount assessed for all future enforcement actions, including those that are non-S&S.

Special Assessments

If MSHA determines that the regular penalty assessment scheme would not yield an appropriate penalty, the Office of Assessments is authorized to disregard the formula and propose a special assessment. This new penalty must be supported with narrative findings by the Office of Assessments based on the penalty assessment criteria. The following categories of violations are reviewed to determine whether a special assessment will be proposed:

- Involving fatalities and serious injuries
- Resulting from an unwarrantable failure (i.e., constituting more than ordinary negligence) to comply with mandatory health and safety standards
- Operating a mine in the face of a closure order
- Failing to permit an authorized representative of the labor secretary to perform an inspection or investigation
- Involving individuals who are personally liable under Section 110(c) of the Mine Act
- Involving an imminent danger
- Discriminating under Section 105(c) of the Mine Act
- Involving an extraordinarily high degree of negligence or gravity or other unique aggravating circumstances

Special Findings

S&S

When investigating a possible violation, an inspector will note, on MSHA's enforcement action form, the level of negligence he or she believes attributable to the operator for the existence of the violation: none, low, moderate, high, or reckless disregard. In addition, the inspector is required to assess the gravity of the alleged violation or the degree of hazard or risk posed by the alleged violation. The term S&S indicates that the alleged violation is of a more serious nature in terms of gravity. Because the Mine Act did not define S&S, it was left to the Review Commission to do so in contested cases:

[A] violation is of such a nature as could significantly and substantially contribute to the cause and effect of a

mine safety or health hazard if, based upon the particular facts surrounding that violation, there exists a reasonable likelihood that the hazard contributed to will result in an injury or illness of a reasonably serious nature. (*Secretary of Labor v. Cement Division, National Gypsum Co.*, 3 FMSHRC 822, 825 [1981]).

As a result, in order to sustain an S&S violation, the labor secretary must prove four conditions: (1) that a mandatory safety standard was violated; (2) that a discrete safety hazard contributed to the violation; (3) the reasonable likelihood that an injury will result; and (4) that the injury will be of a reasonably serious nature.

Unwarrantable Failure

The term *unwarrantable failure*, set forth in Section 104(d) of the Mine Act, refers to the degree of an operator's fault or negligence in causing a violation. Although the term is not defined in the Mine Act, the Review Commission has described it as "aggravated conduct, constituting more than ordinary negligence" (*Emery Mining Corp. v. Secretary of Labor*, 9 FMSHRC 1997 [1987]). Only those violations of a mandatory health or safety standard characterized as resulting from "high" negligence or "reckless disregard" can be issued as an unwarrantable failure.

A MSHA inspector may look at the following factors to determine whether an unwarrantable failure exists:

- The length of time the violation existed before it was discovered by the inspector
- Whether the violation should have been discovered by the operator during required inspections or routine travel or equipment use
- Whether there was a failure to report the condition as required by company policy
- Whether the violation was caused by unforeseeable conduct on the part of a miner
- Whether the facts support a conclusion of aggravated conduct beyond a mere finding that the operator should have known about the violation.

A citation for an S&S violation, caused by the operator's unwarrantable failure to comply with a standard, is issued under Section 104(d)(1) of the Mine Act. The initial citation commences the "d-chain" or "withdrawal order chain." Each time thereafter, during the same inspection or any subsequent inspection within 90 days that an unwarrantable failure violation is observed, an unwarrantable failure order will be issued. After the initial Section 104(d)(1) citation is issued, the subsequent unwarrantable failure orders issued in the chain do not have to be S&S. The operator stays on the d-chain until there is an intervening "clean" inspection (i.e., no unwarrantable failure orders) of the entire mine.

JURISDICTION

The Mine Act's enforcement provisions extend to almost every aspect of the mining industry, and its jurisdictional scope has been broadly interpreted by the courts. The Mine Act's jurisdiction encompasses

Each coal or other mine, the products of which enter commerce, or the operations or products of which affect commerce, and each operator of such mine, and every miner in such mine shall be subject to the provisions of this Act. (Mine Act, Section 4)

The two key terms that must be defined when determining whether the Mine Act applies to a workplace or to an employer are "mine" and "operator."

Definition of "Mine"

Section 3 of the Mine Act defines a *mine* as

(A) an area of land from which minerals are extracted in nonliquid form or, if in liquid form, are extracted with workers underground, (B) private ways and roads appurtenant to such area, and (C) lands, excavations, underground passageways, shafts, slopes, tunnels and workings, structures, facilities, equipment, machines, tools, or other property including impoundments, retention dams, and tailings ponds, on the surface or underground, used in, or to be used in, or resulting from, the work of extracting such minerals from their natural deposits in nonliquid form, or if in liquid form, with workers underground, or used in, or to be used in, the milling of such minerals, or the work of preparing coal or other minerals, and includes custom coal preparation facilities.

The definition includes related milling operations, including the alumina refining process, mine development, rehabilitation activities, and exploration work at an established mine.

MSHA has jurisdiction over lands, equipment, and structures used or to be used in the preparation of the coal. Congress intended that "what is considered to be a mine and to be regulated under this Act be given the broadest possible interpretation" (S. Rep. 95-1919, at 14 [1977], reprinted in 1977 U.S.C.C.A.N. 3401, 3414). (See also, *Marshall v. Stoudt's Ferry Preparation Co.*, 602 F.2d 589, 591-92 [3d Cir. 1979], cert. denied, 444 U.S. 1015 [1980].)

Consequently, the federal courts and the Review Commission have relied on the Mine Act's legislative history to include activities not commonly associated with the definition of a mine. For example, a mine operator's off-mine site central supply shop that warehoused materials and supplies was defined as a mine (*Jim Walter Resources, Inc.*, 22 FMSHRC 21 [2000]).

Further interpretation and explanation of what is considered a mine, and therefore under MSHA's jurisdiction, can be found in an interagency agreement between MSHA and the Occupational Safety and Health Administration (OSHA) (OSHA/MSHA Interagency Agreement *Federal Register* 44, no. 22827 [April 17, 1979, amended February 22, 1983]).

The OSHA/MSHA Interagency Agreement delineates areas of inspection responsibility, sets up a procedure for determining general jurisdictional questions, and provides for coordination between the two agencies in areas of mutual interest.

Definition of "Operator"

When Congress promulgated the Mine Act, it expanded the 1969 Coal Act's definition of *operator* to include independent contractors. Section 3(d) defines an operator as "any owner, lessee, or other person who operates, controls, or supervises a coal or other mine or any independent contractor performing services or construction at such mine" (Mine Act, Section 3[d]). Just as Congress intended a mine to be defined broadly, it also intended that operator be broadly interpreted.

With the inclusion of independent contractors in the definition of operator, the courts and the Review Commission have supported MSHA's authority to cite virtually anyone working on the mine site. For example, a company that provided elevator maintenance services at a mine was found to be a mine operator, because its work was sufficiently related to the extraction of ore to qualify it as an operator and it had a "continuing presence" at the mine (*Otis Elevator Co. v. Secretary of Labor*, 921 F.2d 1285 [D.C. Cir. 1990]). The elevator company's employees worked between 6 to 20 hours

at the mines and their work was performed in the center of mining activities on equipment that was essential to the mining process.

With the Mine Act's expanded definition of an operator, MSHA has the authority to issue enforcement actions directly to an independent contractor for violations committed by the contractor or its employees. According to MSHA, this authority does not, however, lessen the production-operator's overall responsibility for compliance with the Mine Act and the standards. MSHA has taken the position that the production-operator is in the best position to coordinate the contractor's activities and monitor safety performance, because the production-operator has the overall knowledge and daily control of the mine operation. (See *MSHA Program Information Bulletin No. P94-14*, May 20, 1994.) MSHA characterizes this as "overlapping compliance responsibility."

As a result, MSHA may issue citations or orders to both the independent contractor and to the production-operator for a violation. MSHA's guidelines state that it is appropriate to issue an enforcement action to the production-operator for a violation committed by the independent contractor or its employees under any of the following situations:

- When the production-operator has contributed by either an act or by an omission to a violation in the course of an independent contractor's work
- When the production-operator has contributed by either an act or omission to a violation committed by an independent contractor
- When the production-operator's miners are exposed to the hazard
- When the production-operator has control over the condition that needs abatement

PROMULGATION OF REGULATIONS

Regulations

The Mine Act has a complex and comprehensive structure to safeguard the health and safety of miners. One aspect is the specific mandatory health and safety standards that are set forth in Titles II and III of the Mine Act. The Mine Act refers to them as "interim mandatory safety and health standards," recognizing that legislated interim standards should evolve to provide increased safety and, when necessary, to address changes in mining technology.

The Mine Act authorizes the labor secretary to use two procedures for changing the interim standards. The first is notice-and-comment rulemaking, through which the secretary can promulgate new, industry-wide safety or health standards, provided that any new or revised standard does not "reduce the protection" afforded by a mandatory standard. The second procedure, discussed later in this chapter, allows individual mining companies or miners' representatives to "petition for modification" of a particular standard.

Procedures for rulemaking are set forth in Section 101 of the Mine Act. The rulemaking provisions of the Administrative Procedures Act, 5 U.S.C. Section 553, are also applicable. Both acts set forth time frames to follow. Proposed rules promulgating, modifying, or revoking mandatory health or safety standards must be published in the *Federal Register*. Persons interested in providing comments or data are provided an opportunity to submit written information and may also request a public hearing. The labor secretary is required to publish in the *Federal Register* notification of the standards for which comments were received. If a hearing is requested, the secretary must propose a schedule for the hearing, and interested persons must be allowed to present oral or written comments at the hearing. In addition, the secretary is authorized to use a subpoena to compel the attendance of any witnesses (Mine Act, Sec-

tion 101[a][2] and [3]). After the close of the comment period, if no hearing was held, the secretary is required to publish what action will be taken regarding the standard and the reasons for the action. If the secretary decides to delay taking any action or making a decision about the standard, the reasons for the delay must be published in the *Federal Register*. Unless another time frame is specified, a new standard is effective following publication in the *Federal Register*.

Any person (or legal entity) that is adversely affected by a standard promulgated pursuant to Section 101 may file a petition challenging the validity of the standard. The challenge may be filed in either the federal district court for the District of Columbia or the federal court for the circuit where the person who is adversely affected resides or has a principal place of business. Importantly, no objection that has not been raised with the secretary can be considered by a court unless good cause is shown for the failure to raise the objection (Mine Act, Section 101[d]).

The MSHA standards that have been promulgated are found at Title 30 of the CFR. The safety and health standards applicable to surface metal and nonmetal mines are in Part 56. Those applicable to underground metal and nonmetal mines are found in Part 57. Many of the standards in Parts 56 and 57 are identical or substantially similar. Because the standards are primarily performance based, the determination of whether a standard has been violated in a specific situation is typically whether a reasonably prudent person, familiar with mining and the specific circumstance at issue, would find that a violation exists. Other regulatory compliance standards in Title 30 include:

- Part 40—Miners' Representative Requirements
- Part 41—Legal Identity Requirements
- Part 46—Training Requirements for Shell Dredging, Sand, Gravel, Surface Stone, Surface Clay, Colloidal Phosphate, and Surface Limestone Mines
- Part 47—Hazard Communication
- Part 48—Training Requirements for All Underground and Surface Coal and Metal/Nonmetal Mines, except mines covered by Part 46
- Part 50—Accident and Injury Investigation and Reporting
- Part 62—Noise Regulations

Petition for Relief from Requirements of Mandatory Standards

The second procedure for modifying mandatory standards is through a petition for relief from the requirements of mandatory standards. An operator is not permitted to petition for modification of a health standard. The procedure for modifying mandatory safety standards is provided in Section 101(c) of the Mine Act, which allows relief from the application of a safety standard under two circumstances:

1. If the secretary determines that an alternative method guarantees the same measure of protection to the miners as the standard
2. That the application of such standard to the mine will result in a diminution of safety to the miners

Procedures governing petitions for modification are found in the regulations at 30 CFR Part 44. After MSHA receives the petition, a notice is published in the *Federal Register*, and interested persons have 30 days to submit comments or information. In addition, MSHA conducts an investigation into the merits of the petition, which typically includes an on-site examination. MSHA inspectors from the local district office then prepare an investigation report and a draft of their proposed decision. After the investigation,

the appropriate MSHA official issues a proposed decision and order, which becomes final in 30 days unless a hearing is requested. (The MSHA official who issues the proposed decision and order is either the deputy administrator for Coal Mine Safety and Health or the deputy administrator for Metal and Nonmetal Safety and Health.)

Hearings are held before ALJs, not the Review Commission. If no hearing is requested, the terms and conditions of the MSHA official's decision and order become enforceable as a mandatory standard.

A request for a hearing must be filed within 30 days after service of the proposed decision and order and is forwarded to the Department of Labor's chief ALJ for assignment. The ALJ who is assigned to the matter holds a hearing and issues a decision. A party has 30 days to file a notice of appeal of the ALJ's decision with the assistant secretary of labor for mine safety and health. The assistant secretary may affirm, modify, or set aside the decision. For purposes of judicial review, the decision by the assistant secretary is the final agency action. It may be appealed to the U.S. Court of Appeals in the jurisdiction where the mine is located or appealed to the U.S. Court of Appeals for the District of Columbia.

Mine Site Plans

The Mine Act requires operators to submit mine-specific plans addressing such topics as roof control and ventilation. (See, e.g., Mine Act, Sections 302[a], 303[o].) Mine plans are intended to be site-specific plans, taking into consideration the conditions and mining systems of each particular mine, and are enforceable by MSHA as if they were a regulation. Some mine plans are subject to periodic review and/or approval by MSHA. If a mine operator fails to operate in accordance with a plan, the Mine Act requires that the mine operator be cited for that violation (Mine Act, Section 104[a]). As a result, a mine operator should be cautious about agreeing to plan terms about which it has reservations.

The labor secretary has promulgated standards that require a mine operator to develop and adopt mine plans. For example, some of the regulations applicable to nonmetal mines that require plan adoption are the following:

- 30 CFR Section 48.3—training
- 30 CFR Section 49.4—alternative mine rescue capabilities
- 30 CFR Part 62—hearing conservation
- 30 CFR Part 47—hazard communication

SPECIFIC MINE ACT ENFORCEMENT TOOLS

Enforcement Actions against Mine Operators

The types of citations that may be issued to a mine operator include the following:

- Citation for a violation of the Mine Act, mandatory health or safety standard, rule, order or regulation (Mine Act, Section 104[a]).
- Unwarrantable failure citation for a violation that could significantly and substantially contribute to a health or safety hazard. This is the first link in the closure order chain based on unwarrantable failure findings (Mine Act, Section 104[d][1]).
- Citation for exceeding respirable dust standard at underground coal mines (Mine Act, Section 104[f]).

The various orders of withdrawal that may be issued to a mine operator include the following:

- Failure to abate a Section 104(a) or Section 104(d)(1) violation in the time period given (Mine Act, Section 104[b]).
- Unwarrantable failure violation issued subsequent to Section 104(d)(1) citation during same inspection or within 90 days

after issuance of Section 104(d)(1) citation (Mine Act, Section 104[d][1])

- Unwarrantable failure violation issued during a subsequent inspection, after a Section 104(d)(1) order was issued, assuming that no intervening inspection of the mine in its entirety has disclosed further unwarrantable failure violations (Mine Act, Section 104[d][2])
- Pattern-of-violations order issued within 90 days after Section 104(e)(1) pattern notification is given to the operator if violation is found that could significantly and substantially contribute to a health or safety hazard (Mine Act, Section 104[e][1])
- Pattern-of-violations order issued after the Section 104(e)(1) order is issued when a violation is found that could significantly and substantially contribute to a health or safety hazard, assuming that no intervening inspection of mine in its entirety has disclosed further S&S violations (Mine Act, Section 104[e][2])
- Order issued when there is a failure to comply with respirable dust standard by the end of time granted in Section 104(f) citation at underground coal mine (Mine Act, Section 104[f][1])
- Order issued when miners have not received requisite safety training (Mine Act, Section 104[g][1])
- Order issued when an imminent danger is present, defined as a condition or practice that can reasonably be expected to cause death or serious physical injury before it can be abated (Mine Act, Section 107[a])
- Order that may be issued to take action deemed appropriate to supervise and direct rescue and recovery work following an accident (Mine Act, Section 103[j])
- Order issued to ensure safety of persons following an accident and to preserve evidence (Mine Act, Section 103[k])

Civil Penalties Associated with Enforcement Actions against Mine Operators

A director, officer, or agent of a corporate operator who knowingly authorizes, orders, or carries out a violation of a mandatory health or safety standard or who fails to comply with an order issued under the Mine Act or included in a final decision under the Mine Act may be subject to civil or criminal penalties (Mine Act, Section 110[c]). Criminal and civil penalties are generally pursued as a result of special investigations conducted by MSHA to uncover willful and knowing violations of the Mine Act. (See the Special Investigations section of this chapter for more information.)

Section 110(c) is most commonly utilized against management employees, including section supervisors, mine supervisors, safety directors, and other managers of corporate operators engaged in day-to-day mining operations. For purposes of assessing a civil penalty against an individual, "knowingly" means knowing or having reason to know (*Freeman United Coal Mining Co. v. FMSHRC*, 108 F.3d 358 [D.C. Cir. 1997]).

Section 110(c) subjects individuals to "the same civil penalties" that may be imposed on mine operators. However, when assessing civil penalties against individuals, the penalty assessment factors are based on the individual, not the operator; for example, in connection with the size criterion, the inquiry is of the individual's income and net worth.

Criminal Penalties

The Mine Act also allows for a variety of criminal penalties. The provisions of Section 110(c) may be used to pursue either criminal

sanctions or civil fines against agents, officers, and directors, depending largely on the nature of the violation and the evidence. Whether a civil or criminal sanction is imposed rests with MSHA's discretion, with input from the Justice Department. However, because conviction for a criminal act requires proof beyond a reasonable doubt, only those violations with evidence of intentional conduct are pursued criminally.

Under the Mine Act, criminal penalties can be imposed against operators for knowing and willful violations of mandatory health and safety standards (Mine Act, Section 110[d]). In the context of criminal liability, "knowingly" has been defined as an act done voluntarily and intentionally, and not because of mistake, accident, or other reason (*United States v. Jones*, 735 F.2d 785 [4th Cir.], cert. denied, 469 U.S. 918 [1984]). An operator who willfully violates mandatory health or safety standards, or who knowingly violates any order issued pursuant to Section 104 or Section 107, faces a maximum fine of \$25,000, imprisonment up to 1 year, or both for the first conviction. For subsequent convictions, a maximum fine of \$50,000, imprisonment up to 5 years, or both may be imposed.

In addition, the Mine Act allows for criminal sanctions for any person who provides unauthorized advance notice of mine inspections (maximum \$1,000 fine, imprisonment for up to 6 months, or both) or who knowingly makes a false statement, representation, or certification in any application, record, report, plan, or other document filed or required to be kept under the Mine Act (maximum \$10,000 fine, imprisonment for up to 5 years, or both) (Mine Act, Sections 110[e], [f]).

Special investigations are conducted under the general inspection authority of the Mine Act (Section 103[a]). Impeding a MSHA special investigation may constitute obstruction of an agency proceeding and includes witness influence, intimidation, and false statements made to investigators (18 U.S.C. Section 1505 [2004]). Other potential criminal acts relevant to the special investigation process include, but are not limited to, conspiracy (18 U.S.C. Section 371 [2004]), mail fraud (18 U.S.C. Section 1341 [2004]), bribery (18 U.S.C. Section 201 [2004]), concealment of material facts (18 U.S.C. Section 1001 [2004]), and obstruction of a federal criminal investigation (18 U.S.C. Section 1510 [2004]).

Contest of Citations and Penalties

An operator may contest a citation or order, and the associated penalty, by filing a contest with the Review Commission. There are three main methods to initiate review:

1. File a notice of contest under Section 105(d) within 30 days of issuance, modification, or termination of a citation or order issued under Section 104
2. File an application for review pursuant to Section 107(e)(1) within 30 days of issuance, modification, or termination of any order issued under Section 107(a)
3. File a contest of a civil penalty assessment by notifying the labor secretary within 30 days of receipt of the proposed penalty assessment of the operator's intent to contest the penalty

Once an operator initiates a contest of an enforcement action and/or the penalty, the resulting procedures and deadlines will vary, depending on whether it was a prepenalty contest or a contest of the proposed penalties. There are stringent deadlines to follow, as set forth in the Mine Act and the Review Commission's procedural rules found at 29 CFR Part 2700.

In addition, only certain parties may file specific protests. The parties to a contest or penalty proceeding include the operator, the

labor secretary, and any parties that are permitted to intervene. Affected miners or their representatives may intervene in a hearing by filing a written notice with the Review Commission. A miners' representative may only protest the length of the abatement time of a Section 104(a) citation and not the issuance or modification. However, miners or their representatives may challenge the issuance, modification, or termination of withdrawal orders issued under Section 104.

A hearing is held before an ALJ on the issues of fact and law raised by the parties. The ALJ administers the oath to witnesses, issues subpoenas, rules on offers of proof and objections, receives relevant evidence, disposes of procedural requests, and generally regulates the hearing. Often, the ALJ will ask questions of the witnesses for purposes of clarification. The parties may seek to file written posthearing briefs or may make closing arguments at the hearing. The ALJ will issue a written decision that includes findings of fact and conclusions of law. The ALJ has the authority to vacate or uphold a citation, modify the negligence and gravity findings, and reduce or increase the penalty amount.

Any person adversely affected by the ALJ's decision may file a petition for discretionary review with the Review Commission within 30 days of the decision. Because this review is discretionary, the affirmative vote of at least two of the Review Commissioners is required within 40 days of the decision in order for the review to be heard by the commission. Alternatively, the Review Commission may vote to grant review of the decision on its own motion, or *sua sponte*, within 30 days of the ALJ's decision. If review is granted, a person may file a motion to intervene in the proceeding within 30 days of the Review Commission's direction for review. Intervention is also subject to the Review Commission's discretion. The Review Commission's rules set forth the time frames in which parties must file the appropriate written documents relating to the review process.

Any person adversely affected by an order of the Review Commission may file a petition to modify or set aside the order with the U.S. Court of Appeals for the circuit in which the violation occurred or with the District of Columbia Circuit Court of Appeals. This petition for review must be filed within 30 days of issuance of the Review Commission's order. The procedural requirements for a petition for review are set forth in the Federal Rules of Appellate Procedure.

INSPECTIONS AND INVESTIGATIONS

The Mine Act grants broad inspection powers to MSHA, essentially authorizing three types of inspections: (1) routine or regular, (2) spot, and (3) those performed pursuant to a miner's complaint (Mine Act, Sections 103[a], 103[i], 103[g]).

Regular inspections are conducted to determine compliance with the Mine Act and MSHA regulations. MSHA is required to make a complete inspection of all underground mines at least four times a year and of all surface mines at least two times a year (Mine Act, Section 103[a]). Spot inspections are conducted when a mine releases excessive amounts of methane, if the mine has experienced a methane or gas ignition that resulted in a death or serious injury, or when there is some other hazardous condition (Mine Act, Section 103[i]). Finally, a miner may request an inspection if he or she believes there is a condition that violates the Mine Act or MSHA regulations, or that an imminent danger exists.

A common thread that runs through each type of inspection is the intent of Congress, declared in the legislative history of the Mine Act, that the labor secretary be permitted to conduct inspections in the absence of a search warrant. The U.S. Supreme Court has ruled that warrantless inspections under the Mine Act generally do not violate an operator's Fourth Amendment rights (*Secretary of*

Labor v. De wey, 452 U.S. 594 [1981]). Warrantless inspection authority also extends to seizure of records required to be kept under the Mine Act. Courts have been reluctant, however, to extend the inspection exception to records not specifically required to be maintained by the Mine Act. While an operator may make other records available, doing so is voluntary and amounts to a waiver of any privacy rights.

Accident Investigations

In addition to MSHA's broad inspection powers, the Mine Act requires MSHA to investigate the causes of accidents and "other occurrence[s] relating to health or safety" (Mine Act, Section 103[b]). In light of this, every mine operator should have a plan to deal with a serious accident, fatality, explosion, or other disaster.

MSHA has promulgated detailed regulations (found at 30 CFR Part 50) for accident investigations and record keeping in connection with accidents. The regulations require immediate notification to MSHA if an accident occurs. In addition, a mine operator must preserve the accident scene until MSHA has completed its investigation, "except to the extent necessary to rescue or recover an individual, prevent or eliminate an imminent danger, or prevent destruction of mining equipment" (30 CFR Section 50.12). The Part 50 regulations also contain detailed requirements for the reporting and record keeping of occupational illnesses and injuries.

If an accident occurs, MSHA is required to do what is necessary to protect lives, including directing rescue and recovery operations and issuing appropriate safety orders (Mine Act, Sections 103[j], 103[k]). During the course of an investigation of an accident or other occurrence, MSHA, after notice, may also hold public hearings, administer oaths, and issue subpoenas to compel attendance, testimony, and the production of relevant documents and items (Mine Act, Section 103[b]). However, MSHA rarely resorts to these formal hearing mechanisms and prefers a more informal approach to investigations. The agency typically conducts an investigation, issues enforcement actions, and generates a report that outlines its findings and conclusions. The focus of MSHA's investigation is to determine the cause of an accident and prevent recurrences.

The primary device MSHA uses to gather information is witness interviews. Because the interview process is informal and non-custodial, MSHA is not required to inform the witness about the right against self-incrimination (*Miranda v. Arizona*, 384 U.S. 436 [1966]). MSHA usually does not administer oaths and prefers to tape-record the interviews and to have the witness sign a statement. The decision to submit to an interview is voluntary and a witness may refuse to be interviewed or to permit tape recording of the interview. A witness also has the right to refuse to sign a written statement or summary of the interview.

Special Investigations

Investigations under Section 110(c)

As discussed earlier, the Mine Act gives MSHA authority, under certain circumstances, to impose civil penalties and criminal fines against individual managers and corporate operators. These are determined through a process called a special investigation. Actions that are reviewed for possible special investigation include the following:

- All Section 104[d] unwarrantable failures, S&S citations, and orders
- All fatal and serious injury accidents
- All Section 107(a) imminent danger orders that involve a violation of a mandatory standard

Each investigation case file submitted by a MSHA investigator recommending individual civil or criminal penalties must include specific evidence to support the following:

- That the operator is a corporation
- That the violation created was properly cited
- That the violations created a hazard that posed a "high degree of risk" to miners
- That there was an agent of the operator with knowledge of the violation and that persons were exposed to the condition

Targets of special investigations are typically officers, directors, and agents of the company, including supervisors, safety directors, and others involved in the day-to-day supervision of all or part of the mining operations and/or miners. MSHA's special investigation procedures can be summarized as follows:

- The qualifying enforcement action is reviewed in the district office for referral.
- The district manager recommends whether to refer the enforcement action for a special investigation to MSHA's Arlington, Virginia, headquarters.
- If a special investigation is opened, the special investigator obtains the enforcement file and/or the accident investigation file.
- Interviews with all involved persons, witnesses, and potential targets or defendants are voluntary. Investigators generally contact employees directly.

Individuals are never required to talk to a special investigator and have the following rights during a Section 110(c) investigation:

- To counsel or other representatives prior to and during speaking with an investigator
- To speak with an investigator alone
- To refuse to answer certain questions
- To discontinue an interview at any time
- To refuse to have an interview tape recorded
- To refuse to sign a statement taken by the investigator

Investigations under Section 105(c)

The purpose of Section 105(c) of the Mine Act is to protect miners, job applicants, management level employees, and representatives of miners from retaliation for engaging in protected activity. Additional information regarding Section 105(c) is provided later in this chapter.

Under Section 105(c), an initial complaint of discrimination must be filed with MSHA within 60 days after the alleged violation occurs. Within 15 days of receiving the complaint, MSHA special investigators begin researching the allegations in the complaint. The MSHA special investigators may interview the complaining party, the operator, and others having relevant information. No operator can attempt to hinder any investigation of a Section 105(c) complaint or prevent management employees from talking with the special investigator. Front-line managers are the usual and likely targets of investigations and discrimination claims because of their constant interaction with miners in matters involving production and safety.

If MSHA determines that a complaint is valid, a formal complaint will be filed with the Review Commission within 30 days of MSHA's determination. The complaint is filed on behalf of the miner with notification to the operator and the complaining party.

If MSHA determines that a complaint is not valid, the complaining party may pursue his or her own complaint before the Review Commission. The complaint must be filed within 30 days of the complaining party's receipt of MSHA's written determination that

no violation occurred. An operator must respond to a formal complaint within 30 days after receipt. Failure to answer within 30 days may result in the entry of a final order against the operator.

INJUNCTIONS

The Mine Act authorizes MSHA to pursue a civil action seeking relief, including temporary or permanent injunctive relief or a restraining order, in federal district court (Mine Act, Section 108). MSHA may pursue a civil action if a mine operator does one of the following:

- Refuses to comply with an order or decision issued under the Mine Act
- Interferes with, hinders, or delays MSHA from carrying out its duties under the Mine Act
- Refuses to allow an inspection or investigation
- Refuses to provide other information or access to a mine.

However, an operator cannot seek an injunction in advance of enforcement action. Operators are precluded from this avenue of relief by the Mine Act's administrative review scheme under which challenges to enforcement actions must be reviewed first by the Review Commission and then by an appropriate court of appeals.

POSTING AND RECORD-KEEPING REQUIREMENTS

Posting Requirements

As part of the regulatory scheme of the Mine Act, mine operators are required to provide certain information to MSHA and to the miners. Mine operators must post on the mine bulletin board all citations, orders, notices, and decisions that are required by the Mine Act or regulations to be given to the operator, pursuant to the posting requirements of Section 109(a) of the Mine Act. Mine operators are required to maintain the bulletin board at the mine office or "at a conspicuous place near an entrance of" the mine; the above-described documents are to be posted "immediately;" and the posted documents must be "easily visible" and "protected against damage by weather and against unauthorized removal" (Mine Act, Section 109[a]). The Mine Act does not state how long such information must remain posted. Because the Mine Act does not specifically require that decisions and orders of the Review Commission or courts be given to the operator, they do not have to be posted to comply with Section 109(a) (*Secretary of Labor v. Thunder Basin Coal Co.*, 18 FMSHRC 582 [1996]). However, it is common that the decision or order requires that it be posted at the mine site.

In addition to the requirements of Section 109, a number of standards have specific posting requirements. For example, the miners' representatives must file specific information with MSHA's district manager and provide a copy of that information to the operator. The mine operator is then required to post this information on the mine bulletin board (30 CFR Section 40.4). Generally, mine operators must also post the training plan (30 CFR Sections 46.3[g], 48.3[n], and 48.23[n]). A comprehensive discussion of all of the posting requirements under Title 30 of the CFR is beyond the scope of this chapter. Mine operators should review the specific regulations to determine if any document is required to be posted.

Record-Keeping Requirements

MSHA may make requests and demands for a broad range of company records. Many of these records are written by a management official in an effort to analyze the cause of an event and/or prevent its recurrence and are expected to be private. Unfortunately, in the hands of an opposing party, some records may be utilized to support allegations against the company or individual managers.

Records requested by MSHA inspectors may include

- Injury- and illness-related documents (workers' compensation records, insurance forms, medical reports, personnel records, supervisory reports of accidents and incidents, and safety department audits or evaluations)
- Operations records (production and progress reports, maintenance records, equipment manuals, equipment purchase orders, mine policy or procedural memos, and mine logs or summary books used for shift-to-shift communication)

Required records and those kept in the ordinary course of business may be used to establish heightened negligence under the Mine Act by establishing *actual or constructive* knowledge of hazards and violations. Therefore, a record retention policy should be considered for mine-site implementation that retains required records for mandated time frames and limits retention of other records to their useful life. Such a record retention policy will assure compliance with legal requirements and prevent the accumulation of old records. Such a record retention policy will assure compliance with legal requirements and prevent the accumulation of old records, which may jeopardize the company's interest if discovered during litigation.

MINERS' RIGHTS

The Mine Act contains a wide range of protections and noncontractual rights for miners. Some are quite complex. Following is a brief overview of miners' rights under the Mine Act.

Protection against Discrimination

In general, Section 105(c) states that no person may discharge or otherwise discriminate against a protected individual who exercises any of the rights set forth in the Mine Act, or who files or makes a complaint regarding a safety or health hazard. In order to prevail, the protected individual must establish that he was discriminated against because he engaged in some type of statutorily protected activity. If a finding of discrimination is made, the Mine Act authorizes the Review Commission to take whatever steps are appropriate to return the miner to his former position, including, but not limited to, rehiring or reinstatement with back pay and interest.

In cases brought by the miner through his private counsel under Section 105(c)(3), an award of attorney's fees and costs in prosecuting the claim may be granted. An award may include fees incurred through the appellate stage and are usually calculated by multiplying the prevailing rate in the community for similar work by the number of hours worked.

A discrimination claim brought pursuant to Section 105(c) has three essential elements: (1) protected activity, (2) adverse action, and (3) causal nexus between the protected activity and the adverse action. In other words, in order to prevail, a complaining miner must establish that he suffered adverse action because he engaged in some type of statutorily protected activity.

Initially, the complaining miner must make out a *prima facie* case of discrimination by establishing that the protected activity in some way motivated the adverse action. The burden then shifts to the operator to demonstrate that the activity was not protected, or that the activity was protected but did not in any way lead to the adverse action, or that a "mixed motive" was involved. In mixed-motive cases, the adverse action is caused, at least in part, by the unprotected activity which, by itself, would have caused the mine operator to take the alleged adverse action. The majority of discrimination cases involve such mixed-motive determinations.

If the claim involves a discharge or suspension, an application for temporary reinstatement may be requested by the labor secretary

and heard, on an expedited basis, within 10 days after the request is filed, to determine whether the miner's complaint was "frivolously brought." If no hearing is requested, the ALJ will review the secretary's application and required accompanying affidavit supporting the secretary's findings before making a decision on temporary reinstatement. If the ALJ concludes that the complaint is not frivolously brought, temporary reinstatement may be ordered. A temporary reinstatement order either granting or denying the relief may be appealed to the full Review Commission but will not stay the effect of the order unless directed by the Review Commission.

Protected Work Refusals

Miners have the right to refuse to work in unusually hazardous conditions. Although this right is not specifically spelled out in either the Mine Act or MSHA regulations, its basis may be found in the legislative history and in the Review Commission and court decisions interpreting that history. The exercise of this right may be particularly troublesome because of its effect on production and control of the work force. A four-part test has evolved for determining whether a work refusal is protected activity under Section 105(c). (The right was first recognized by the Review Commission in *Secretary of Labor ex rel. Pasula v. Consolidation Coal Co.*, 2 FMSHRC 2786 [1980], *rev'd sub nom. Consolidation Coal Co. v. Marshall*, 663 F.2d 1211 [3d Cir. 1981].)

That test requires a miner to have (1) a good faith (2) and reasonable belief (3) that a hazard exists, (4) which is ordinarily communicated to the mine management.

Defining the extent or degree of the perceived hazard necessary to support a protected work refusal has proved to be an evolutionary process and fact-dependent. The facts of each case obviously will vary, and whether a hazard exists sufficient to support a work refusal is determined on a case-by-case basis. But when issues are raised by a miner concerning a hazard, and management adequately addresses the concerns, a protected work refusal will not be supported.

Rights to Contact MSHA

A miner has the right to request a MSHA inspection if the miner believes there is a violation of the Mine Act or a health or safety standard, or that an imminent danger exists (Mine Act, Section 103[g]). MSHA is required to conduct an inspection as soon as possible and to withhold the name of the miner who filed the complaint. As a result of a Section 103(g) investigation, MSHA can issue enforcement actions.

Transfer Rights

The Mine Act has two provisions regarding a miner's transfer rights, Sections 101(a)(7) and 203(b). Section 101(a)(7) addresses promulgation of mandatory health or safety standards for toxic substances and warning of hazards and symptoms. If it is determined that "a miner may suffer material impairment of health or functional capacity by reason of exposure to the hazard covered by the mandatory standard," then the miner is to be "removed from such exposure and reassigned" (Mine Act, Section 101[a](7)). MSHA has not promulgated any standards under this section of the Mine Act.

On the other hand, Section 203 provides for medical examinations of miners working in coal mines. If a miner shows evidence of lung disease, the miner is to be given the option of transferring to a position in another area of the mine where the concentration of respirable dust is lower. A miner so transferred "shall receive compensation for [work in the new area of the mine] at not less than the regular rate of pay received by him immediately prior to his trans-

fer" (Mine Act, Section 203[b](3)). MSHA's regulations that address miners' transfer rights are codified at 30 CFR Part 90.

Walk-Around Pay Rights

The Mine Act provides that mine operators and representatives of miners have the right to accompany MSHA inspectors during inspections or investigations (Mine Act, Section 103[f]). MSHA has promulgated standards regarding this issue at 30 CFR Part 40 to encourage miner participation in the process. Section 103(f) states that if a miner's representative is an employee of the mine operator, the representative "shall suffer no loss of pay during the period of his participation in the inspection." Case law addresses the complexities under this provision, such as what the operator is required to do when separate MSHA inspection teams are carrying out different activities.

Compensation When Mine Is Idled by Withdrawal Order

Under the Mine Act, miners who are idled by withdrawal orders are entitled to certain statutorily mandated levels of compensation. Section 111 of the Mine Act provides for three classes of idlement compensation. These classes are differentiated by the types of closure orders that caused the idlement and affect the level of compensation.

1. Miners idled by any closure order issued during their shift are entitled to receive pay for up to the remainder of the shift plus up to 4 hours into the next shift if the order remains in effect.
2. Miners idled by a Section 104 or 107 closure order predicated on a violation of a mandatory health or safety standard are entitled to receive pay for the period idled for up to 1 week.
3. Miners working while any closure order is in effect, who should have been withdrawn from the area affected by the order, are entitled to full compensation for the time worked, in addition to their regular pay, from the date of the order until the date of compliance, vacation, or termination.

Any order issued under the first or second classification requires that miners be compensated at their regular rate of pay for the period idled by the order or until the end of the shift, whichever is shorter. If an order continues in effect on the next shift, miners on that shift idled by the order must be paid for the period idled, up to a maximum of 4 hours. According to Section 111, the right to this compensation accrues regardless of whether the violation is sustained following review.

The provision for compensation of up to 1 week described in the second classification is commonly referred to as "augmented" compensation. It is only available after the withdrawal order is final. If the order is contested and invalidated, the augmented compensation is not paid, but the basic compensation is still payable (i.e., remainder of the shift plus up to 4 hours). However, the validity of the order of withdrawal cannot be challenged for the first time in the compensation proceeding. Consequently, if an operator believes that an order was issued erroneously, the challenge must be made in a contest or penalty proceeding under Section 105(d), or, in the case of a Section 107(a) order, in an application for review filed within 30 days.

Right to Participate in Litigation

Miners are entitled to participate in the litigation of citations, penalty assessments, and orders issued under the Mine Act, Section 105[d]. Miners may also seek and receive party status in litigation (see 29 CFR Section 2700.4[a][b]). However, miners and their representatives do not have the right to contest citations (*UMWA v. Secretary of Labor*, 5 FMSHRC 807 [1983], *aff'd* 725 F.2d 126 [D.C. Cir. 1984]).

Right to Paid Training

The Mine Act requires mandatory training of miners (Mine Act, Section 115). New miners who have no prior underground experience must receive at least 40 hours of training before they work underground. Training must include several topics, including the statutory rights of miners under the Mine Act, hazard recognition, and the health and safety aspects of the tasks to which they will be assigned. New miners who will work at surface operations must receive at least 24 hours of training that covers generally the same topics covered for new underground miners. Newly hired, experienced miners also must receive training, which includes mine-specific information, such as escape ways, mine transportation, and emergency medical procedures. In addition, all miners must receive a minimum of 8 hours of refresher training at least once every 12 months. When a miner is assigned to a new task, he must be provided with task training.

The training requirements are set forth in 30 CFR Parts 46 and 48. The standards contain detailed requirements, including those for a training plan approved by MSHA. Part 46 requirements apply to all persons at shell dredging, sand, gravel, surface stone, surface clay, colloidal phosphate, and surface limestone mines. These are generally small mines with fewer employees than those covered by Part 48. Part 48 applies to all underground and surface coal and metal and nonmetal mines, except for those covered by Part 46. The standards also require mine operators to maintain records of miner training.

Additional Rights

The Mine Act has other specific provisions for miner participation. Those include

- The right to participate in inspections
- The right to contest the reasonableness of the length of time for abatement specified in a citation (Section 105[d])
- The right of an any representative of miners to apply for reinstatement, modification, or vacation of an imminent danger order (Section 107[e][1])

SUMMARY

The Mine Act is a complex piece of legislation that covers all mine operators and miners throughout the United States and that holds mine operators responsible for the safety and health of miners. It sets mandatory safety and health standards, mandates miners' training requirements, prescribes penalties for violations, and enables inspectors to close dangerous mines. The Mine Act requires that MSHA inspect all mines each year and requires or authorizes additional inspections and investigations to ensure safe and healthy work environments for miners.

To promote compliance with the provisions of the act and its safety and health standards, all violations found during inspections and investigations must be cited. All violations are subject to civil penalties and must be corrected within the time frames established by MSHA. In addition, the act provides for either civil penalties against individuals for "knowing" violations or criminal sanctions against mine operators that "willfully" violate safety and health standards. The Mine Act gives individual miners, as well as their representatives, and job applicants many specific employment rights. It requires MSHA to

- Provide compliance assistance through development of safety and health training programs in cooperation with industry and labor
- Test new mining equipment
- Work with other agencies to advance safety and health research programs
- Compile and analyze accident, injury, and illness data to better address serious workplace hazards



Environmental Law for Industrial Minerals and Rocks

Kurt E. Blase and James P. Ryan

This chapter summarizes federal environmental laws and regulations with significant effects on mining, processing, and use of industrial minerals. It is intended as a primer for mining engineers who are not attorneys but need a basic understanding of the federal environmental requirements that apply to their operations. It provides a comprehensive summary of the major environmental requirements and issues that a mining engineer is likely to face in the industrial minerals sector, though not in great detail. Although this chapter may not answer all pertinent questions, it should provide the information necessary for a productive search.

This chapter is organized along media lines, with separate discussions of air quality, water quality, waste disposal, and product regulation. The focus is primarily on summaries of existing regulatory requirements, though relevant legislative developments and judicial opinions are discussed as warranted. Where possible, references that provide more detailed information are listed. The preference is for references that are generally available, such as the Code of Federal Regulations (CFR) and the *Federal Register*. The conclusion of the chapter discusses some of the more controversial environmental issues in the industrial minerals sector at the time of this writing.

The discussion is limited to federal laws, but states have complementary and parallel laws that can differ from federal requirements and must always be consulted as well. As a general rule, state environmental programs are organized in the same manner as federal requirements, and the standards or other substantive requirements contained in federal laws and regulations are the minimum requirements for state programs. In most cases, however, federal law permits states to adopt more stringent requirements if they choose to do so. Accordingly, the federal requirements discussed in this chapter should be viewed in most cases as a minimum, and the possibility that more stringent requirements may be applied under state law should always be considered.

Where a state is proposing to adopt requirements more stringent than federal law, several legal remedies may be available. The state's proposal must be permissible under federal law, and it must also be consistent with state law. Some states have adopted state laws that prohibit deviation from federal requirements. Others have not gone to that length but also have not adopted state laws that expressly allow deviation from federal law. In states where state law expressly allows deviation from federal requirements, the proposal must be consistent with the applicable state law and must have a reasonable factual basis.

AIR QUALITY

The current federal Clean Air Act (CAA) was initially adopted in 1970 and substantially amended in 1977 and 1990 [42 U.S.C. § 7401 *et. seq.* (2004)]. An earlier statute, the Air Quality Act of 1967, directed the Department of Health and Human Services (then the Department of Health, Education, and Welfare) to set federal ambient air quality standards based on public health concerns and divided the United States into air quality regions for purposes of attaining the standards. Impatient with the states' progress under the 1967 act, Congress adopted the 1970 act to "take a stick to the states" to improve air quality. Shortly after the 1970 act was adopted, President Nixon created the federal Environmental Protection Agency (EPA), by Executive Order, to oversee administration of the CAA and, ultimately, the other environmental laws adopted in the early 1970s and discussed throughout this chapter. The 1977 amendments strengthened various portions of the 1970 CAA and added new authority to address air quality in areas that meet or exceed the ambient standards ("prevention of significant deterioration") and air quality in areas not attaining the ambient standards ("nonattainment areas"). The Clean Air Act Amendments of 1990 (CAAA) again strengthened the prior provisions and added new provisions governing acid deposition control, operating permits, and stratospheric ozone protection.

The CAA provisions of greatest interest in industrial minerals sectors are the following: (1) ambient air quality standards and state implementation plans, (2) prevention of significant deterioration (PSD) and nonattainment rules, (3) new source performance standards, (4) hazardous air pollutant (HAP) standards, (5) permitting, (6) mobile source standards, and (7) enforcement. These are discussed in the sections that follow.

Ambient Standards and State Implementation Plans

The backbone of the federal CAA is the program for national ambient air quality standards (NAAQS), and state/regional implementation of those standards, first adopted in the 1967 act. Under the current act (CAA), the NAAQS are set by EPA, but the plans for attaining the standards are adopted by the states, subject to EPA oversight and approval.

Sections 108 and 109 of the CAA govern establishment of NAAQS for so-called conventional pollutants (42 U.S.C. §§ 7408 and 7409). As a general matter, these are pollutants that are found pervasively in the air throughout the country and have

Table 1. National ambient air quality standards

Pollutant	Primary NAAQS	Secondary NAAQS
SO _x	0.030 ppm (annual mean) 0.14 ppm (24-hour average)	0.5 ppm (3-hour average)
Particulate matter, PM ₁₀ *	150 µm/m ³ (24-hour average) 50 µm/m ³ (annual mean)	Same† Same
Particulate matter, PM _{2.5} *	15 µm/m ³ (annual mean) 65 µm/m ³ (24-hour average)	Same Same
CO	9 ppm (8-hour average) 35 ppm (1-hour average)	None
Ozone	0.12 ppm (1-hour average) 0.08 ppm (8-hour average)	Same Same
NO ₂	0.053 ppm (annual mean)	Same
Pb	1.5 µg/m ³ (quarterly average)	Same

* There are currently two types of standards for particulate matter (PM): one covers particles with diameters in the range of 0–10 µm (PM₁₀), and another for particles with diameters in the range of 0–2.5 µm (PM_{2.5}; also known as *fine particulate*). At the time of this writing, EPA is preparing to revise these standards, as discussed further in text.

† Indicates the secondary value is the same as the primary value.

been demonstrated to cause adverse health or environmental effects as a result of chronic exposure. EPA is to maintain a list of pollutants that are present in “ambient air” as a result of “diverse mobile or stationary sources” and that “cause or contribute to air pollution which may reasonably be anticipated to endanger public health or welfare” (42 U.S.C. § 7408(a)).* For each of these, EPA must develop “air quality criteria” that “reflect the latest scientific knowledge useful in indicating the kind and extent of all identifiable effects on public health or welfare which may be expected from the presence of such pollutant in the ambient air” (42 U.S.C. § 7408(a)). Thus, the pollutants for which ambient standards have been developed are often referred to as *criteria pollutants*.

Based on the air quality criteria, EPA must set primary standards at levels that, “allowing an adequate margin of safety, are requisite to protect the public health” (42 U.S.C. § 7409 (b)). Secondary standards must be set at levels “requisite to protect the public welfare from any known or anticipated adverse effects” (42 U.S.C. § 7409 (b)). “Welfare” is defined to include effects on all aspects of the environment, including “economic values” and “personal comfort and well being” (42 U.S.C. § 7602(h)). EPA also is directed to develop information on control technologies for conventional pollutants (42 U.S.C. § 7408(b)). A number of guidance

documents on control techniques for various mining segments and processes are available on EPA’s Web site (www.epa.gov).

The NAAQS are codified in EPA’s regulations at 40 CFR Part 50, which includes appendices containing detailed federal reference methods for determining compliance with the standards. Table 1 gives the primary and secondary standards applicable at the time of this writing.

Section 109(d) of the CAA requires EPA to review the ambient standards at least every 5 years and revise them if necessary. The ozone and particle standards are now being revised. Once an area has attained the 1-hour ozone standard, it no longer applies and the area is governed by the 8-hour standard (40 CFR 50.9(b)). In reviewing each ambient standard, EPA issues a revised Criteria Document that contains the updated scientific basis for the standard, and a revised Staff Paper that applies legal and policy considerations to the science in the Criteria Document to recommend revisions to the standard, if appropriate. Several drafts of these materials are generally made available for public review and comment, and for review by EPA’s Clean Air Scientific Advisory Committee. The Criteria Document and Staff Paper are excellent sources of detailed scientific and legal information about the ambient standards and the pollutants they address, as are the preambles to the *Federal Register* notices in which EPA proposed and adopted the standards.

The measures necessary for attainment of the ambient standards are specified in State Implementation Plans (SIPs). Section 110 of the CAA requires states to adopt plans adequate for attainment and maintenance of the ambient standards in the state. There are specific deadlines for attainment of the primary standards and the secondary standards must be attained “as expeditiously as practicable.” States generally use detailed emissions inventories to construct regional and state wide emissions “budgets” for emissions from stationary and mobile sources. The combination of the budgets for mobile and stationary sources must be demonstrated to meet the standards, and the SIP will include the emission limits and other emission controls necessary to ensure that emissions stay within the budgets. As a general rule, site-specific emission limits for existing stationary sources must be based on reasonably available control technology (RACT). EPA has issued RACT guidelines for many categories of sources that are available through EPA’s Web site. Although EPA cannot consider costs or other economic factors in setting the ambient standards, costs can be considered in developing source-specific emission limits in SIPs based on RACT. The SIP development documents compiled by state air quality agencies are an excellent resource for detailed information on the emission limits and budgets applicable at a particular site. SIPs must be revised as necessary when standards change or it becomes clear that the current measures in the SIP are not adequate (or not necessary) to ensure attainment of the standards.

EPA is required to approve SIPs and SIP revisions, and has adopted detailed regulations for doing so (40 CFR Part 51). EPA’s files on proceedings to approve SIPs or SIP revisions, generally located at the relevant EPA regional office, are also good sources of information on the basis for SIP requirements. If EPA disapproves a SIP or SIP revision, and the state fails to make the necessary corrections, the state will lose its authority to implement that portion of the SIP and EPA will impose a Federal Implementation Plan (FIP) provision. EPA’s regulations for FIPs are codified at 40 CFR Part 52.

PSD and Nonattainment

The CAA contains special requirements for areas that do not meet the ambient standards (nonattainment areas, Part D) and areas that exceed the ambient standards (PSD, Part C). The general idea is to require rapid progress toward attainment in nonattainment areas,

* The act does not define ambient air, but it is defined in EPA’s regulations as “that portion of the atmosphere, external to buildings, to which the general public has access” (40 CFR 50.1(e)). Thus, it is possible to create “non-ambient air,” in which the national standards do not apply, by denying public access to company property. This company property rule, in conjunction with the purchase of surrounding land, has been relied on by some large mining operations to a void applicability of the standards in areas near mines or mineral processing facilities where compliance would be difficult. Regulators historically have frowned on this approach but have been forced to allow it in the face of sound evidence that public access to the land is in fact denied. For a good discussion of the company property rule, see 49 *Fed. Reg.* 10946 (March 23, 1984) (sulfur dioxide plan for Kennecott Utah smelter). The definition of ambient air also has been relied on to mark the jurisdictional boundaries for occupational (Occupational Safety and Health Administration [OSHA]), Mine Safety and Health Administration (MSHA) and environmental (EPA) regulation at mining facilities.

and to keep air quality from deteriorating in areas that are attaining the standards.

EPA's PSD regulations are contained in the Part 51 regulations for SIP approvals (40 CFR 51.166) and are quite complex. Most states simply parrot these requirements in their SIPs and related state regulations. The regulations that apply under FIPs are similar (40 CFR 52.1029). PSD goals are attained by two types of requirements: (1) construction permits for new or expanded facilities and (2) air quality "increments" that limit deterioration and act as substitutes for the ambient standards. Attainment areas are placed into one of three classes: Class I, the most pristine areas; Class II, areas in which some deterioration (and hence some development) is allowed; and Class III, areas in which the most deterioration is allowed. For each class, increments have been established for PM, SO₂, and NO₂. The increments are expressed as the "maximum allowable increase above baseline." For example, the PM₁₀ increments (in µg/m³) are

	Class I	Class II	Class III
Annual:	4	17	34
24-hour:	8	30	60

The state adopts the classification for an area. Certain types of areas, such as national parks that exceed 6,000 acres and wilderness areas that exceed 5,000 acres, must be designated as Class I. All other areas are initially designated as Class II but can be redesignated by the state. When states attempt to reclassify areas that are near federal lands, the federal land manager generally plays a significant role. The PM increments historically have played a major role in limiting mine expansion, particularly for large mines in arid western regions. The PSD requirements, including permitting requirements, should be reviewed carefully in connection with any new mining or mine expansion project.

The provisions for nonattainment areas in Part D of the CAA were amended substantially in 1990 and are now quite complex. There are now specific nonattainment requirements for specific criteria pollutants. In general, they classify nonattainment areas as "moderate," "serious," or "severe," with escalating requirements for each classification. The primary requirements are to reduce emissions sufficiently to produce attainment within specified time periods, and to attain interim benchmarks that demonstrate "reasonable further progress." This involves a continuous "ratcheting down" of the SIP emissions budgets until the interim and final budgets are achieved. Special requirements also apply to construction permits for new or expanded sources in nonattainment areas. For facilities in nonattainment areas, the specific SIP provisions and underlying documents should be consulted.

New Source Performance Standards

Section 111 of the CAA requires EPA to adopt minimum standards of performance for new sources in major industrial categories, known as new source performance standards (NSPSs). The NSPSs generally are implemented in construction permits. NSPSs are emission standards that are based on the "best available technology adequately demonstrated." The underlying policy is that the most cost-effective time to install or upgrade emission controls is when a facility is initially built or is renovated in some manner for production purposes.

EPA's NSPS regulations are codified in 40 CFR Part 60. The standards apply to new, reconstructed, and modified sources. A source is modified if it undergoes a physical change or change in the method of operation that actually or potentially increases emissions of any regulated air pollutant. A source is reconstructed if the

cost of renovation exceeds 50% of the cost of a new unit. Under these rules, NSPSs will be applied to a modified source, even without a potential increase in emissions, if the source is reconstructed. On the other hand, if the renovation results in an emissions decrease, NSPSs will not apply as long as the facility has not been reconstructed. There are also a number of exemptions, including routine maintenance, an increase in the hours of operation, changes in ownership, and pollution control projects. An unusual aspect of NSPSs is that they apply to facilities that are constructed, reconstructed, or modified after the NSPS is proposed, whereas most standards do not apply until final standards have been adopted.

EPA's Part 60 regulations include NSPSs for most types of major industrial facilities. The standards are updated periodically as new technologies become available. EPA's regulations include NSPSs for metallic and nonmetallic mineral processing plants, calciners and dryers in certain mineral industries, lime-manufacturing plants, and phosphate rock plants, among other types of facilities that may be relevant to industrial minerals operations. The standards for nonmetallic mineral processing plants in 40 CFR Part 60, Subpart OOO, are representative. They apply to the following "affected facilities" in fixed or portable plants that crush or grind a list of non-metallic minerals: crusher, grinding mill, screening operation, bucket elevator, belt conveyor, bagging operation, storage bin, enclosed truck, and railcar loading station. Stack emissions of PM from these facilities are limited to 0.05 g/dscm and 7% opacity. Fugitive emissions are limited to 10% opacity, with some exceptions. Detailed requirements for monitoring, testing, record keeping, and reporting also are imposed.

Air Toxics Standards

Section 112 of the CAA provides for establishment by EPA of national emission standards for HAPs. These are not ambient air quality standards but source-specific emission standards that apply to categories of sources that emit HAPs. Unlike the conventional pollutants subject to the ambient standards, which are pervasive but harmful primarily in chronic exposure situations, HAPs are substances that are emitted primarily in local "hot spots" (such as near an industrial facility) and can be acutely toxic.

The original version of Section 112, enacted in 1970, required EPA to set health-based standards that provide an "ample" margin of safety (as opposed to the "adequate" margin required for NAAQS) for all acutely toxic pollutants and sources that emit them. The 1970 provision proved extremely difficult to implement, and only a few standards (known as NESHAPs, national emission standards for hazardous air pollutants) were set under that provision. They remain applicable and are codified in 40 CFR Part 61. One of them applies to arsenic emissions from primary copper smelters and essentially requires use of primary and secondary hooding systems in smelters where the quantity of arsenic in the feed exceeds a specified level. Other NESHAPs apply to uranium mines, mills, and tailings piles, and facilities containing asbestos.

The need to revise the HAP provisions was a primary driving force behind the 1990 CAAA, and Section 112 was revised extensively. It now contains a list of more than 400 HAPs for which standards may be set. EPA has authority to revise the list administratively. The list includes asbestos, fine mineral fibers (average diameter 1 µm or less), and a number of metals considered to be toxic, in addition to numerous other organic and inorganic chemicals and compounds. EPA is to set emission standards for categories of industrial facilities that include "major sources" of one or more listed pollutants. A major source is one that emits 10 tpy or more of any single listed pollutant, or 25 tpy or more of a combination of listed pollutants. EPA is allowed to change the se major

source thresholds for specific pollutants by rule. The source is any single facility or a group of facilities located within a contiguous area and under common control (the so-called co-location rule). Unlike the operating permit scenario, discussed later, fugitive emissions are counted in the major source determination for HAPs.

EPA's emission standards for various categories of industrial facilities that emit HAPs are codified in 40 CFR Part 63. The standards are set in two phases: (1) an initial technology-based standard is set on the basis of EPA's determination of the maximum available control technology (MACT); and (2) within 10 years after setting the initial standard, EPA is to determine whether additional measures should be required on the basis of an assessment of the residual risk that remains after the technology-based standards are implemented. Costs can be considered in setting MACT standards, but standards for new sources must reflect at least the degree of control that is achieved in practice by the best-controlled similar source. MACT standards for existing sources must reflect a degree of control that is an average of the best performing sources in the category.

HAP standards are implemented in SIPs and permits. All of EPA's current standards are MACT standards, and the agency is only just beginning the residual risk determinations for the initial MACT standards, while continuing to establish MACT standards for categories of sources not yet regulated. The CAAA provides specific deadlines for establishment of MACT standards that have, in some cases, been implemented through court orders that place EPA on a specific timetable. If EPA misses an applicable deadline to set standards for a source category, states are to set source-specific standards for sources within the category that are located in the state. Section 112 also requires EPA to establish a program for prevention of accidental releases of HAPs, and the agency has adopted implementing regulations at 40 CFR Part 68.

Most types of industrial minerals operations are not subject to MACT standards at present, though EPA may develop them in the future. Existing standards that may be of interest apply to facilities that manufacture bricks and structural clay products (subpart JJJJ), clay ceramics (subpart KKKK) or refractory products (subpart SSSS), and to asphalt plants (subpart LLLL).

Permitting

Before the 1990 amendments, the CAA required construction permits for major new sources or source modifications in PSD and non-attainment areas but did not require existing sources to obtain operating permits. Most states developed operating permit programs of some type, and Congress added a federal operating permit program to the act in 1990 (Title V). Both programs are summarized.

Construction Permits. The construction permit program, also known as new source review (NSR), is generally implemented by states with substantial review by EPA regional offices. EPA's NSR regulations are part of the SIP regulations and are codified at 40 CFR 51, subpart I (SIPs), and 40 CFR 52.1026 (FIPs).

The construction permit program applies to "major sources" that are newly constructed or modified in a manner that produces a significant net increase in emissions. As with NSPSs, modification is defined as any physical change or change in the method of operation of the source, including the exemptions described in the NSPS discussion. A construction permit is required, however, only if the modification produces a "significant net" emissions increase, unlike the NSPS program, which applies to a modification that produces *any* emissions increase. There are two major differences between the NSPS and permitting programs in this respect. First, the permit program applies only where there has been a "net" increase, meaning that an increase in emissions from one piece of

equipment at a source (for example, a crusher) could be offset with a corresponding decrease from another piece of equipment at the same facility (e.g., a conveyor belt or loading station). This is called "bubbling," and it is allowed in determining the applicability of permitting requirements but not NSPSs. Second, a permit is not required unless the net emissions increase is "significant." EPA's regulations define "significant" increases for criteria pollutants and certain HAPs. Accordingly, under the scenario described, if the crusher were modified in a manner that increases emissions (or reconstructed, as explained in the NSPS discussion), the modified crusher would need to comply with NSPSs. If corresponding emission reductions from a conveyor belt are sufficient to avoid a significant net emissions increase, however, no construction permit would be required. EPA has published detailed guidance on bubbling and emissions trading that should be consulted in making these determinations.

In addition, federal construction permits are required only for a "major source" or a "major modification" of a major source. These are defined in EPA's regulations (e.g., 40 CFR 51.166(b)(1)). In general, a major source is any source with the potential to emit 250 tpy or more of any regulated pollutant, except for a list of source categories that are considered to be "major" if potential emissions are 100 tpy or more. The list includes lime plants, phosphate rock plants, large boilers, and other types of sources that might be found at industrial minerals operations. A major modification is one that creates a major source or causes a significant net emissions increase from a major source. The major source thresholds for HAPs are 10 tpy of any single HAP or 25 tpy of a combination. Under the co-location rule, the source is any stationary source or group of sources located on contiguous property and under common control.

The construction permit regulations also define "source" as facilities within the same two-digit Standard Industrial Classification (SIC) code. Thus, at an integrated facility that contains, for example, a mine, a concentrator, and a smelter all under common control, the mine/concentrator unit is one source and the smelter is a different source, meaning that emission from all could not be aggregated for purposes of determining the major source emissions threshold. The SIC code rule is also used in the operating permit regulations, but it does not appear in the HAP regulations.

In determining emission rates from particular pieces of equipment for determining the major source, EPA and states generally rely on the EPA compilation of emission rates known as AP-42 (available from <http://www.epa.gov/ttn/chief/ap42/>). That document should be consulted for emission rates that are likely to be used by permitting authorities, absent site-specific data. In the past, many of the emission rates in AP-42 were notoriously inaccurate, often based on one or two data points taken years ago from out-moded facilities. In recent times, however, various segments of the mining and mineral processing industries have made it a priority to ensure that the AP-42 emission rates for facilities at their operations are accurate and up to date. Many states also use AP-42 emission rates to compute operating permit fees. As specified in the preamble to AP-42, site-specific emission rates can be used in lieu of the AP-42 rates provided they are scientifically sound.

As a matter of federal law, fugitive emissions from mining and mineral processing operations generally are not counted in the major source determination. EPA's regulations contain a list of fugitive emissions sources for which fugitive emissions are counted, and it includes some facilities that may be found at industrial minerals operations (40 CFR 51.166 (b)). Under Section 302 (j) of the CAA, EPA is not permitted to count fugitive emissions unless it has determined by rule that they should be counted for the particular

source category at issue. The list of fugitive emissions sources includes any source subject to an NSPS adopted before August 7, 1980. That does not include metallic or nonmetallic mineral processing plants, because both of those NSPSs were adopted after that date. From time to time, EPA has considered a "Section 302(j) rule-making" to add these facilities to the list, but has not yet done so. The only category of facilities for which EPA has held such a rule-making is surface coal mines, which EPA decided not to place on the list of fugitive emissions sources. In practice, the rule against consideration of fugitive emissions often means that mining or mineral processing operations are not major sources that are required to obtain permits. This federal rule, however, can be overridden by state rules under which fugitive emissions are considered.

The substantive requirements for construction permits differ depending on whether the source would be located in (or significantly affect) a nonattainment area or a PSD area. Permits in nonattainment areas are governed by Section 173 of the CAA. The source is required to comply with the "lowest achievable emission rate" (LAER), which is generally determined by the state in accordance with EPA guidance that can be obtained from the EPA Web site. At a minimum, LAER must comply with any applicable NSPSs, in addition to any other control technologies or measures that may be relevant and available. The owner of the source also must obtain, from other sources in the area, an "emissions offset" under which the combined emissions of the new source and the other sources in the area are sufficiently reduced to show "reasonable further progress" toward nonattainment goals. Some of the nonattainment provisions in the act provide pollutant-specific permit and offset requirements. For example, the major source threshold for PM₁₀ in a "serious" nonattainment area is reduced to 70 tpy.

In addition, the owner of a source seeking a construction permit in a nonattainment area must certify compliance with all applicable regulations at other facilities under common control, and EPA must determine that the state is adequately implementing the SIP. The owner also must demonstrate that the benefits of the source outweigh the environmental costs. Provisions necessary to implement these requirements will be placed in permits generally issued by state permitting authorities subject to regional EPA review.

Permits in PSD areas are governed by Section 165 of the CAA as implemented in EPA's Part 51 regulations for PSD and NSR. The permit must contain conditions sufficient to ensure that the new or modified facility will not cause or contribute to NAAQS violations and will not cause exceedance of the applicable PSD increments, including those for any Class I areas that might be affected. Compliance with these requirements, and related requirements for source monitoring and other air quality impact analyses, often requires a year or more of advance air quality monitoring or modeling work.

PSD permits also must require use of the best available control technology (BACT). BACT is, at a minimum, compliance with applicable NSPSs, plus any additional level of control that the state may determine is a viable considering costs. The primary difference between BACT and LAER is that BACT is a "technology," whereas LAER can require other types of control measures as well. In concept, BACT is "NSPS plus," and LAER is "BACT plus." RACT, the level of control required for existing sources that are not newly constructed or modified (and therefore not subject to these NSR control requirements), can be something less than NSPSs, though it could also be NSPSs if the necessary technology is determined to be "reasonably available." Guidance for determining compliance with all of these various control requirements at particular sources is available on EPA's Web site.

Operating Permits. The federal operating permit program was added in 1990 to require all major sources to have operating permits in which all of the applicable air quality requirements in the SIP or in applicable construction permits are gathered in one place and kept current. It is primarily a state program subject to EPA approval, and EPA's regulations for approving state programs are codified in 40 CFR Part 70. Permits eventually will be required for some types of minor sources as well, and many states already have minor source NSR and operating permit programs.

Detailed requirements for operating permit applications, issuance, and renewal are presented in EPA's Part 70 regulations. The rules for determining major sources and consideration of fugitive emissions are the same as previously described with respect to construction permits. As a result of litigation filed by the mining industry over the original Part 70 rules, EPA has issued guidance indicating that the co-location rules cannot be used to require a permit for an unlisted source of fugitive emissions that would not otherwise be considered a major source that requires a permit. The guidance does not apply to construction permits and indicates that EPA may revisit this issue in the context of a Section 302(j) rulemaking.

Operating permits must be renewed periodically, and procedures for permit amendments following operational changes also are specified. Operating permits are not to impose any new substantive requirements, though state agencies often find ways to do so (e.g., updating requirements said to be outdated). In addition, permits must include monitoring requirements sufficient to ensure compliance, as regulated under EPA's compliance assurance modeling (CAM) rules codified at 40 CFR Part 64. Some state agencies use this requirement to impose new or revised monitoring provisions in operating permits. Permit applications must certify that the facility is in compliance with all applicable requirements or must include a compliance schedule for doing so. States are allowed to charge permitting fees that reflect the costs of administering the operating program. Fees often are assessed on the basis of the quantity of emissions, as determined by the emission rates provided in AP-42.

Mobile Sources

Under federal law, mobile source emissions that occur within a stationary source (e.g., heavy mining equipment) are not subject to regulation in stationary source permits and are not to be counted in determining the applicability of permit requirements. But state regulators often find creative ways to do so, and mobile source emissions must be examined as part of a National Environmental Policy Act (NEPA) analysis if it is required (as discussed further in the following sections). EPA has established, and is now in the process of updating, emission standards for heavy- and light-duty vehicles, heavy-duty diesel engines, and off-road engines. The purchase or use of equipment that meets the applicable standards is the primary consideration with respect to mobile source emissions at industrial minerals operations. In addition, use of such equipment can be limited by state mobile source emissions budgets.

Another mobile source requirement that can affect industrial minerals segments is "conformity." One of the conditions for release of federal funds for highway or transit projects is a requirement to demonstrate that mobile source emissions generated by the project (e.g., increased automobile emissions from expansion of a highway) would "conform" to the applicable state mobile source emissions budget. If not, no federal funding can be provided for the project. In recent years, antidevelopment groups have used the conformity rules effectively to delay road construction and other projects that cannot proceed without federal funding, with a significant effect on some industrial minerals sectors.

Enforcement

Section 113 of the CAA imposes civil penalties up to \$25,000 per violation per day for violations of the act or the implementing regulations. Criminal penalties, including imprisonment and fines under the federal criminal statutes, are provided for “knowing” violations, and for negligent release of a HAP that poses imminent danger. Intentional release of a HAP that poses imminent danger is punishable by imprisonment and fines up to \$1 million. EPA has issued civil and criminal penalty policies that specify how various mitigating factors will be taken into account in the assessment of penalties.

An EPA enforcement action begins with issuance of a Notice of Intent to initiate an investigation under Section 114 of the CAA. Companies or individuals who receive a Section 114 notice should involve experienced counsel as quickly as possible. If EPA believes, as a result of the Section 114 investigation, that a violation has occurred, a notice of violation will be issued. As a general rule, in civil cases, EPA will then commence an administrative enforcement action and attempt to negotiate a settlement. If a settlement is concluded, the terms will be embodied in a consent decree that will be entered as an order of the appropriate court. Typical settlement terms include compliance plans, remediation measures, and supplemental environmental projects (SEPs), in addition to penalties. A SEP is an environmental project that is not otherwise required by law and essentially is financed in lieu of penalty payments. Criminal cases are handled separately by EPA's Office of Criminal Enforcement.

If a settlement cannot be reached, EPA generally will initiate the administrative enforcement process before an administrative law judge at EPA. If the administrative process fails, or the penalty is very large, or injunctive relief is necessary, EPA will refer the case to the Department of Justice for prosecution in the appropriate federal court. In addition to these provisions, Section 303 of the CAA allows EPA to issue orders or bring civil actions to address actions believed to be causing imminent and substantial danger. In addition, Section 304 of the act allows private citizens to file enforcement actions if they have given 60 days' notice to EPA and the agency is not diligently prosecuting the action. Section 304 also allows private citizens to file actions to force EPA to perform non-discretionary actions under the act.

WATER QUALITY

The current federal Clean Water Act (CWA) was enacted in 1972 and substantially amended in 1987. It grew from the prior attempts of Congress to regulate waters that are “navigable in fact” under the Rivers and Harbors Act of 1899. The regulatory reach of the current act, however, extends far beyond such waters, as discussed in more detail in the text that follows. The primary focus of the 1972 act was establishment by EPA of technology-based effluent standards for categories of industrial sources and implementation of the standards in a national system of discharge permits. With adoption of the 1987 amendments, the focus has shifted to adoption of water quality standards designed to protect public health and aquatic ecosystems and development of permit terms necessary for compliance with the standards.

The primary components of the CWA are (1) effluent guidelines and standards; (2) water quality standards; (3) discharge permits; (4) “dredge or fill” permits; (5) oil spill responses; and (6) enforcement. These are discussed in the sections that follow.

Effluent Guidelines and Standards

Section 301 of the CWA requires EPA to establish technology-based effluent standards for a wide array of categories of industrial

facilities. The standards apply nationwide and are implemented in permits issued under the National Pollutant Discharge Elimination System (NPDES). The limits are designed to be technologically and economically feasible for the affected industry segment.

For conventional pollutants discharged to surface waters from existing sources, initial standards were to be based on the “best practicable technology currently available” (BPT), to be followed within a few years by new standards, generally more stringent, based on the “best conventional pollutant control technology” (BCT). For toxic pollutants, the standards are to be based on the “best available technology economically achievable” (BAT). Under Section 306 of the CWA, new source performance standards must be based on the “best available demonstrated control technology” (BDT). Sources that are “fundamentally different” from the facilities on which the standards were based may be eligible for a variance based on such differences.

EPA's national effluent guidelines and standards are codified in 40 CFR beginning at Part 400. Categories that are subject to standards and may be of interest in industrial minerals sectors include cement manufacturing (Part 411), phosphate manufacturing (Part 422), asbestos manufacturing (Part 426), mineral mining and processing (Part 436), centralized waste treatment (Part 437), ore mining and dressing (Part 440), transportation equipment cleaning (Part 442), and asphalt paving and roofing materials (Part 443). The background information documents compiled by EPA in setting these standards and the *Federal Register* notices proposing and promulgating the standards are excellent reference sources for understanding the basis for the standards and the details of the regulated processes.

Water Quality Standards

Water quality standards can be established by EPA or states. EPA has published federal guidance, available on the agency's Web site, on appropriate standards for some pollutants. Most applicable water quality standards are now set by states under state law.

Water quality standards serve two purposes: (1) they define the water quality goals for a specific body of water based on designated uses identified by the state; and (2) they are the basis for permit limits designed to make sure that the standards are not exceeded. Section 303 of the CWA requires states—or EPA if a state does not comply—to designate uses for all water bodies and stream segments in the state. Representative uses include industrial use, domestic use, recreation, and fish habitat, among others. The general goal of the act as stated in Section 101, however, is to ensure that all national waters are “fishable” and “swimmable” where this goal is attainable.

After the designated use of a water body has been established, ambient water quality standards are then imposed at levels necessary to maintain and protect the designated use. The standards can take several forms, including numeric concentration limits for specific substances, numeric toxicity levels, or narrative statements. In some cases, whole effluent toxicity (WET) tests are required that measure the effects of effluent on aquatic organisms in the receiving waters. In addition, EPA has adopted an antidegradation rule that requires protection of current uses (40 CFR 131.12). Water quality that exceeds an applicable standard cannot be degraded to the level of the standard absent social or economic justification.

Water quality standards are the “second wave” of protection under the CWA and increasingly drive permit limits. In many cases, the technology-based effluent standards that were adopted during the early years of the act assist in attainment of water quality standards but are not capable of producing full compliance and must be

augmented with additional permit conditions necessary to attain the applicable water quality standards.

Permitting

The CWA imposes strict liability for discharge of any pollutant by any person into the “navigable waters of the United States,” except in compliance with a valid discharge permit. Historically, EPA has interpreted this to extend to all surface water bodies that Congress can reach under the Commerce Clause of the Constitution, that is, all waters with any connection to interstate commerce. The act does not regulate groundwater, though the Safe Drinking Water Act provides for regulation of “sole-source aquifers” under some conditions, and state water quality or mining and reclamation laws often include requirements for groundwater protection.

In the 2001 case of *Solid Waste Agency of Northern Cook County v. U.S. Army Corps of Engineers*, S.Ct. No. 99-1178, however, the Supreme Court held that EPA’s jurisdiction under the act does not extend to isolated intrastate ponds or other state waters that do not affect interstate waters. The effect of this decision is to remove some isolated state waters from the purview of the federal program that previously were thought to be subject to the program. The precise scope of the Court’s decision remains a matter of debate within EPA and the Army Corps of Engineers, though more recent lower court decisions have generally interpreted the Supreme Court’s decision narrowly. It is likely to be some time before the precise effect of the Supreme Court’s decision is known, and Congress is considering legislation in reaction to the Court’s decision.

The CWA establishes two types of permits: (1) NPDES permits for discharges into navigable waters under Section 402; and (2) “dredge or fill” permits under Section 404. These are discussed in the following sections.

NPDES Permits

Permits under Section 402 are required for any “discharge of a pollutant” from a “point source” into the navigable waters of the United States. They are issued by EPA or by states with EPA-approved permit programs, which are now in place in most states. Permits contain discharge limits as necessary to comply with applicable effluent and water quality standards, monitoring and reporting requirements, and various “standard conditions.” The usual permit term is 5 years, after which the permit must be renewed, and amendment is required following significant changes in operations. EPA has issued extremely complex regulations for permit application, issuance, amendment, and renewal, codified at 40 CFR Part 122. Standards and criteria for permits are codified in Part 125.

There are two types of NPDES permits: (1) individual permits issued to a facility based on site-specific information, and (2) general permits that cover discharges from categories of industrial sources. A facility operator generally can choose between the two. For general permits, no application is required, but the operator must file a Notice of Intent to proceed under the general permit. In the past, general permits were used fairly widely at some mining or mineral processing operations. EPA recently revised the general permit for mining activities, however, and greatly reduced its utility for some operations. This action is currently subject to litigation.

Section 502 of the CWA defines “discharge” as “any addition” of a pollutant to regulated waters. The courts have generally focused on whether the activity introduces a pollutant from outside of the water body at issue. “Pollutant” is defined very broadly and can include temperature, fish or other organisms, or water of varying quality. A point source is a pipe, ditch, channel, tunnel, well, conduit, or other synthetic structure, excluding irrigation return flows and agricultural stormwater discharges. Stormwater

runoff is subject to special permit regulations codified in 40 CFR Parts 122–124.

Nonpoint-source pollution includes runoff from agricultural and silvicultural operations (crops, fields, forested lands) and runoff from mines; mining activities that release pollutants from discernible conveyances, however, are point sources. It can also include changes in flow or circulation caused by dams, levees, channels, or other diversions. The 1987 amendments added Section 319, which requires states to identify actions necessary to improve the quality of waters impaired by nonpoint-source pollution. In addition, Section 303 of the CWA, as amended in 1987, requires waters not protected by effluent limitations to be listed as impaired. For such waters, EPA or the states must establish total maximum daily loads (TMDLs) that apply to both point and nonpoint sources. A TMDL is the largest amount of pollution that a water body can receive daily without violating the applicable water quality standards. The objective of the TMDL program is to identify, for specific water bodies and locations, an appropriate division of water quality control efforts among point and nonpoint sources, and to impose related controls on both types of sources. In some cases, the existing requirements for point sources in permits will need to be strengthened. In many parts of the country, the effect of the TMDL program is only just beginning to be felt.

Under Section 307 of the CWA, special standards and permit requirements are applied to sources that discharge into publicly owned treatment works. These are called “pretreatment requirements,” and EPA’s regulations governing them are codified at 40 CFR Part 403.

Dredge or Fill Permits

Section 404 of the CWA requires issuance of permits for any dredging or filling operations that affect regulated waters. Section 404 permits are issued by the Army Corps of Engineers, in consultation with EPA. As with the NPDES program, discharge is defined broadly as any addition of pollutants. Dredged material is material excavated from water, including some fallback material. Fill material is material used to create dry land or alter the bottom elevation. This generally includes activities involving wetlands, which are defined as areas “inundated or saturated by surface or groundwater at a frequency and duration sufficient to support, and that under normal circumstances do support, a prevalence of vegetation typically adapted for life in saturated soil conditions” (33 CFR 328.3(b)). In 1998, a federal court invalidated the Corps’ so-called Tulloch rule, which required a permit for incidental fallback at mining and other operations. EPA and the Corps have interpreted that court’s decision very narrowly, however, and the issue remains uncertain and in litigation at this time.

As with the NPDES program, there are two types of Section 404 permits: (1) nationwide permits for classes of dredge-and-fill activities, and (2) individual permits. Nationwide Permit 44 (NWP 44), which governs mining activities, was revised and severely limited in 2002, including limitation to activities involving a half acre of wetlands or less. The NWP 44 that was issued in 2002 is currently in litigation. Nationwide permits include general provisions that require avoidance of adverse impacts where possible and mitigation where impacts are unavoidable. Permit provisions also include verification and state certification requirements, and some require preconstruction notice to the state or the Corps.

The Corps has adopted detailed regulations for individual permits, codified in 33 CFR Parts 325 and 327. The permit process includes NEPA and public interest review, and permits are required to include mitigation provisions to avoid, minimize, or compensate

for adverse impacts. An administrative appeal and veto process also is provided.

Oil and Hazardous Substances

Section 311 of the CWA, a precursor to the federal Superfund law, prohibits discharges of oil or hazardous substances into regulated waters in quantities that violate water quality standards or create a sheen or sludge. EPA's regulations for implementing this program appear in 40 CFR Part 112. They include requirements for development of spill prevention plans, reporting of spills, and reimbursement of removal or other cleanup costs.

Enforcement

Sections 309 and 505 of the CWA govern enforcement actions, which are similar to the actions permitted under the CAA as described earlier in this chapter. Administrative penalties up to \$12,000/day can be assessed by EPA, with a maximum of \$31,500 for informal proceedings and \$157,500 for formal proceedings. SEPs are allowed and mitigating factors are considered, including the gravity of the violation, the economic benefit the violation produced, prior violations, good faith, and ability to pay. Cases involving larger penalty amounts or injunctive relief are referred to the Department of Justice for prosecution in the federal courts.

Criminal penalties may be assessed for negligent violations (\$2,500 to \$25,000/day and imprisonment up to a year), knowing violations (\$15,000 to \$50,000/day and up to 3 years' imprisonment), and knowing endangerment (up to \$250,000 and 15 years' imprisonment for individuals and \$1,000,000 for organizations). Citizen suits can be filed against violators or EPA in cases where EPA or the state fails to prosecute diligently after receiving notice of a violation.

WASTE DISPOSAL

Congress enacted the Resource Conservation and Recovery Act of 1976 (RCRA) to establish a comprehensive federal program to regulate the handling of solid wastes. RCRA amended the Solid Waste Disposal Act and was the first substantial effort by Congress to establish a regulatory structure for the management of solid and hazardous waste. RCRA's primary goals are to protect human health and the environment from the potential hazards of waste disposal, to conserve energy and natural resources, to reduce the amount of waste generated, and to ensure that wastes are managed in an environmentally sound manner. In 1984, Congress enacted the Hazardous and Solid Waste Amendments (HSWA), which significantly expanded the scope and requirements of RCRA.

To achieve these goals, Congress established three distinct, yet interrelated programs under RCRA. Of those three programs, only two are relevant in the context of the mining industry. Those sections are Subtitle C, the hazardous waste program (42 U.S.C. § 6921–6939(b)), and Subtitle D, the solid waste program (42 U.S.C. § 6941–6949(a)). Subtitle C was implemented to address “cradle-to-grave” requirements for hazardous waste from the point of generation to the ultimate disposal and requires EPA to promulgate regulations to govern the treatment, storage, and disposal of these wastes. Subtitle C requires EPA to develop criteria to identify hazardous wastes and authorizes the agency to list particular wastes as hazardous according to certain enumerated criteria. Generally, wastes are considered hazardous under Subtitle C if they are listed as hazardous by the administrator of EPA or they are found to have one of four technical characteristics that make them hazardous. Those four characteristics are ignitability, corrosivity, reactivity, and extraction procedure (EP) toxicity, which EPA separately defined as the leaching of toxic residues into surrounding liquid.

Under Subtitle D of RCRA, states are allowed and in fact encouraged to use federal financial and technical assistance to develop comprehensive solid waste management plans in accordance with guidelines promulgated by EPA. EPA has authority under Subtitle D to promulgate criteria for classification of waste facilities as sanitary landfills or open dumps. Facilities can be classified as sanitary landfills only if there is no possibility that the facility poses a danger to health or the environment from deposits made at those sites. Subtitle D prohibits open dumping of potentially dangerous solid wastes and requires states to submit for EPA approval comprehensive solid waste disposal plans that include a prohibition of such unregulated dumping. Subtitle D of RCRA regulates only nonhazardous solid wastes and hence its requirements are less restrictive than those found in Subtitle C.

Regulation of Mining Wastes

Congress enacted Subtitle C to address the hazards of industrial and manufacturing process wastes. When RCRA was enacted, however, Congress recognized that it lacked sufficient information to bring mining wastes within the purview of Subtitle C. As a result, Congress included a statutory provision directing EPA to conduct a detailed study of mining waste to evaluate the potential danger to human health and the environment and, ultimately, whether such wastes should be subject to Subtitle C and the related regulatory scheme. The study provision mandates investigation into the following factors: the sources and volume of mining waste and the present disposal practices; alternative practices and costs of the alternatives; potential dangers to human health and the environment; possibilities for use of discarded material; and adequacy of state or other federal regulatory programs to meet the problem.

Notwithstanding the mandate of Congress concerning the study of mining waste and the deferral of regulation of such waste until the results of the study were evaluated, at the time Congress enacted Subtitle C of RCRA, there was no provision that permitted EPA to defer the regulation of mining waste until the study mandated by the statute was complete. As a result, EPA instituted a stopgap measure whereby in December 1978 it proposed regulations to govern hazardous waste under which mining waste from the extraction, beneficiation, and processing of ores and minerals would be considered “special wastes,” defined as wastes that were generated in high volumes but were considered low hazard. These high volume, low hazard special wastes were to be subject to separate standards from waste that otherwise fell within the scope of Subtitle C.

The new special wastes provision was abandoned by EPA in 1980 before it came into effect because EPA had narrowed the EP toxicity and corrosivity criteria for Subtitle C regulation, the anticipated result being that the special wastes would no longer qualify for stringent regulation under Subtitle C (i.e., they would no longer meet the criteria of wastes that were subject to Subtitle C). Certain mining waste streams from primary metal smelting and refining operations that satisfied the revised criteria for hazardous wastes, however—specifically, copper blowdown wastes, lead impoundment solids, and zinc wastewater sludges—were proposed to be listed as hazardous waste by EPA.

Shortly before these new regulations were to take effect, Congress enacted the Solid Waste Disposal Act amendments of 1980, which included what has come to be known as the Bevill Amendment. The Bevill Amendment added two key provisions to RCRA. First, in addition to extending the deadline on the study of mining waste required by RCRA, it added a new section that required EPA to conduct a comprehensive study of the adverse environment and health effects of the disposal and utilization of solid wastes from

the extraction, beneficiation, and processing of ores and minerals, including phosphate rock and overburden from uranium mining, among solid wastes from mining operations. Second, it required EPA to defer, for a period of at least 6 months after the completion of the studies, the imposition of the Subtitle C regulation on solid wastes that resulted from the extraction, beneficiation, and processing of ores and minerals. The Bevill Amendment also required EPA to determine whether regulation of those wastes under Subtitle C of RCRA was warranted. This determination had to be made by EPA within 6 months of the completion of the statutorily mandated study.

To incorporate the Bevill Amendment's exclusion of certain mining wastes from regulation under Subtitle C, and therefore maintain consistency between the statutory requirements and the EPA regulations, EPA published an amendment to its hazardous waste regulations in November 1980. The regulatory amendment tracked the language of the Bevill Amendment and extended the mining waste exclusion to apply to solid waste from the exploration, mining, milling, smelting, and refining of ores and minerals. Since it excluded smelting operations from the purview of Subtitle C, EPA also temporarily suspended the listing under Subtitle C of three of the hazardous waste streams that resulted from smelting operations: copper blowdown waste, lead impoundment solids, and zinc treatment sludges. EPA also went further and temporarily suspended the remaining three types of hazardous waste that resulted from smelter operations.

In 1984, Congress enacted the HSWA. These amendments strengthened the RCRA regulatory scheme and specifically gave EPA the flexibility to fashion Subtitle C standards for wastes from the extraction, beneficiation, and processing of ores and minerals. In particular, EPA was given the authority to modify the various standards for hazardous waste disposal under Subtitle C to take into account the special characteristics of such wastes.

Although the hazardous and solid waste amendments broadened EPA's authority to include its ability to regulate mining waste, it could not use its broadened authority until it completed the study required by the Bevill Amendment. The statutorily mandated deadline for the study was October 21, 1983, which EPA missed. As a result of its failure to complete the study, EPA was sued by a concerned citizens group in September 1984. The citizens group suit sought to have EPA either list aluminum pot liners as a hazardous waste, which would then be subject to regulation under Subtitle C of RCRA, or include those wastes in the required study. During that case, EPA indicated that it would reinterpret the mining waste exclusion to at removed certain smelting and refining wastes from the scope of Subtitle C, and since those wastes would again be subject to Subtitle C regulation, they would not be included in EPA's study of mining waste. Based on this representation by EPA, a federal court awarded judgment to the plaintiffs and ordered EPA to abide by the schedule it proposed. Specifically the court ordered EPA to propose its reinterpretation of the mining waste exclusion by September 30, 1985; to complete the studies mandated by the RCRA statute by December 31, 1985; and to take final action on the proposed reinterpretation by September 30, 1986. In keeping with the court-ordered timetable, in October 1985, EPA proposed to narrow the scope of the exclusion of mineral processing wastes from Subtitle C. EPA subsequently withdrew this proposal in October 1986.

Also in keeping with the court-ordered schedule, EPA submitted to Congress and published the statutorily required study on December 31, 1985. The study included an evaluation of, among other types of wastes, mining waste from the early processing stages of extraction and beneficiation as required by Subtitle C but did not include any study of processing wastes because those

wastes were the subject of EPA's proposed reinterpretation of the Bevill Amendment and would have ultimately come back within the regulatory purview of Subtitle C. Although the report estimated that 755 Mt of waste produced yearly by the nonfuel mining industry potentially qualifies as hazardous waste, it recognized and acknowledged that this figure was an overestimate because the conventional testing for EP toxicity—one indicator of whether a waste is a hazard under Subtitle C—did not reflect real conditions. A modified test revealed that no mining waste samples tested were in fact toxic.

Relying on the results from the modified testing method, EPA then concluded that mining waste was not hazardous and that it was not going to regulate mining waste under Subtitle C of RCRA. Although EPA acknowledged that some of the wastes generated from the two categories were clearly hazardous, it concluded that a large segment of the industry could not afford to manage and treat these wastes if they were regulated under Subtitle C. EPA indicated it would attempt to develop a regulatory program for these two types of waste under the less stringent Subtitle D of RCRA. Although EPA's determination was challenged in court, it was upheld (see *Environmental Defense Fund v. EPA*, 852 F.2d 1309 (D.C. Cir. 1988)).

In October 1986, EPA withdrew its proposed reinterpretation of the Bevill Amendment exclusions. EPA asserted that there was no standard for ascertaining specifically what a "high volume-low hazard" waste was in the context of "special wastes," and thus there were no criteria for distinguishing processing waste from nonprocessing waste. EPA simultaneously reaffirmed its 1980 interpretation of the Bevill Amendment exclusions of processing wastes from regulation under Subtitle C. EPA was again sued on the ground that its decision was arbitrary and capricious. This time the court awarded judgment to the plaintiffs, requiring EPA to regulate smelting waste under Subtitle C (see *Environmental Defense Fund v. EPA*, 852 F.2d 1316 (D.C. Cir. 1988)). Subsequent to this decision, EPA engaged in a rulemaking process, the results of which were to list certain smelting wastes as "hazardous wastes" that were not exempt from regulation under Subtitle C of RCRA.

Mining on Federal Land

The policy governing mining on federal land is laid out in the Federal Land Policy and Management Act of 1976, which sets forth that the public lands, those owned by the federal government, remain under the stewardship of the federal government, and that although these lands belong ultimately to the American people, their resources can be managed under a multi-use principle that will allow the federal government to use these lands to meet the present and future needs of the American public (43 U.S.C. § 1701, *et. seq.*). Three different sets of federal laws and regulations govern the exploration, development, and production of minerals on federal lands: (1) hard-rock (generally metallic) claims under the General Mining Law of 1872; (2) mineral leasing under the Mineral Leasing Act of 1920; and (3) the minerals disposal system under the Mineral Materials Act of 1947.

The primary federal law governing minerals on federal lands is the Mining Law of 1872 (30 U.S.C. § 22–54). The Mining Law provides citizens in the United States with the opportunity to explore for, discover, and purchase certain valuable mineral deposits on those federal lands that remain open for the purpose of mining. The Mining Law also contains provisions that provide for the enactment of state laws that are consistent with federal law. As a result, most states have enacted laws that prescribe the manner of locating and recording mining claims, tunnel sites, and mill sites on federal lands within their boundaries. There are federally

administered lands in 19 states where mining claims or sites are allowed: Alaska, Arizona, Arkansas, California, Colorado, Florida, Idaho, Louisiana, Mississippi, Montana, Nebraska, Nevada, New Mexico, North Dakota, Oregon, South Dakota, Utah, Washington, and Wyoming.

In these states, the Bureau of Land Management (BLM) of the Department of the Interior manages the surface of public lands and the Forest Service of the U.S. Department of Agriculture manages the surface of National Forest System lands. The BLM is also responsible for subsurface mining on both public lands and lands within the National Forest System.

Proposed mining activities on federal lands trigger the application of the BLM and Forest Service regulations (see 43 CFR § 3809 for the BLM's regulations and 36 CFR § 228 for the Forest Service's counterpart regulations). The BLM's regulations establish guidelines intended to ensure compliance with the federal land policy and management act prohibition against "unnecessary or undue degradation of public lands." The following sections in 43 CFR relate to and govern mining claims under the mining laws of the United States:

- 3800 Mining claims under the general mining laws
- 3810 Lands and minerals subject to location
- 3820 Areas subject to special mining laws
- 3830 Location of mining claims
- 3840 Nature and classes of mining claims
- 3850 Assessment work
- 3860 Mineral patent applications
- 3870 Adverse claims, protests, and conflicts

In addition, the 1976 National Forest Management Act provides the statutory framework for lands within the jurisdiction of the Forest Service. The regulations are contained in 36 CFR § 228 and establish guidelines intended to ensure compliance with its regulatory requirement to "minimize adverse environmental impacts on national forest subsurface resources." In addition to the regulations, mining on lands within the domain of the Forest Service is also controlled by the National Forest Management Act (16 U.S.C. 1600–1640).

In addition to the BLM and Forest Service regulations, NEPA is a broad statutory scheme that requires evaluation of certain environmental issues with regard to mining proposals on private as well as federal lands. Any anticipated actions or operations, including mining activity, on federal lands that are expected to have a significant impact on the environment require under NEPA that an environmental impact study be performed. After the study is conducted, the results are issued in an environmental impact statement (EIS). Depending on the results of the EIS, an entity planning such activity may be required to enact measures to prevent destruction or harm to the environment. For small operations on federal lands, NEPA allows the use of an environmental assessment (EA) as a preliminary study in lieu of the EIS. The EA is intended to assist the relevant federal land management agency or agencies in determining whether environmental impacts will be significant and, if so, whether a full EIS will be required.

REMEDIATION OF CONTAMINATED SITES

The evolution of the application of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund) to mining waste did not have the long and drawn-out course as did the history of the application of RCRA to such waste. When it was enacted in 1980, CERCLA was designed to address the growing problem of inactive hazardous waste sites throughout the United

States. CERCLA authorizes EPA to respond to the release of "hazardous substances" that may present "an imminent and substantial danger to the public health or welfare." The term *hazardous substances* is defined by CERCLA to mean

"(A) any substance designated pursuant to § 1321(b)(2)(A) of Title 33; (B) any element, compound, mixture, solution, or substance designated pursuant to § 9602 of this Title; (C) any hazardous waste having the characteristics identified under or listed pursuant to § 3001 of the Solid Waste Disposal Act (but not including any waste the regulation of which under the Solid Waste Disposal Act has been suspended by act of Congress); (D) any toxic pollutant listed under § 1317(a) of Title 33; (E) any hazardous air pollutant listed under § 112 of the Clean Air Act; and (F) any imminently hazardous chemical substance or mixture with respect to which the Administrator has taken action pursuant to § 2606 of Title 15. The term does not include petroleum, including crude oil or any fraction thereof which is not otherwise specifically listed or designated as a hazardous substance under subparagraphs (A) through (F) of this paragraph. ..."

A superficial reading of the definition of hazardous substance, particularly subsection (C), may lead one to believe that those mining wastes excluded from regulation under RCRA are likewise excluded from regulation under CERCLA by virtue of the language of subsection (C) of the definition of hazardous waste that excludes any waste the regulation of which under RCRA has been suspended by Congress. As previously discussed, the current regulatory scheme under RCRA excludes certain types of mining waste, specifically extraction and beneficiation waste, although certain smelting wastes are specifically regulated by virtue of the specific waste being listed.

Notwithstanding the attractiveness of this interpretation, such is not the current state of the law. This issue came to a relatively quick resolution when a number of parties, including mining companies, sued EPA when it put their facilities on the National Priorities List (NPL) of releases or threatened releases throughout the United States (*Eagle-Picher Industries, Inc. v. EPA*, 759 F.2d 922 (D.C. Cir. 1985)). The NPL is the list of national priorities among the known releases or threatened releases of hazardous substances, pollutants, or contaminants throughout the United States and its territories. The NPL is intended primarily to guide the EPA in determining which sites warrant further investigation and possibly remedial action.

The plaintiffs relied on the basic wording of subsection (C) of the definition of hazardous waste in arguing that mining waste was not excluded from regulation under RCRA by Congress, at least until the study discussed in the RCRA section cited was completed, and thus mining waste should be excluded from regulation under CERCLA. The court concluded the plaintiffs' position was incorrect and ruled in favor of EPA on the following rationale. The plaintiffs were correct, in the narrow sense, with regard to the argument that subsection (C) was meant to exclude from regulation under CERCLA those same wastes that were excluded from regulation under RCRA. The court, however, concluded that the exception set forth in subsection (C) does not prevent a waste from being labeled as a hazardous substance if it falls within another subsection of the definition of hazardous waste.

Accordingly, although extraction and beneficiation mining waste and certain smelting waste are not subject to regulation under RCRA and therefore are not captured in the definition of hazardous waste by virtue of its subsection (C) exclusion, if constituents of

those wastes contained elements that otherwise meet CERCLA's definition of hazardous waste, then those wastes will be considered to be a hazardous substance under CERCLA. The RCRA/CERCLA dichotomy treatment of mining waste seems to be a quirk in the law; the reader must recognize that RCRA and CERCLA serve two similar although distinct purposes. RCRA is designed to regulate the generation, storage, and ultimate disposal of wastes and to ensure in doing so that those wastes do not pose a danger to the public health. By virtue of the high-volume and low-hazard nature of mining wastes, it was determined by Congress and EPA that these wastes do not pose a danger to the public health and therefore do not warrant regulation by EPA. CERCLA, on the other hand, regulates certain specific substances that are deemed to be hazardous by their very nature, and, as such, if these substances are found in any waste, be it mining or otherwise, an "imminent and substantial danger to the public health or welfare is deemed to exist." Mining waste can be analogized to the disposal of water down the drain in residential houses: when an individual drains a bathtub of water, that waste is not regulated by CERCLA; however, if gasoline is mixed with the bath water, which is ultimately drained down the sewer, that waste is regulated by virtue of the gasoline being the constituent of the bath water.

Apart from the requirements previously discussed, CERCLA Sections 102 and 103 require operators to report discharges of hazardous materials into the environment in quantities that exceed "reportable quantities" established in EPA regulations (see 40 CFR Part 302). Further, the Superfund Amendments and Reauthorization Act of 1986 (SARA) included a new statute now commonly known as the Emergency Planning and Community Right-to-Know Act (EPCRA), which imposes additional requirements for reporting of listed toxic chemicals stored on site, spills of such chemicals, and related emergency response procedures. The EPA regulations implementing these requirements are codified at 40 CFR Parts 355, 370, and 372.

NATIONAL ENVIRONMENTAL POLICY ACT

NEPA requires federal agencies to

"include in every recommendation or report on proposals for legislation and other major federal actions significantly affecting the quality of the human environment, a detailed statement by the responsible official on—

- the environmental impact of the proposed action;
- any adverse environmental effects which cannot be avoided should the proposal be implemented;
- alternatives to the proposed action;
- the relationship between local short-term uses of man's environment and maintenance and enhancement of long-term productivity; and
- any irreversible and irretrievable commitments of resources which would be involved in the proposed action should it be implemented" (42 U.S.C. § 4332).

Before taking the action, the responsible official must consult with various affected federal, state, and local governmental representatives, and public review and comment is required. NEPA review often is used to delay or prevent significant industrial or other development.

A NEPA review is required for all "major federal actions" that "significantly affect the environment." This includes mineral leases on federal lands, actions involving expenditure of federal funds, and issuance of many types of federal permits, though most environmental permits are excluded from NEPA review. NEPA review is required for dredge or fill permits under Section 404 of the CWA

and for new source permits under the act. It is not required for air quality permits, or for any permits issued by states (though many states now have their own state NEPA laws).

The White House Council on Environmental Quality (CEQ) has issued the primary set of regulations implementing NEPA, which are codified in 40 CFR Part 1500 *et. seq.* Most federal agencies have adopted complementary NEPA regulations, which include "categorical exclusions" of agency actions for which NEPA review is not required. If NEPA review is required, the first step generally is preparation of an EA, which is designed to determine whether an action might cause significant environmental impacts that should be reviewed in more detail. If so, an EIS is required. Preparing an EIS today is usually an extremely complex task that requires at least a year or more, and EAs are becoming more detailed as well. Agency-specific NEPA regulations often will specify classes or types of agency actions for which an EIS is presumed to be required.

If a completed EA or EIS predicts no significant impacts, the lead agency will issue a "finding of no significant impact" (FONSI), and the project will proceed. If significant impacts are predicted, NEPA does not expressly require mitigation, but the CEQ regulations require the EIS to state whether all practicable means to avoid or minimize environmental harm from the alternative selected have been adopted, and if not, why not (40 CFR 1505.2(c)). If mitigation measures are adopted, a monitoring and enforcement program is required (40 CFR 1505.2(c)). Some agency regulations, such as those of the Federal Highway Administration, independently require mitigation measures for impacts identified in NEPA analyses (23 CFR 771.105(d)). Even where no such mitigation provision is involved, the social and political leverage provided by NEPA analyses often is enough to delay or prevent controversial projects.

TOXIC SUBSTANCES CONTROL ACT

The Toxic Substances Control Act (TSCA, 15 U.S.C. § 2601 *et. seq.*) is a comprehensive program for regulation of toxic materials in products. It is aimed at "chemical substances," which are defined in Section 3 to include, with some exceptions, "any organic or inorganic substance of a particular molecular identity, including any combination of substances occurring in whole or in part as a result of a chemical reaction or occurring in nature." EPA is given a wide array of tools to regulate chemical substances that may pose "unreasonable risk of injury to health or the environment." These include authority to require product testing (Section 4), regulate new products and new uses of existing products (Section 5), ban or otherwise regulate existing products (Section 6), and address imminent hazards (Section 7). Section 8 includes a variety of reporting requirements, including a requirement to inform EPA whenever new information (e.g., scientific studies) becomes available suggesting that a product may pose an unreasonable risk. Under TSCA Section 11, in an appropriate case EPA can use TSCA as a conduit to regulation under other statutes administered by the agency or, in cases involving occupational exposures, to OSHA or MSHA. EPA's TSCA regulations are codified at 40 CFR Part 700 *et. seq.*

TSCA was intended primarily to regulate the chemical industry and has rarely been used in the context of mining or mineral processing. EPA's asbestos and polychlorinated biphenyl (PCB) regulations are issued under TSCA, though the asbestos ban was invalidated by a federal court. In practice, the "unreasonable risk" standard for TSCA regulation is not as stringent as the standards for issuing similar environmental regulations (e.g., ambient air quality standards) because it requires balancing the potential risks against the benefits of the product and requires EPA to adopt the least burdensome effective regulatory alternative. Early in the process, EPA attempted to regulate lead concentrate and other lead products

under TSCA, but that did not result in significant regulation of mining or mineral processing operations. Similar attempts have been made over the years with respect to asbestos and other toxic materials in ores or concentrates but have generally not come to fruition. Efforts to regulate products containing industrial minerals have occasionally produced meaningful results. For example, in the early 1990s, EPA considered several types of TSCA regulation for refractory ceramic fibers, but the industry was able to avoid additional regulation by adopting acceptable measures in a voluntary product stewardship program.

Currently, it appears that the primary TSCA concern for operators of industrial mineral mining or processing facilities is compliance with any applicable reporting requirements for their products. Compliance with the PCB regulations is also an occasional concern. Whether the future may hold additional regulation of industrial mineral products under TSCA remains to be seen.

FUTURE OUTLOOK AND TRENDS

At the time of this writing, operators of industrial minerals facilities are facing several significant public health regulatory issues. EPA is in the process of revising the ambient air quality standards for PM, and is considering replacing the PM₁₀ standards with new coarse PM standards that would regulate the fraction PM_(10-2.5). The most recent drafts of the agency's PM Criteria Document and Staff Paper (unpublished) contain the strongest findings to date that coarse crustal PM is not likely to be harmful. EPA, however, is considering recommending coarse PM standards that are significantly more stringent than the current PM₁₀ standards and may adopt more stringent standards for fine particles as well.

Fibers in mineral particulate or products are another regulatory concern that crosses over several agency jurisdictions. So-called nonasbestiform minerals, which are essentially nonfibrous forms of asbestos, are now being investigated for further regulation, as are microscopic structures in ores and minerals that have not previously been classified as fibrous. EPA is investigating these issues under the TSCA and Superfund programs, and OSHA and MSHA are investigating them in the occupational exposure context. Similar investigations are underway with respect to crystalline silica, though they are largely confined at present to occupational exposure scenarios. Many independent companies and trade associations have begun work on comprehensive product stewardship programs designed to address these issues voluntarily in advance of additional regulatory measures.

Other "hot" issues include the establishment of TMDLs and related permit limitations under the CWA, the ability of EPA and the Army Corps of Engineers to require water permits for isolated intrastate waters, and assessment of natural resource damages under Superfund. Although it does not directly affect most industrial minerals operations, the ability of interest groups to continue or expand use of the CAA conformity requirements to delay or defeat major highway projects is also a matter of serious concern.

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Sustainable Development and Industrial Minerals

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INTRODUCTION

The President's Council on Sustainable Development (PCSD) envisioned a sustainable America that would offer a dignified, peaceful, and equitable existence for all Americans (PCSD 1996). It would have a growing economy but also protect the environment, natural resources, and natural systems. The council acknowledged that economic prosperity necessitates the use of natural resources; the issue of minerals in a sustainable America, however, was never directly raised. Although the council did not explicitly exclude minerals from the national discussion of sustainability, the reality is that many individuals define resource sustainability narrowly as sustaining renewable resources—forests, grasslands, ecosystems, species, and so forth. From this perspective, the goal of sustainable resource management is to sustain resource stocks and ecosystem functioning over the long term by controlling anthropogenic impacts such as emissions and regulating harvests of timber, forage, fish, and wildlife.

Clearly, it is inappropriate to speak of mineral resources as being sustainable in the same way as are ecosystems or biological resources. Mining does, however, impact the environment. Together these facts have led many people to express the simplistic view that mining is inconsistent with sustainability (once extracted, the resource is “gone”), anathema (primarily a source of pollutants and environmental degradation), or of secondary importance (merely a source of virgin materials for which recycled materials or renewable resources can be substituted).

One source of this misunderstanding is the use of the terms *sustainability* and *sustainable development* interchangeably. Sustainability is an inherent characteristic of healthy social and environmental systems. It is achieved by maintaining or enhancing various system capacities (such as family structure and community institutions in social systems or energy flows and carbon cycling in environmental systems) so that the system can withstand external shocks and return to normal functioning. It depends on healthy, functioning social, institutional, and economic relationships in human systems and on ongoing, natural, regenerative processes in biological systems. Mineral deposition is a natural, physical process, sometimes an ongoing one, but not one that is based on short-term biophysical interconnections or system dynamics. Defined in this way, sustainability is not a characteristic of most of the earth's resource systems, which can lead people to think that minerals are not part of a sustainable future.

Conversely, mineral resources are unquestionably part of sustainable development, a commitment to which necessitates integrating

environmental policies and development strategies so as to satisfy current and future human needs, improve the quality of life, and protect the environment. Essentially, sustainable development involves managing resources in a way that is conducive to long-term wealth creation and the maintenance of capital (natural, social, human, economic, and physical). This perspective extends naturally to mineral resources, which are themselves a form of endowed, natural wealth and are an important source of monetary wealth creation (Shields and Šolar 2000). These resources are vital to human well-being. They are integral components of economic systems; the driving force for some local, regional, and national economies; the basis of the built environment; and the material embodiment of our cultural history. The mineral sector is an integral part of developed, modern societies, and a sustainable future is unachievable without its services. Mining and mineral use will continue.

Societal priorities influence how industrial companies behave (i.e., business must be conducted within the legal and ethical frameworks and limits set by society). Because the business situation and societal requirements change over time, both the costs the company must cover and the constraints on their actions change as well. How companies respond to societal expectations must make good business sense. Companies have an obligation to their shareholders and employees to achieve legitimate corporate goals such as profitability and growth. They cannot manage based on philanthropic principles alone (WBCSD 2000).

Beginning in late 1980s, the influence of the sustainable development paradigm on societal thinking began to spread, in part because its overarching goals are widely acceptable and understandable across cultures. These goals—economic prosperity, environmental health, and social equity—have influenced the public's expectations with respect to all industrial sectors, including mining. Although concern about environmental protection has been increasing ever since the emergence of the environmental movement in the 1960s, its importance has been magnified as sustainable development concepts have spread. The fundamental environmental sustainability goal is to protect natural systems (terrestrial and aquatic) that support life on Earth. The negative impacts of products and production are to be minimized. To this, sustainability has added an additional social imperative to minimize negative impacts of economic activities on employees, consumers, suppliers, the local community, and other stakeholders. There is also pressure to distribute the benefits and the costs of economic activities fairly across all affected stakeholders.

These changes have been gradual and progressive, and responding to them requires much more time and attention from the company than previously was the case. The reality is that industrial companies no longer exist as isolated islands, if they ever did. Businesses are now seen as part of society and are expected to behave responsibly toward the environment and reach out to the community.

This is clearly the case for the minerals industry. In many locations the mining sector has lost the trust of people with whom it must deal every day. In the worst-case scenarios, mining companies have failed to convince governments, lenders, shareholders, and stakeholders that they can be trusted or deserve a social license to operate. This has led to revised expectations of the industry, which the Mining Minerals and Sustainable Development project (IIED and WBCSD 2002, p. xiv) cataloged:

- “Countries [and communities] expect that minerals development will be an engine of sustained growth.
- Local communities expect that the industry will provide employment, infrastructure, and other benefits that counter the risks and impacts they will experience and will leave them better off than when the project started.
- The industry’s employees expect safer and healthier working conditions, a better community life, and consideration when their employment ends.
- Local citizens and human rights campaigners expect companies to respect and support basic human rights, even when they are operating where government does not.
- Environmental organizations expect a much higher standard of performance and that the industry will avoid ecologically and culturally sensitive areas.
- Investors expect higher returns and have shown considerable concern about the industry’s financial results.
- Consumers expect safe products produced in a manner that meets acceptable environmental and social standards.”

What does this mean for the industrial minerals sector? How will companies be affected? The bottom line is that there is a new business reality. Having a legal license to operate is no longer adequate because that, by itself, will not guarantee the existence of a social license to operate. The latter is an upgrade of the former and is granted by society, not the government. To gain a social license to operate, minerals companies must interact with a broader set of constituents than was the case in the past. In addition to legal authorities, shareholders, and lenders, the company’s management must now respond proactively to the concerns of employees, the local community, and other stakeholders. Further, the company must integrate social and environmental concerns in their operations and in their interactions with all their stakeholders (i.e., they must practice corporate social responsibility) (European Commission 2001).

The links between corporate social responsibility and profitability are becoming increasingly clear (WBCSD 2001; Sustainability, the International Finance Corporation, and the Ethos Institute 2002). In the absence of a social license, the company will face opposition to its presence as well as legal, and possibly even physical, attempts to disrupt, temporarily block, or terminate legitimate business activities. Moreover, financial institutions are insisting that companies implement sustainable practices, including gaining prior consent from impacted communities for their presence and operations (World Bank 2003). Financing options are becoming more limited for those companies who refuse to do so, with the result that their cost of capital increases, negatively affecting profitability and potentially even the economic feasibility of mine development. Inevitably, a company’s long-term viability is

undermined if it is unable or unwilling to adapt to a changing business environment, one part of which is responding to societal expectations.

This chapter presents basic sustainability principles and describes in more detail how they apply to the mining industry. It also draws a distinction between sustainability performance and a sustainable industry. The concept of sustainable industrial mineral resources management is introduced, a process for implementing the practices in the mining company is set forth, and major themes that are part of the minerals sustainability dialogue are briefly described.

PRINCIPLES OF SUSTAINABLE DEVELOPMENT

Sustainable development, according to a common definition, strives to improve the economy, environment, and quality of life for the current generation without compromising the ability of future generations to meet their needs. The foundation of sustainable development is reconciliation of a society’s development goals with Earth’s environmental limits (NRC 1999). The world’s nations have agreed on the need to transition to a sustainable development path, first at the Earth Summit held in Rio de Janeiro, Brazil, in 1992 (United Nations 1992) and again in 2002 at the World Summit on Sustainable Development held in Johannesburg, South Africa (United Nations 2003).

One reason the sustainable development paradigm has been so widely embraced is that it explicitly recognizes the interconnectedness of social, economic, and environmental systems (Moldan and Billharz 1997; Funtowicz and Ravetz 2001). Because of the holistic nature of sustainable development, many authors recommend a systems approach for such studies (Meadows et al. 1972; Allen, Tainter, and Hoekstra 2003). Erikson, Loucks, and Strafford (1999) describe three principles of systems thinking that are relevant in this context:

- Systems thinking is applicable in situations where groups of interdependent and interacting parts are linked by exchanges of energy, matter, capital, values, and information.
- A system is healthy and sustainable when variables are resilient (i.e., they can accept externally imposed stress or intervention and return to characteristic levels or patterns).
- Boundaries of sustainable systems should allow measurement of stocks and flows among the components of subsystems, identifying externalities and feedbacks and determining whether cycles and loops are open or closed.

Gunderson and Hollings (2002) argue that systems exhibit endless cycles of growth, adaptation, restructuring, and renewal, and define sustainability as the capacity to create, test, and maintain adaptive capability. This description can be applied to the minerals industry just as it can to social and biological systems; to be sustainable, companies need to adapt, restructure, and renew. At its core, the goal of sustainable development is to foster adaptive capabilities that ensure survival.

Liverman and colleagues (1988, p. 133) offer a more comprehensive description of the goals of sustainable development, one that is also consistent with systems thinking: “the indefinite survival of the human species (with a quality of life beyond mere biological survival) through the maintenance of basic life support systems (air, water, land, biota) and the existence of infrastructure and institutions which distribute and protect the components of these systems.”

This general statement leads to a variety of different, and in some cases even conflicting, understandings of sustainable development (Shields 1998). A lack of agreement notwithstanding, certain basic principles underlie virtually all definitions of sustainable development (Shields and Šolar 2004).

General sustainability principles are as follows:

- Sustainability should seek the appropriate integration of political, social, economic, biophysical, and ecological factors.
- The spatial and temporal scales of decision making, management, and regulation should be compatible with the physical, ecological, and socioeconomic scales of activities in question and their impacts.
- Adaptive management, relying on an iterative process of timely and transparent feedback from socioeconomic, resource, and ecological monitoring, is essential.

Social and economic sustainability principles are as follows:

- Progress toward sustainability should generate direct economic value as well as noneconomic values, which may be intrinsic, recreational, or aesthetic.
- Decisions and actions must be equitable and just, both intra- and intergenerationally.
- Members of the public, particularly local communities, should be empowered to participate fully in decisions that will affect their lives and the lives of their descendants.
- Information relevant to decision making should be made available to all who may be affected so that they can participate effectively.
- Governance, both governmental and corporate, must be honest, open, and fair.
- Individuals should take responsibility for the environmental and social impacts of their personal consumption and behavioral choices.

Environmental sustainability principles are as follows:

- Sustainability depends on conserving ecosystem structure and function in order to maintain ecosystem services needed for both humans and the ecosystems that provide them.
- Ecological sustainability depends on maintaining biological diversity and adequate populations of target species for long-term viability.
- Users of natural resources must recognize that there are limits and boundaries of natural resource consumption beyond which ecosystem behavior might change in unanticipated ways.
- Polluters should be responsible for environmental remediation, reclamation, and aftercare.
- Decisions on environmental protection should not be delayed, even in the absence of full information, if doing so will seriously endanger the structure and function of ecosystems.

The next section discusses in more detail how these principles can be applied in the context of mineral resources in general and minerals companies in particular.

SUSTAINABLE DEVELOPMENT AND MINERALS

There is considerable disagreement as to how minerals should be treated in the sustainable development paradigm. Conflicting views reflect the reality that value orientation affects priorities. One individual's values might lead him or her to place more emphasis on environmental protection (a biocentric viewpoint), whereas another's values might lead to greater emphasis on the benefits of extraction (an anthropocentric viewpoint). Extreme proponents of the former perspective seek to ban mining; extreme proponents of the latter demand the right to mine anywhere they choose, in any manner that they deem most profitable. Sensible sustainable development takes a middle road, acknowledging the need for resource extraction, use, and disposal, while insisting on environmental and social protections.

Not surprisingly, initial discussions about minerals and sustainable development focused on the need for a steady supply of minerals, the consequences of resource depletion, and the need for environmental protection (NASCER 1996; NRC 1999). Some authors then turned to the issue of mineral development as a source of wealth creation and, by extension, the use of mineral extraction as a tool for the eradication of poverty (Auty and Mikesell 1998; Auty 2003). A different perspective has focused on the environmental and social consequences of mineral development, use, and disposal and argues that the achieving environmental sustainability will necessitate significant reduction in the per capita use of materials (Spaargaren 2000; Bartelmus 2002).

More recent work has extended the basic principles of sustainability to mineral resources in a comprehensive manner (Shields and Solar 2000; World Bank 2003). For example, the Mining Minerals and Sustainable Development project created a set of sustainability principles relevant to the minerals situation, a subset of which follows (IIED and WBCSD 2002):

- Maximize rents to ensure efficient use of resources.
- Ensure a fair distribution of risks, costs, and benefits.
- Replace depleted natural resources with other forms of capital so as to ensure that future generations are not deprived of the benefits of current extraction.
- Promote responsible stewardship of natural resources and the environment, including remediation of past damage.
- Minimize waste and environmental damage along the whole supply chain.
- Price commodities, products, and services at levels that reflect the full cost of their provision.
- Maintain and enhance conditions for a viable enterprise.

The preceding discussion focuses on the role of the minerals sector in a sustainable future. The principles in these bullets are phrased as actions that need to be taken by government, society, or industry. Each will inevitably affect the mining company—how it does business, its profitability, and its long-term viability. Each is complex and multifaceted and can be interpreted differently by different stakeholders. For example, there is less than universal agreement as to what fair distribution means. Similarly, responsible stewardship can legitimately be interpreted in multiple ways. A full discussion of the ramifications of each is beyond the scope of this chapter. The last two principles, however, deserve further comment.

First, mineral commodities are sold in competitive markets and prices are set in those markets, not by any governmental authority. Current market prices for most, if not all, mineral commodities do not cover the full, long-term environmental and social costs of their provision (IIED and WBCSD 2002), but no individual company can rectify that situation. At a minimum, it will require an industry-wide commitment to full cost accounting and in some instances advances in national and corporate governance. Second, a viable minerals sector is essential to a sustainable future. Sustainable behaviors are undertaken by profitable companies, seldom by marginal companies or those losing money. It is in society's best interests to ensure the existence of institutional and market conditions that enable companies to stay in business and make profits adequate to enable them to both provide mineral resources and embrace sustainable performance.

SUSTAINABLE INDUSTRIAL MINERALS RESOURCE MANAGEMENT

The goal of sustainable industrial minerals resource management is not to sustain a single deposit or mine but rather to sustain the flow of benefits and services from those resources in such a way that

their contribution to society over the life cycle is net positive (IIED 2002; Shields and Šolar 2005).

Each of the primary stakeholders—government, industry, the public, and nongovernmental organizations (NGOs)—must accept certain responsibilities, and they must cooperate at the regional and local planning levels (Langer, Giusti, and Barelli 2003). The government provides the climate for success through its policies, regulatory framework, and economic incentives. The industry must work to be recognized as a responsible corporate and environmental member of the community. The public and the NGOs need to become informed about mineral resource management issues. All stakeholders have the responsibility to constructively contribute to a decision-making process that addresses not only their own but also a wide range of objectives and interests.

The U.S. government, along with many state, province, or territorial governments in Canada and Australia and many of the federal governments within the European Union and elsewhere, have national minerals policies that recognize minerals and mining as key sectors contributing to jobs, wealth, and a high quality of life for its citizens. Governments have a variety of tools that they can use to encourage sustainability, including laws, policies, guidelines, and incentives. Many countries, including the United States, have enacted laws at different levels (e.g., national, state, regional, provincial, municipal) to protect water, air, endangered species, and other aspects of the environment. These laws are an integral part of sustainability.

Some industrial minerals companies in the United States have begun implementing sustainability concepts without waiting for government intervention. These include companies that produce abrasives (Imerys), aggregates (Aggregate Industries, Lafarge, Vulcan), cement (Cemex, Holcim, Lafarge), clay (Imerys), gypsum (U.S. Gypsum), industrial sands (Fairmount Minerals), phosphate (Agrum), and talc (Luzenac)—all of whom post their annual sustainability reports or policy statements on company Web pages.

At the level of the company, key tenets commonly include that (1) the industry must strive to be recognized as a responsible corporate citizen and member of the community; (2) resource development must meet the needs of the community as well as those of the company; and (3) all stakeholders must be offered the opportunity to have a voice in decisions that will affect them and to participate in the sustainable resource management process (Langer and Tucker 2003; United Nations 2003).

Sustainable industrial mineral resources management commonly is iterative and adaptive, but it does not require than any specific process be followed. Successful management can be achieved in a practical sense by adopting some simple principles (after Plant and Haslam 1999):

- The government should strive to minimize social and environmental impacts by forward-looking planning that protects important resources from urban encroachment and protects growing communities from the nuisance impacts of poorly designed, poorly located, and poorly managed mineral operations.
- Industry should strive to minimize social and environmental impacts by using best practice designs and operations to control the effects of blasting, noise, dust, sediment erosion, and visual scarring in extractive and transport operations, and by providing for conservation of natural values by management of buffer areas that maintain or enhance vegetation and wildlife habitats and corridors.
- Industry, as enabled by governmental permitting decisions, should strive to maximize the economic value of the resource—by extracting as much material as possible from the area that

has to be disturbed, by using it for the most economically valuable use it can accommodate, and by finding uses and markets for all the material disturbed (e.g., turning crusher fines into “manufactured sand,” thus taking the pressure of natural sand sources in more environmentally sensitive areas).

- Industry should strive to maximize rehabilitation of disturbed areas by considering reclamation as part of the quarry/pit design process before extraction begins, by starting rehabilitation from day one, and by being flexible to allow advances in technology and for changing local needs.
- Industry should strive to maximize community engagement—by involving the local community in planning activities through open visit days and community awareness and educational activities. This may lead to a measure of community acceptance and a “social license to operate,” which can be just as important as the official, legal permits.

Langer and Tucker (2003) transformed the tenets of community involvement into a set of operational concepts for the social dimension of mining operations. Their work has been generalized here:

- Establish community relationships: It is never too early for a company to get involved in the community in which they do business, want to do business, or hope to stay in business. In today's world it is through the permission of neighbors that industrial minerals companies are able to continue doing business. Company strategies for each of their principal markets need to include continued community involvement by key employees. Those key employees also need to assist other employees in developing and maintaining long-term community relationships.
- Obtain executive support: The company president, his or her management team, and other appropriate managers must support the implementation of sustainability principles. Develop a sustainable business plan with input from both operations and management. Schedule team meetings regularly so that team members can exchange information and keep each other up to date.
- Create benefits for the community: Understand how your operation fits into the larger community plan and offer the community compensating, long-term advantages.
- Communicate: Identify the tools you will use to communicate the business plan, such as videos, computer presentations, pamphlets, and field trips to the site. Be open; share as much information as possible. Make sure that your message to every community group, elected official, and business leader is consistent. Keep elected officials informed, but also identify the real decision makers; sometimes they are different from the obvious ones. Know who influences the decision makers and why they have the influence.
- Solicit feedback from the community: Listen actively, take notes, ask questions, and show true interest in the communication. Make every effort to work in harmony with those of opposite views. Try to view your operation through the eyes of your stakeholders, and analyze and address their issues and concerns.
- Be visible and accessible: Be available beyond just normal business hours, Monday through Friday. Maintaining availability requires commitment of team members' personal time outside normal business hours, on a regular basis, over the term of this project proposal.
- Maintain your public trust: Remain active in the community over the life of the operation and during aftercare.

These actions are not without cost, and there remains among some in management positions the view that engaging and responding to the community represents an effort that has no added value (Galea 2004). More generally, there is considerable discussion within industry and in academic literature about the relationship between sustainability performance and business competitiveness (Porter 1991; Wagner and Wehrmeyer 2002; Ziegler, Rennings, and Schröder 2002). The traditionalist view draws a parallel between the effects of sustainability performance on the company and the effects of environmental regulation. It is argued that environmental regulation is intended to correct for negative externalities and market failures and in so doing forces companies to absorb additional costs. Companies facing higher production costs because of environmental compliance are seen as having a competitive disadvantage compared with the companies that do not face those same regulatory burdens.

There is, however, a revisionist view of environmental regulation as a policy instrument that drives innovations, which in turn lead to competitive advantage (Porter and van der Linde 1995). The analogy with sustainability is clear. The more traditional view sees additional activities focused on the range of sustainability issues as a drain on corporate profits. Alternatively, the actions can be seen as increasing the company's competitiveness, name recognition, access to markets and capital, and desirability as an employer and neighbor (Wagner and Schaltegger 2004).

SUSTAINABLE DEVELOPMENT THEMES

The literature on sustainable development is vast, and reporting on all the concepts contained therein is beyond the scope of this chapter. Rather, several important themes are described that recur in discussions of sustainable development and minerals. Four are core concepts that play out similarly across all commodities: corporate social responsibility, transparency, best practices, and risk assessment.

Corporate Social Responsibility

Corporate social responsibility (CSR) is a form of business behavior that leads companies to voluntarily contribute to a better society and a cleaner environment. Businesses take on commitments beyond common regulatory and conventional requirements, which they would have to respect in any case (European Commission 2001). The goal of CSR is to raise standards of social development, environmental protection, and respect of fundamental rights by embracing open governance, reconciling the interests of stakeholders, and taking an overall approach to quality. CSR requires company owners (shareholders) and management to act more responsibly toward employees in areas of working conditions, health, and safety, but also with regard to professional development (education), health insurance, and retirement funds. The rights and obligations of local communities, NGOs (mostly environmental), and other traditionally external stakeholders are recognized and respected.

The definition of CSR is context dependent and varies for companies in different economic situations. CSR is an interactive process among management, worker representatives, workers, public authorities, and others that requires commitment, trust, and accountability (European Commission 2001). Organizations need standards by which levels of performance can be measured (e.g., auditable standards).

Corporate culture is the very basis for corporate social responsibility. Corporate culture is determined by written, and in particular unwritten, rules that have great impact on the behavior of each company employee. The company's management sets the framework for corporate culture through corporate governance. Corporate governance is essentially about business leadership in

efficiency, responsibility, and probity. Current calls for higher standards in corporate governance have grown out of public displeasure with corporate scandals (Galea 2004) and debates about several key questions (Corporate Social Responsibility Forum 2000):

1. To whom are companies accountable—shareholders or stakeholders?
2. For what are companies responsible—financial performance or performance more broadly defined?
3. Where are companies accountable—in their home country or everywhere they operate?
4. Who sets company standards—the company, government, business associations, or NGOs?
5. Who monitors the company and what should be disclosed—self-monitoring with only legally required disclosure or external monitoring and full disclosure?

Companies that have embraced CSR, and that are implementing sustainable practices, define themselves as accountable to stakeholders, responsible for social and environmental as well as financial performance, accountable everywhere they do business, and open to external codes of conduct. Such companies institutionalize sustainability at all levels of the organization, putting clear behavioral standards and operational goals in place for field supervisors, middle managers, and upper-level managers to make clear that the commitment to CSR is real (WBCSD 2000; Dunnett 2004). They are also willing to adopt codes of conduct aimed at influencing the practices of their suppliers in both developed and developing countries by providing them with a baseline of expected standards. These are typically based on international labor standards regarding child labor, wages and benefits, working hours, disciplinary practices, the right to freedom of association, health and safety, and environmental practices (Mamic 2004).

Companies implement and promote their CSR strategies for very pragmatic reasons. Doing so is good business. It can increase long-term business viability, including growth and profits, and it sends a signal to stakeholders that the company is a good and responsible corporate citizen.

Transparency

One of the core concepts of CSR, and sustainable development in general, is information flow. The government, the financial sector, shareholders, communities, and other stakeholders need information about proposed or existing mineral operations to ensure both sound decision making and effective engagement in negotiations. In the past, however, companies shared information either because they were legally compelled to do so (i.e., compliance with environmental reporting and financial disclosure requirement) or because doing so supported core business goals (e.g., enhancing profitability, maintaining reputation, or managing risk). Achieving these latter goals in the future is going to entail a much greater degree of openness than was deemed necessary in the past.

Historically, information flow has not been equal to all stakeholders. As Thomson and Joyce observed in a presentation at the Monitoring Science and Technology Symposium (Denver, Colorado, 2004), "Information flows from companies to regulators and shareholders and trickles to all other stakeholders." This reality, combined with the legacy of past mining practices and attempts to cover up problems (successful cover-ups are unknown to the public), has led to public mistrust of mining companies. Now the industry is being asked to be more transparent (IIED and WBCSD 2002). Paragraph 46 of the *Report of the World Summit on Sustainable Development* (United Nations 2003) addresses mining and specifically calls for the promotion of transparency and accountability.

And, increasingly, stakeholders are asserting their right to information about business actions that have the potential to affect their lives and the environment.

Deeply rooted mistrust between environmental NGOs, local communities, and other stakeholders on one side and industry (and sometimes regional or national governments) on the other side can be overcome through transparency of intents and actions—from both sides. Industry has rightfully pointed out that they are sometimes held to higher standards than their critics; both corporations and their critics must meet the same standards of honesty and disclosure (IIED and WBCSD 2002).

There are many ways to increase transparency if the will to do so exists. Guidance is available from Transparency International (<http://www.transparency.org/>) in the United Kingdom, a global NGO dealing with transparency in industry, including the extractive sector. More mining oriented is the multistakeholders' Extractive Industry Transparency Initiative (EITI; <http://www.eitransparency.org/index.htm>) launched in 2002 after the World Summit on Sustainable Development. It aims to increase transparency in transactions between governments and companies within extractive industries. The EITI Secretariat is based in the United Kingdom's Department for International Development.

The core element of transparency is providing access to information. Information flow can increase understanding of the state of the world and, in the process, facilitate an iterative process of learning in the face of uncertainty and change (Bass and Dalal-Clayton 2001). The information provided should be relevant to the questions at hand and meaningful to the intended audiences. Sometimes that means sharing raw data, but raw data are seldom meaningful to the general public, decision makers, or other stakeholders. Rather, meaning emerges through analysis. In many instances it is the analyzed data that need to be shared with stakeholders. In some instances, however, indicators are needed. Effective indicators turn vast amounts of analyzed data into meaningful and relevant information that reduces complexity and brings clarity. Indicators display or predict the state of a given system or phenomenon. More important, indicators have significance extending beyond that directly associated with the measured property or properties (DETR 1997).

Some companies have developed their own sets of indicators for reporting to their publics and stakeholders. Others are using the reporting process developed by the Global Reporting Initiative (GRI 2004b). The GRI is an independent, multistakeholder process that is developing and sharing sustainability reporting guidelines for many industrial sectors, including minerals. They have created the final draft *Mining and Metals Sector Supplement* (GRI 2004a) and are developing technical protocols for indicator measurement.

The "Seven Questions to Sustainability" process offers another approach to reporting (IIED 2002). The seven questions are intended to assess the contribution of mining and mineral activities over the life cycle of the operation. The questions involve (1) public engagement; (2) human well-being; (3) environmental protection; (4) economic viability; (5) traditional and nonmarket activities; (6) institutional arrangements and governance; and (7) synthesis and continuous learning. The process was used successfully to review the Area Structure Plan that was created in response to conflict over development of an aggregate deposit in Alberta, Canada (Richards and Peel 2003).

Information sharing can also be part of best practice and certification processes.

Best Practice

One of the ways mining companies demonstrate CSR is by adopting best practice as part of their overall business strategy. Best practice

is often thought of narrowly as the process through which companies implement the most appropriate and technically effective solutions to engineering and environmental problems. Standards, handbooks, guidelines, and voluntary codes of conduct exist for every aspect of the mine life cycle, published by organizations as diverse as the United Nations Environment Programme (UNEP), the United Nations Economic and Social Commission, the World Bank, the U.S. Environmental Protection Agency, various industry associations, professional groups, and NGOs, among others. Many have been collected and categorized at the United Nations Conference on Trade and Development (UNCTAD) Mineral Resources Forum web site (<http://www.natural-resources.org/minerals/csr/practices.htm>).

Widely applied environmental standards have been built on the Berlin II Guidelines (UNEP 2002a,):

- Recognize environmental management as a high priority.
- Establish environmental accountability.
- Encourage employees at all levels to recognize their responsibility for environmental management.
- Adopt environmentally sound technologies.
- Adopt risk analysis and risk management.

Accountability in this context means both giving an account of what has happened and being responsible for one's actions (Gray, Owen, and Adams 1996). It often involves external verification of the company's activities (Epps and Solomon 2000). Increasingly, companies in the mining sector are seeking certification from the International Organization for Standardization (ISO) that they have complied with a voluntary international standard for environmental management called ISO 14000 (ISO 2005). This standard is primarily concerned with what the organization does to minimize harmful effects on the environment caused by its activities and how it will continually improve its environmental performance. The ISO also has a standard for quality, ISO 9000, that addresses what the organization does to enhance customer satisfaction by meeting customer and applicable regulatory requirements and how it will continually improve its performance in this regard (ISO 2005).

In 2004, the ISO published its *2005–2010 Strategic Plan* (ISO 2004). Their organizational vision is to facilitate trade; improve quality, safety, security, environmental and consumer protection, and the rational use of resources; and disseminate good practices. They lay out seven key objectives, which explicitly include stakeholder involvement. The stated purpose of this plan is to ensure that the ISO contributes to the achievement of a sustainable world economy. It reflects the fact that the original environmental focus of best practice has broadened in recent years to encompass all aspects of resource projects. This is exemplified by the following sustainability-based principles of best practice (Environment Australia and UNEP 2002):

- Ecologically sustainable development
- Intra- and intergenerational equity
- Accountability and compliance with international human rights and environmental standards and principles
- The precautionary principle
- Well-informed and -trained staff
- Effective communication and openness
- Flexibility
- Continual improvement

The last two principles are included in recognition of the fact that circumstances differ from mine to mine, technology advances over time, and sustainable practices require learning and adaptation.

Companies are also looking into certification of their products, or business processes and practices, as “sustainable.” In the former case, this would mean that the product has been produced or manufactured according to some agreed-on sustainable best practice, and uses inputs that were themselves produced in the same manner. In the latter case, the operation itself would be certified as using sustainable best practice. This trend toward certification has progressed rapidly in forestry, and certification bodies exist for forests themselves and for wood products (the web site of the Forest Certification Resource Center compares certification methods; <http://www.certifiedwood.org/search-modules/CompareCertSystems.asp>).

Voluntary certification is beginning to take hold in the mineral sector as well. Mining companies see this as a potential tool for “branding” an otherwise fungible commodity and also differentiating themselves from competitors who do not behave responsibly. Whereas seeking and maintaining such certification could be costly and time consuming, it could also give the company a competitive advantage. One recent example is the International Cyanide Management Code, intended to control cyanide use in gold mining (UNEP 2002b). Mines would be certified as compliant with the code by the International Cyanide Management Institute. Another example is the Mining Certification Evaluation Project (MCEP), which is evaluating the potential for a third-party certification program for the mining industry (Rae, Rouse, and Solomon 2002). The MCEP is a joint exercise among the mining industry, NGOs, labor, government agencies, the financial accounting sector, and research institutions. Four tests of the protocol took place in 2004 and results will be reported in 2005 (CSIRO 2005).

Risk Assessment

The terms *risk assessment*, *risk analysis*, *risk characterization*, *risk management*, and *risk distribution* recur in discussions of sustainable development, CSR, and best practice. Risk is the possibility of an unwanted outcome in an uncertain situation. Every action in life has an associated risk: eating, travel, the type of physical activity in which one engages, how much sleep an individual gets. Each can directly influence one's life in a positive or adverse manner. It cannot be known for certain what the influence will be, though outcomes can be predicted to a greater or lesser extent depending on past experience, knowledge of circumstances, and an understanding of the consequences of alternative choices.

The same is true for mineral extraction, which by definition takes place in a location that can be only partially characterized in biophysical and socioeconomic terms. A degree of uncertainty inevitably exists about the true nature and extent of the deposit or the type and extent of adverse environmental and social impacts from mining. That being the case, companies assess risk to identify potential sources of harm to people and the environment from all aspects of their business, with the goal of determining whether sufficient precautions or preventive measures have been taken (Health and Safety Executive 1999).

Risk assessment is a multiphased process of (1) scoping and problem formulation, (2) analysis, and (3) risk characterization (EPA 2003). The first step, defining the problem to be assessed, depends on input from experts other than those who know how to do risk assessments, including persons who are knowledgeable about the potentially affected community and its values. The analysis phase is given over to the analytic process, where risk assessment experts apply science to a problem. It requires the use of rigorous, replicable methods that are evaluated under agreed-on protocols of an expert community, which results in a systematic use of information to identify hazards and to estimate the likelihood and consequences that they will be realized. Environmental risk

analysis separates risk to the environment from other mining risks such as occupational safety and health issues and risks to community stability.

Finally, risk characterization is a deliberative process that integrates and interprets the results of the analysis phase and addresses the problems formulated in the planning and scoping phase. The qualitative or quantitative risk assessment results are described; assumptions, limitations, and uncertainties are listed and associated with results; and ultimate uses of results are considered. Thus the process in its entirety uses a systematic approach to identify and evaluate potential environmental and social impacts, the consequences of those potential impacts, the likelihood that those potential impacts will happen, and ways to reduce the seriousness of those impacts.

The next step is risk management. Risk managers use the results of risk assessments, plus economic, social, and legal considerations, to make decisions (Kamrin, Katz, and Walter 1996). When implemented, monitored, and reviewed, risk management can reduce the uncertainty of the business. The goal is reduction of risk and related costs through education, regulation, and cleanup. Uncertainty is unavoidable, but keeping it within tolerable limits is very beneficial for the company performance. The “polluters pay” principle, widely accepted and legalized, states that those who pollute should pay to clean up after themselves. Failing to manage the risk of environmental damage can thus lead to the imposition of significant, unexpected costs that can heavily damage the company and may even cause bankruptcy.

Another, more complex definition of risk management was originally developed by the Presidential Commission on Risk Assessment and Risk Management (PCRRM 1996). They proposed a process that starts with risk assessment, but goes further to add making decisions, taking action, conducting ex post evaluation, and, most important, involving stakeholders in every step of the process. This approach is consistent with the principles of sustainability on public participation and transparency. It is not, however, without difficulties.

Risk means different things to different people, and there are wide variances between “experts” and the lay public. Engineers view risks as a numerical value: a function of probability and consequences. The public's understanding of risk is contextual and typically nonmathematical. An individual's subjective definition of risk may be influenced by a wide array of psychological, social, institutional, and cultural factors. The hazards and risk that are likely to be of most concern are those that pose threats to locally valued social and institutional arrangements.

Moreover, it has long been recognized that people tend to be poor risk estimators (Tversky and Kahneman 1981). They overestimate the likelihood of some accidents (motor vehicle, tornadoes, or venomous bites and stings) but underestimate the risk of other potentially dangerous events (lightning strikes, asthma attacks, or complications from diabetes) (Slovic, Lichtenstein, and Fischhoff 1979). This occurs because people assign greater probabilities to events to which they are more frequently exposed, and they judge the risk of an event based on reference to other events that they think resemble it, even if the resemblance carries little or no relevant information (Montgomery 1995). In addition, people are very averse to risks that could result in catastrophic outcomes or outcomes that they do not understand well, even if the likelihood of occurrence is very low (Montgomery 1995).

For the company, communication of risk information depends on the perceived credibility and unbiasedness of experts. If there is no trust in experts, there will be no trust in the risk estimate. What risks the public considers tolerable or acceptable depends on how

they view the data on which the risk measure is based and whose values were considered. These factors bring us back to the core debates of sustainability: Whose value system counts and who gets to judge the importance of loss?

Increasingly, communities want to see the risks (real or perceived) to which they are exposed matched by comparable benefits (IIED and WBCSD 2002). As in the case of risk alone, people base their judgments about risk/benefit relationships not only on what they think but also on what they feel (Slovic et al. 2003). "If they like the activity, they are moved toward judging the risks as low and the benefits as high; if they dislike it, they tend to judge the opposite—high risk, low benefit (Slovic et al. 2003, p. 5)." This reality complicates the situation and makes the effective communication of risk challenging for the company, but also essential.

MATERIAL TRACKING AND LIFE CYCLE ASSESSMENT

The National Research Council (NRC) report entitled *Materials Count: The Case for Material Flows Analysis*, by the Committee on Material Flows Accounting of Natural Resources, Products, and Residuals of the Committee on Earth Resources (NRC 2004), recommended that the nation develop material accounts that would track the sources, flows, and dispositions of materials (including minerals) to determine more effective strategies for improving environmental and economic performance and efficiency of resource use. These accounts would provide information to legislators and decision makers as they devise and implement policies intended to support our transition to sustainability.

Tracking flows already takes place at the company level in the form of life-cycle assessment (LCA). LCA is an objective process to evaluate the environmental burdens associated with a product, process, or activity by identifying energy and materials used and wastes released to the environment and to evaluate and implement opportunities to affect environmental improvements (Barnhouse et al. 1998). The process has four steps (UNEP and WBCSD 1996, p. 8):

1. Goal and Scope Definition, the product(s) or service(s) to be assessed are defined, a functional basis for comparison is chosen and the required level of detail is defined;
2. Inventory Analysis of extractions and emissions, the energy and raw materials used, and emissions to the atmosphere, water and land, are quantified for each process, then combined in the process flow chart and related to the functional basis;
3. Impact Assessment, the effects of the resource use and emissions generated are grouped and quantified into a limited number of impact categories which may then be weighted for importance;
4. Interpretation, the results are reported in the most informative way possible and the need and opportunities to reduce the impact of the product(s) or service(s) on the environment are systematically evaluated.

An outgrowth of LCA is the emerging concept of product stewardship, or extended product responsibility. Stewardship appears to have first been used in an environmental context by the Canadian Chemical Producers Association (CCPA) in their Responsible Care Code in the late 1970s (CCPA 2000). The term *extended producer responsibility* originated in Sweden, with the goal of decreasing environmental impacts of products by assigning responsibility for take-back, recycling, and disposal (Lindhqvist and Lindgren 1990). The PCSD (1996) identified extended product responsibility as a tool for reducing waste, conserving resources, and preventing pollution. This version of the concept is voluntary; shares responsibility among consumers, government, and industry rather than focusing exclusively on one part of the

supply chain (Lewis 2005); and, in addition, omits the postconsumer stage (Fishbein 2000).

Companies in the industrial minerals sector are beginning to embrace product stewardship. Rio Tinto Borax, for example, commits in Corporate Policy No. 410 to "the responsible and ethical management of our products from the extraction of natural resources, through design, processing, marketing, distribution, use, and disposal" (Goldberg 2004).

Another outgrowth of LCA is the shift from perceiving mining companies as mineral extraction companies to seeing them as material suppliers. The business activities of this type of company could include a mixture of extraction, trade, and recycling, and the remanufacture and processing of minerals for reuse. For example, many quarries use their processing equipment for recycling construction and demolition waste that has technical characteristics similar to the primary aggregate. Steps (voluntary or legislated) intended to increase the percentage of recycled materials support this trend (HM Customs and Excise 2004).

CONCLUDING REMARKS

To ensure the sustainability of mineral resources, each of the primary stakeholders—government, industry, the public, and NGOs—must accept certain responsibilities:

- The government is responsible for developing the policies, regulatory framework, and economic climate that provide conditions for success.
- The industry must work to be recognized as a responsible corporate and environmental member of the community with a social license to operate.
- The public and NGOs have the responsibility to become informed about natural resource management issues and to constructively contribute to a decision-making process that addresses not only their own but also a wide range of objectives and interests.
- All stakeholders have the responsibility to identify and resolve legitimate concerns, and the government, industry, and the public must cooperate at regional and local levels in planning for sustainable minerals extraction.

Sustainable minerals resource management would be less difficult if all conflicts between regional minerals resource needs and local impacts had solutions that would leave everyone better off. This is seldom the case, and there are usually winners and losers. But as the amount of accessible land that is underlain with suitable industrial minerals resources diminishes, inequalities increase. The longer that implementation of sustainable resource management principles is delayed, the more difficult it will become.

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PART TWO



Commodities

Abrasives

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INTRODUCTION

Abrasives are substances, both natural and synthetic, used to grind, polish, abrade, scour, clean, or otherwise remove solid material, usually by rubbing action (as in a grinding wheel) but also by impact (pressure blasting). Facts about the discovery, early use, adaptation, and development of abrasives before the 20th century are few. From the sparse, earliest information that is available, it appears that the science of abrasives began when, to fashion tools, humans selected certain rocks over others because of their useful properties. There is evidence that some sort of grinding machine sawed stones as early as 4000 BC in Egypt. The real expansion of abrasives use coincided with the beginning of metallurgy in the Middle East around 2000 BC. The earliest confirmed use of abrasives for grinding metal comes from a steel dagger found along with a sharpening stone that dated to 1500 BC.

Natural and manufactured abrasive substances play an important role in fashioning and finishing numerous products with a wide variety of applications. The mining and preparation of crude, natural abrasives for market and the manufacture of synthetic and other abrasive materials contribute significantly to the U.S. economy (Table 1). Just as sawing to specific dimensions enhanced the value of Egyptian stone, the use of abrasives in the fabrication of modern products and the addition of abrasives to others add value. The following discussion draws heavily from Hight (1983) and Wellborn (1994).

GENERAL CONSIDERATIONS

The most important physical properties of materials that qualify as abrasives are hardness, toughness (or rigidity), grain shape and size, character of fracture (or cleavage), and purity (or uniformity). To fabricate bonded abrasive products such as grinding wheels, additional considerations include stability under high heat and bonding characteristics of grain surfaces. The economic factors of cost and availability are always important.

No one singular property is paramount for any use. Some applications require extreme hardness and toughness, as in diamonds for drill bits. For other uses, factors of greatest importance are hardness, the ability to break down slowly and, in the process, develop fresh cutting edges when grains become worn. In garnet sandpaper, for example, highly cleavable, friable, or extremely tough grains are not desirable. For other uses, extreme hardness may be objectionable, such as abrasives for dentifrices and for glass-

Table 1. Salient U.S. abrasives statistics

Natural Abrasives Production	1999	2000	2001	2002	2003
Tripoli (processed), t*	84,900	72,000	60,500	66,600	68,800
Value, 1,000 US\$	20,200	15,900†	15,000	16,600	17,700
Special silica stone (crude), t*	697	553	705	748	1,070
Value, 1,000 US\$	183	158	234	240	313
Garnet, t‡	60,700	60,200	52,700	38,500	29,200
Value, 1,000 US\$	6,170	7,060	6,430	4,500	3,170
Manufactured abrasives, t§**	160,000	145,000	100,000	60,000	60,000
Value, 1,000 US\$§**	73,085	61,775	44,520	26,320	26,665

Adapted from Dolley 2003 (tripoli and special silica stone); Olson 2003a, 2005a (manufactured); Olson 2003c (garnet).

* Includes amorphous silica and Pennsylvanian rottenstone.

† Value calculated from price per ton for fused aluminum oxide, regular and high-purity, and silicon carbide (Olson 2004, 2005a).

‡ Primary garnet; denotes first marketable product. Includes crude concentrates.

§ Includes Canadian production of crude silicon carbide and fused aluminum oxide and shipments of metallic abrasives by producers.

** Excludes U.S. and Canadian production and value of aluminum-zirconium oxide.

cleaning soaps. For efficiency uses in critical applications, different types of abrasives rarely can be completely interchangeable. Although both crushed quartz and garnet are used in sandpaper, the two abrasives are not interchangeable in their applications.

In the final analysis, the choice of a high-grade abrasive depends on the quality and quantity of work performed by the abrasive per unit of cost. Initial cost of an artificial abrasive may be much greater than that of a natural abrasive, but the artificial mineral may do better work faster, so the ultimate cost is less. For this reason artificial abrasives have largely replaced natural abrasives.

Abrasive Value

Mineralogical hardness, or “scratch” hardness, as expressed in Mohs scale is an important property in evaluating abrasive materials, but it

Table 2. Relative hardness of abrasive materials on the Knoop scale

Substance	Knoop Hardness (K100)
Quartz	820
Garnet	1360
Alumina/25% zirconia	1450
Alumina/40% zirconia	1600
Aluminum oxide, brown	1850
Aluminum oxide, pink	1900
Aluminum oxide, white	1950
Al ₂ O ₃ + 3% TiO ₂	1950
Corundum	2050
Aluminum oxide, Sol-Gel	2100
Corundum (perpendicular to C axis)	2150
Silicon carbide	2480
Boron carbide	2760
Cubic boron nitride	7800
Diamond	8000

Adapted from Wellborn 1994 and Harris 2000.

is only one of several essential properties. The mineral hardness of pure crystal almandine garnet is about 7.5. The useful hardness may be much lower if incipient fracture planes cross the crystal, or if it contains inclusions of other minerals. Although the quartz grains in sandstone have a hardness of 7, the bond holding the grains together may be so weak that the stone is valueless as a commercial abrasive. The hardness, strength, and character of the bond in artificially bonded wheels and stones are fully as important as the hardness of the abrasive grains. For abrasive hardness of loose grains, both scratch hardness and toughness must be considered. In natural or artificially bonded abrasive stones, the character of the bond is of equal, if not greater, importance.

The problem of abrasive hardness is further complicated by the shortcomings of methods for testing hardness and expressing relative values. The Mohs scale is inadequate because the methods of testing are very crude and the intervals between steps in the scale are not uniform. There is far less difference between a hardness of 6 and 7 on the scale than between 9 and 10. Numerous attempts have been made to remedy these deficiencies. Knoop, Peters, and Emerson (1939) devised a diamond indentation method of measuring hardness that gives reproducible results on a wide variety of materials and definite numerical values over a wide range, up to diamond hardness, that is still currently used. Table 2 lists Knoop hardness values of various abrasive materials. Other methods of testing hardness are Vickers and Rockwell. The Vickers indenter is shaped like a square pyramid, whereas the Knoop diamond is an elongated pyramid shape; the Rockwell test uses a diamond cone or hardened steel-ball indenter.

Toughness or friability are perhaps more important than true hardness in appraising abrasive value. Very hard materials are necessarily neither tough nor resistant to fracture. Diamond is the hardest material known, yet it fractures easily under impact. Several techniques for testing friability are in widespread use in the quality control of abrasive grains. The basic operating principle common to all strength-of-grain tests is to impact a given sample of abrasive grain under a set of standardized conditions and then measure the amount of breakdown. The higher the survival rate, the tougher the grain, other factors held constant.

A simple and inexpensive device for testing friability is an ordinary ball mill. The standard *Ball Mill Test for Friability of Abrasive Grain* outlines this test (ANSI 1987).

Grain shape is another fundamental physical property that must be considered in selecting the best abrasive for a particular application. Blocky and nearly equidimensional grains are identified as strong-shaped and are less friable than slivery or flakey grains, which are considered weak-shaped. In grinding wheels, strong-shaped grains are preferred in extra-heavy-duty applications involving high heat and pressure, and weak-shaped grains are selected for precision grinding to close tolerances and where highly polished surfaces are required.

Close control of abrasive shape is necessary in modern abrasive technology. The bulk density of an abrasive is a dependable indicator of shape, because bulk density is a function of shape. A sample of weak-shaped grains will not pack as efficiently and will have a lower bulk density than the same abrasive with a strong shape.

Various techniques are used to measure the bulk density (shape) of abrasive grain. The loose-pack density test is described in ANSI B74.4-1992 (R2002), *Procedure for Bulk Density of Abrasive Grain* (ANSI 1992). In performing this test, care must be taken to avoid vibration. The container is filled to overflowing and then carefully leveled with a straight edge. The grain filling the container is weighed and the bulk density calculated using the conventional formula:

$$D = W/V,$$

where D = bulk density of the sample, in g/cm³

W = weight of the grain, in g

V = volume of the cylinder, in cm³.

Characteristics other than shape also influence the strength of abrasive grains. The manufacture and processing of aluminous abrasives permit control of some of these important characteristics. For example, laboratory and field tests have clearly established that the finer the crystal size of an abrasive the stronger that abrasive will be. The cooling history of a fused alumina melt is the dominant factor influencing the crystal size of the finished product. Generally, rapid cooling will result in finer crystals (400 µm) and slow cooling will produce coarser crystals (3,000 µm).

A rapid and inexpensive quality control check for crystal size is the monocrystalline count. Any convenient grit size can be used, but 24-grit is ideal. A petrographic microscope can reveal whether a grain consists of a single crystal (monocrystalline) or two or more crystals (polycrystalline). A count is made of 100 grains and the percentage found to be monocrystalline is the monocrystalline count. The higher the monocrystalline count, the weaker the grain. A polycrystalline grain is less apt to disintegrate because a fracture passing through one crystal in the grain is deflected on encountering another crystal not in crystallographic continuity with the first.

Heat treatment or roasting strengthens fused aluminum oxide abrasive grain. The heated slag (impurities between crystals) softens and flows on to the surface of the grain, cementing imperfections and sealing incipient fractures.

TYPES OF ABRASIVE PRODUCTS

Loose Abrasive Grains

Abrasive grains are produced from a wide variety of materials for use as grains and for incorporation into other products. Abrasive grains are important products and are the starting point for making bonded shapes, coated abrasives, abrasive tools, polishes, cleaners, grinding pastes, and other compounds. Garnet, flint, and chert are used for pressure-blasting silica sand and other natural mineral

grains such as corundum. Manufactured grains such as fused alumina, silicon carbide, and steel shot are also employed. Each use has its own special requirements. All grains except steel shot have a Mohs hardness of 7 or more. Besides hardness, the physical properties of toughness, grain shape, grain size, uniformity, and specific gravity are important. Grains should be tough so that they will not disintegrate readily under impact. For some uses, rounded grains are considered desirable. For others, sharp cutting edges are favored. Uniformity of grain size and other physical properties are always desirable. The higher the specific gravity, the greater the force of impact for grains of equal size.

Pressure blasting is used to clean stone and concrete, clean metal castings, prepare surfaces for painting, and etch glass and plastics. Relatively coarse grain sizes are used for sawing stone, rough grinding plate glass, and surfacing stone. Quartz sand, garnet, corundum, emery, aluminum oxide, and silicon carbide are common materials used. Slag abrasives dominate the blast cleaning market in Europe (Labrakis, An dronikos, and Kaliampakos 2002). Recently, sodium bicarbonate has been used as an alternative to silica sand for cleaning, buffing, degreasing, polishing, and coating removal. It is biodegradable, water soluble, and safe for most surfaces.

Smaller abrasive grains are used for grinding lenses, rough-polishing gems and ornamental stones, and dressing and polishing wood surfaces.

Fine-grained powders are specified for polishing and lapping glass, tile and artificial stone flooring, gems, semiprecious stones, and wood surfaces. Fine abrasives are rouge, crocus, tin oxide, aluminum oxide, chromium oxide, cerium oxide, diamond dust, feldspar, garnet, rottenstone, pumice, diatomite, tripoli, ground silica, clay, whiting, and zirconium oxide. Most automobile body cleaners and polishes contain diatomite. A familiar bathroom and kitchen scouring powder for glass and porcelain items contains feldspar or pumice. One method of drilling small holes in glass, porcelain, gemstones, and similar materials uses a brass tube. It is charged with diamond, corundum, emery, aluminum oxide, silicon carbide, or boron carbide dust in a water, oil, or grease carrier. Diamond-tipped drills are also used for this purpose.

Emery, magnetite, silicon carbide, and aluminum oxide are cast into the treads of steps and ramps to increase traction.

Bonded Abrasives

Abrasive grains, closely sized, are bonded and pressed or molded into a wide variety of bonded abrasives such as grinding wheels, honing stones, and tumbling media. The abrasives in such products were originally corundum or emery. The use of natural abrasives has declined greatly with the introduction of electric-furnace abrasives (aluminum oxide and silicon carbide).

Five main types of bonded abrasives, depending on the type of bond and method of manufacture, are as follows:

1. Vitrified wheels with a clay-feldspar bond that is made in ceramic kilns. Because of their high rigidity and dimensional stability, vitrified bonded wheels are preferred for precision grinding operations. They are unaffected by water, acids, oils, and ordinary temperature variations.
2. Resinoid wheels with a hard synthetic resin bond. These are high-speed wheels used in foundries and in welding shops, and for billet conditioning. They are also used in cutoff and thread-grinding operations.
3. Rubber wheels, bonded with natural or synthetic rubber. These are somewhat elastic in nature. They are used for grinding ball races, most centerless feed wheels, and for portable snagging operations where finish is an important

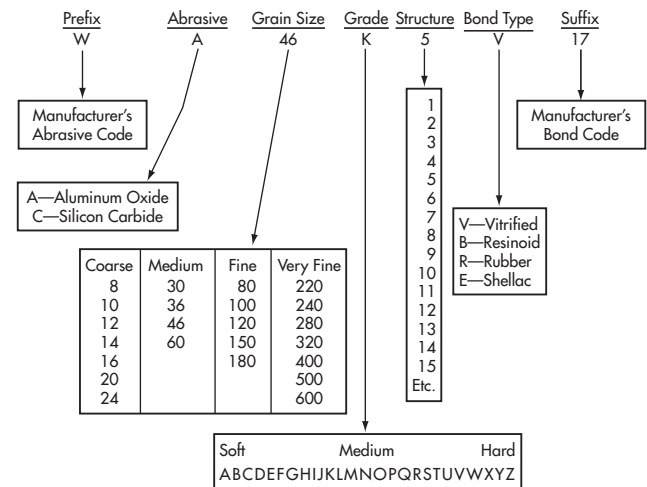


Figure 1. Wheel-marking system used in the abrasives industry

consideration. Rubber-bonded cutoff wheels can be made very thin.

4. Shellac wheels used for producing high finishes on items such as camshafts and paper mill rolls.
5. Silicate bonds for applications where heat generated in grinding must be kept to a minimum. Silicate bonded wheels are mild acting and are used in grinding-edge tools of all kinds.

Wheels vary in at least five physical properties aside from size and shape:

1. Type of abrasive grain (aluminum oxide, silicon carbide, diamond, etc.)
2. Grit (size of abrasive grains ranging from 8 to 1,500 mesh)
3. Grade (strength of bond encompassing 18 to 20 grades)
4. Structure (grains with 10 to 12 spacings)
5. Bond (vitrified, etc., in five bond types)

Figure 1 shows a wheel-marking system that is widely used in the abrasives industry.

When all these variables are combined with an almost infinite number of sizes, shapes, and spindle diameters that are either standard or available on special order, the complexity of the abrasive wheel business becomes apparent.

In addition to grinding wheels, bonded abrasives are made into blocks, bricks, and sticks; used as sharpening and polishing stones (oil stones or scythestones); and as razor and cylinder hones. Curved blocks and segments can be combined into large wheels such as pulpstones, or used mounted or unmounted for grinding or polishing the interior or exterior of curved surfaces.

Structured abrasives consist of fine abrasive grains mixed uniformly with a binder and shaped using microreplication techniques to form small geometrically shaped protrusions on a flexible backing. A 0.33-mm mineral height allows a continuous fresh supply of sharp minerals. Rubber pencil and ink erasers contain abrasive grains, and similar soft rubber wheels, sticks, and other forms are made for finishing soft metals.

Coated Abrasives

Coated abrasives consist of sized abrasive grains cemented to a paper, woven cloth, polyester film, or vulcanized fiber backing.

Sandpaper was originally coated with silica sand, but today crushed quartz is used on silic a-type paper because its grains have much sharper cutting edges. The principal abrasives used for this purpose are aluminum oxide, silicon carbide, alumina–zirconia, Sol-Gel alumina, crushed quartz, and garnet. Most emery cloth is now coated with silicon carbide or aluminum oxide. Flint paper in the United States is coated with crushed quartz, but true flint is used in Europe.

With the exception of sintered abrasives, all abrasive grains, natural or artificial, are made by graded crushing and close sizing. Crushing usually is done in two rolls to a void extreme fines—for which there is little demand—with close screening between. Products are passed through magnetic separators to remove iron-bearing material abraded from the rolls, and again precisely sized on screens. Careful sizing is essential to prevent contamination of grain grades. The finest powders are sized by air or water flotation and sedimentation.

In earlier practice, grade numbers were more or less arbitrarily assigned to grain sizes and garnet, flint, and emery scales were all different. Artificial abrasives were given numbers based on screen mesh designations now specified in ANSI B74.18 (ANSI 1996). Several grit grain-sizing standards exist worldwide. In Europe, the Federation of European Producers of Abrasives (FEPA) and International Organization for Standardization (ISO) are recognized. In Japan and Asia, the Japanese Industrial Standard (JIS) is recognized. Table 3 shows the relationship between the scales.

The bond for coated abrasives can be either glue or a synthetic resin. An initial coating—the *make coat*—of resin or glue is applied to the backing, and the grain is then electrocoated onto the surface. This electrostatic process ensures uniform distribution and optimum positioning of the grains. A second coating—the *size coat*—of resin locks the particles into place on the backing. The bonded material is cured and processed into various belts, rolls, discs, or wheels. Garnet and flint papers and cloths are most widely used for wood, leather, hard rubber, plastics, felt, and rubbed paint and varnish finishes on metals. Cloth, coated with silicon carbide, is used chiefly in the metal working industries. Alumina–zirconia and Sol-Gel abrasives are finding increasing use in heavy-duty cloth belts for industrial purposes.

Grains and Powders for Soap, Cleaners, and Polishes

Many different materials—mostly natural, but some manufactured—are used in making soaps, cleaners, and polishes. Feldspar, pumice and pumicite, sand, ground quartz, tripoli, diatomaceous earth, clay, and wood flour are ingredients in hand and scouring soaps. Low price is often the primary factor in the selection of the abrasive. Occasionally, the abrasive is an important factor in the formulation and use of a product. A household cleanser should contain neither quartz nor any mineral of hardness equal to or greater than that of glass or enamels, nearly all about a Mohs hardness of 6 or lower. Otherwise, the glass or enamel surface would be readily scratched. Such cleansers should not contain calcium carbonate, calcium sulfate, or other easily reactive lime compounds because lime reacts with most soaps to form insoluble substances that are difficult to remove from glass or enamel surfaces.

An ideal mineral abrasive for soaps, cleaners, and polishes would be a mineral or rock between 3 and 5 in hardness, occurring in abundance in easily mined deposits, close to rail transportation, and within a reasonable freight-haul distance of important markets. The material should be uniform in texture and physical properties.

The ultimate grain size of abrasives in this group depends on the finished product. Sizes range from extremely fine, air-separated and water-floated particles with sizes expressed in micrometers

Table 3. Size grades for abrasives*

Industrial U.S. Mesh	Micrometer Grade	FEPA or P-Grade†	JIS Grade
400	30		500
360		P500	400
320		P360	360
280	40		320
240		P280	280
220	60	P240	240
180	80		
150	100		
120			
100	150		
80	300	P80	
60		P60	
50			
40		P40	
36		P36	
30		P30	
24		P24	

Modified from Avonite Surfaces 2004 and Massasoit Tool Company 2005.

* Blanks indicate that there is no equivalent size in that particular sizing system.

† P series is used only in micrograins. FEPA has an F series whose equivalents in micrometers are different.

(much finer than 325 mesh) up to 100 mesh or even coarser for heavy-duty scouring soaps.

CLASSIFICATION

Abrasives can be divided into two general classes, natural and manufactured. The former includes all rocks and minerals used for abrasive purposes without chemical or physical change other than crushing, shaping, or bonding into suitable forms. Manufactured or artificial abrasives are made by either heat or chemical action from metals or mineral raw materials. Table 4 lists most of the important abrasives, classified by inherent type and the forms in which they are used industrially.

Manufactured products can be substituted for most natural products, usually at higher initial cost but with greater efficiency. This is not always the case. For example, there is no satisfactorily manufactured garnet substitute for making coated abrasive paper and cloth. For some abrasives such as chaser stones and others with declining use, the production of manufactured substitutes has not been economically attractive. For a low-priced commodity such as pressure-blasting steel shot, fused aluminum oxide and silicon carbide may be substituted.

The use of many natural abrasives such as sand and quartz has seriously declined because of government regulation of free crystalline silica (a carcinogen). The siliceous abrasives have been replaced with manufactured abrasives. The transition has not been a net loss to the mineral industry because virtually all manufactured abrasives are made from mineral raw materials.

Natural Abrasives

This book devotes separate chapters to such commodities as diamonds, diatomite, tripoli, pumice and pumicite, silica sand, and quartz. Thus, this chapter discusses these rocks and minerals only as abrasives.

Table 4. Classification of abrasives

Natural Abrasives						
Superior Hardness (>7.0 on Mohs scale)	Intermediate Hardness (H 5.5 to 7.0)		Inferior Hardness (H < 5.5)	Manufactured Abrasives		Types of Abrasive Products
	Silica Abrasives	Other Rocks and Minerals				
Diamond 10.0	Buhrstone	Argillaceous limestone	Apatite	Boron carbide	Lampblack	Abrasive grains and powders, loose
Corundum 9.0	Chalcedony	Basalt	Calcite	Boron nitride	Lime	Abrasive grains bonded into wheels, blocks, and special shapes
Emery 7.0 to 9.0	Chert	Feldspar	Chalk	Calcium carbonate (pptd*)	Magnesia (pptd)	Coated abrasives; grains bonded to paper and cloth
Garnet 6.5 to 7.5	Flint	Granite	Clay	Calcium phosphate	Manganese dioxide	Abrasive grains and powders; paste form; oil or water vehicles
Staurolite 7.0 to 7.5	Novaculite	Mica schist	Diatomite	Cerium oxide	Periclase (artificial)	Abrasive grains and powders; brick and stick form; grease, glue, and wax binders
	Quartz	Perlite	Dolomite	Chromium oxide	Silicon carbide	Natural rocks shaped into grindstones, pulpstones, chaser stones, millstones, etc.
	Quartzite	Pumice and pumicite	Iron oxides	Clay (hard burned)	Tantalum carbide	Natural rocks shaped into sharpening stones such as oil stones, whetstones, scythestones, razor hones, etc.
	Sandstone	Quartz conglomerate	Limestone	Diamond	Tin oxide	Natural stones shaped into rubbing and polishing stones such as holystones and pumice scouring blocks
	Silica sand		Rottenstone	Fused alumina	Titanium carbide	Natural stones shaped into blocks for tube-mill and pebble-mill liners
			Siliceous shale	Glass	Tungsten carbide	Pebbles, natural and manufactured, for grinding mills
			Silt	Iron oxides	Zirconium oxide	
			Talc		Zirconium silicate	
			Tripoli	Metallic abrasives, including steel wool, steel shot, angular steel grit, brass wool, and copper wool		
			Whiting	Porcelain blocks for mill liners and grinding pebbles		

Adapted from Wellborn 1994.

* pptd = precipitated.

Corundum and Emery

Corundum and emery have become relatively unimportant. Most of the emery is used as hardener for heavy-duty concrete floors and as nonskid material on bridges and at tollbooths. The competition from synthetic abrasives eliminated most of the markets for the se materials; only niche markets remain (Harben 2002). There is some limited use of the material as tumbling media.

Production. No corundum is currently mined in the United States or Canada. No production or imports of emery or corundum are reported for the United States. Turkey, the largest producer, reported 14.5 Mt of emery in 2003 (Mobbs 2003) and Greece produced an estimated 8 Mt (Newman 2003).

Diamonds—Industrial

The United States has no production of natural diamonds and is therefore dependent on imports.

Natural Industrial Diamonds. The four major types of natural industrial diamonds are as follows:

1. Bort, which includes off-color, flawed, or broken fragments of diamonds unsuitable for gems
2. Carbonado or black diamond, which is a very hard and an extremely tough aggregate of very small diamond crystals
3. Ballas, a very hard, tough, globular mass of diamond crystals radiating from a common center
4. Diamond crystals used for grinding wheel dressing

Carbonadoes come only from Bahia, Brazil. Ballas comes chiefly from Brazil, but some is from South Africa. Bort comes from all diamond-producing centers. There is a considerable production of diamond dust and powder waste from cutting gem diamonds. Several new diamond operations have opened in the Northwest Territories of Canada and exploration continues. In 2003, Canada produced about 15% of the world's diamond production (Olson 2003b).

Uses. The industrial diamond has become one of the most important and essential materials in modern industry. Diamond drilling, once used only for locating metallic ores, is now widely used for exploring geologic structures for oil and gas; testing foundations of dams, buildings, and heavy machinery; exploring the internal condition in heavy concrete structures such as dams, step mining, and explosive demolitions under special conditions; and for miscellaneous other purposes.

Some of the most important uses are as follows:

- Diamond drill bits for drilling rock and concrete
- Diamond dies for wire drawings
- Diamond-tipped tools for truing abrasive wheels and for turning and boring hard rubber, fiber, vulcanite, hard plastics, and so forth.
- Diamond-toothed (segmented) saws and rim-impregnated (continuous rim) saws for sawing stone, glass, quartz, and metals, and for slicing expansion joints in concrete highways, etc.

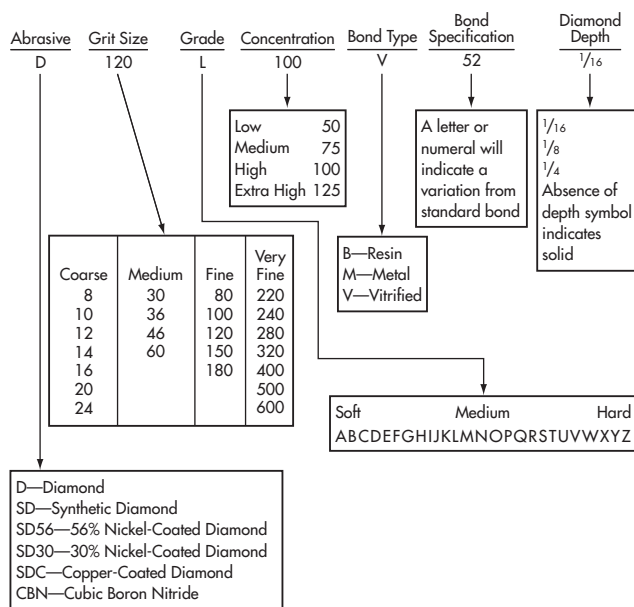


Figure 2. A diamond wheel-marking system

- Abrasive wheels, both for grinding and cutoff work in which the working face consists of diamond grit bonded with a metal or ceramic resinoid
- Diamond-tipped tools for cutting glass and for engraving gems
- Diamond powder for cutting gems

Cemented carbides and other exceedingly hard, tough alloys can be cut and shaped efficiently with diamond tools. Diamond-tipped tools are essential for the rapid and accurate shaping, truing, and dressing of abrasive wheels.

Quality Control and Testing. A diamond wheel-marking system (Figure 2), analogous to that previously shown for ordinary grinding wheels, is used by the abrasives industry. With diamond, as with ordinary abrasives such as aluminum oxide and silicon carbide, the previously mentioned properties of size, shape, and friability must be closely controlled so that diamonds with the proper physical properties can be selected for a particular application.

Resinoid or vitrified bonded diamond wheels require a fairly friable, weak-shaped, diamond abrasive grain. Metal bonded wheels require a more durable, strong-shaped grain.

A device similar to the bulk density apparatus used for ordinary abrasives is applied to diamond abrasives (Hight 1971). The cardinal rule in any determination is close reproducibility of conditions from one test to another. Another shape test is a microscopic technique developed at the Diamond Research Laboratory, Johannesburg. It is fast and inexpensive, but quite subjective. Custers and Raal (1959), who recognized four shape categories, further refined this method. Shape No. 1 is a near perfect cube or sphere whereas shape No. 4 is a thin flake or a needlelike grain. Shape Nos. 2 and 3 are intermediate. The arithmetic mean of 100 grains is calculated, and this number becomes the “shape count” for that particular sample. Belling and Dyer (1965) devised a friability test at the Diamond Research Laboratory.

Imports. The United States is the largest single consumer of industrial diamonds. It is estimated that apparent domestic consumption of both natural and synthetic industrial diamonds in 2004

was approximately 423 million carats (Olson 2005b). U.S. imports of natural diamond stones in 2004 were 2 million carats with a value of \$11.7 million (Olson 2005b). The United States was a net exporter of synthetic diamond grit and powder, and a net importer of natural industrial stones.

Garnet

The name *garnet* is given to a group of iron–aluminum silicate minerals having similar physical properties, crystal forms, and general chemical formulae.

Composition. In garnet, the general formula is $A_3B_2(SiO_4)_3$, where the *A* divalent element can be calcium (Ca), magnesium (Mg), ferrous iron (Fe^{2+}), or manganese (Mn). The *B* trivalent element includes aluminum (Al), ferric iron (Fe^{3+}), or chromium (Cr), and rarely, titanium (Ti). Further, titanium also replaces silicon in some examples. There are three prominent groups—aluminum, iron, and chromium—and various subdivisions under each, many of which blend into each other (Table 5).

Properties. Minerals of the garnet group have specific gravities that range from 3.4 to 4.3; have vitreous, resinous, or dull luster; and are transparent to opaque. Garnets have a cubic crystal system that is commonly rhombic dodecahedrons, tetragonal trisoctahedrons, or a combination of the two. They have a glassy structure and usually have a marked conchoidal fracture. Sometimes, however, the mineral tends to break into thin flakes. In some garnets the fracture is sharp and uneven. Index of refraction of the garnet group ranges from 1.735 to 1.94. Occasionally an indistinct dodecahedral cleavage is observed. Some species of almandine possess a pronounced laminated structure; the laminae are planes of weakness along which the mineral separates. This parting is not related to the crystal form and is not a true cleavage. Garnets having high iron content, such as almandine, fuse at about 1200°C. White garnets containing a considerable percentage of chromium are infusible. Aggregates of garnets are composed of individual crystals of various sizes, are brittle, and shatter readily. Massive garnet and well-formed crystals are remarkably tough and shatter with difficulty.

Occurrence. Garnet commonly occurs as an accessory mineral in a large variety of rocks, more particularly in gneisses and schists. It also occurs in contact with metamorphic deposits, crystalline limestone, pegmatites, and serpentines, and as gangue in ore veins formed at high temperatures. Most varieties of garnet are resistant to chemical and mechanical erosion and tend to be concentrated in sand of present-day or ancient beaches, streams, or other alluvial deposits.

Garnet is found in many foreign countries and in nearly every state in the United States. Large domestic resources of garnet occur in coarsely crystalline gneiss near North Creek, New York; other significant domestic resources occur in Idaho, Maine, Montana, New Hampshire, North Carolina, and Oregon (Olson 2005c).

Recent production has come from three companies, two operating in New York and one in Idaho. Montana had garnet production in 2002, but operations are now closed. Imports primarily from Australia, China, and India have displaced the domestic market.

According to data from Willis (2003) and Austin (1991), Barton Mines Corp. produces almandine garnet from an igneous–metamorphic rock of uncertain origin in Warren County, New York. It is used in sand blasting, precision powders for glass grinding and polishing, and water-jet cutting. The NYCO Division of Processed Minerals Inc., Essex County, New York, recovers and sells crude garnet concentrate, a by-product of its wollastonite operation, for additional refining and use as blasting and filtration media. Reserves in New York are large—more than

Table 5. Garnet classification

Mineral	Formula	Color	Specific Gravity	Mohs Hardness
Almandine, iron aluminum	$3\text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$	Deep red, brownish red to black	4.1–4.3	7.0–7.5
Grossular, calcium aluminum	$3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$	White, pale green, or yellow	3.4–3.6	6.5–7.0
Pyrope, magnesium aluminum	$3\text{MgO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$	Deep red to black	3.5–3.8	6.5–7.5
Spessartine, manganese aluminum	$3\text{MnO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$	Brown to red	3.8–4.3	7.0–7.5
Andradite, calcium iron	$3\text{CaO} \cdot \text{Fe}_2\text{O}_3 \cdot 3\text{SiO}_2$	Yellow-green, black, green	3.7–4.1	6.5–7.0
Uvarovite, calcium chromium	$3\text{CaO} \cdot \text{Cr}_2\text{O}_3 \cdot 3\text{SiO}_2$	Emerald green	3.4–3.8	6.5–7.0

Adapted from Harben 2002.

600,000 kt of high-quality garnet are recoverable from the Barton Mines' Ruby Mountain deposit. Similar deposits occur in the area (Austin 1991).

WGI Heavy Minerals Inc. has mining operations in northern Idaho at Emerald Creek, two jigging plants, and a mill in Benewah County, where garnet recovered from garnet-bearing gravels is used primarily for blasting and filtration media and water-jet cutting (Austin 1991). In March 2005, WGI was re-permitted by the U.S. Army Corps of Engineers at a current mine life of about 10 years. This will extend the reserve of garnet grades for two of their target markets, water-jet cutting and oil industries (U.S. Army of Corps of Engineers 2004).

Garnet is or has been commercially mined in Madagascar, Japan, Argentina, India, and Tanzania. Alluvial almandine garnet is mined in Western Australia (Port Gregory), and a hard-rock operation produces almandine garnet in New South Wales in Australia. In Australia, GMA Garnet of Geraldton, Washington, is the world's largest producer at more than 100 ktpy (Cullen 2004). Barton Mines Co. LLC of the United States owns the company along with Garnet International Resources based in Perth. India's garnet production is concentrated in southern India in Tamil Nadu and is primarily for export. The major producers in India are Vetri Vel Minerals Ltd. (VVM), Indian Ocean Garnet Sands Co., and Transworld Garnet India, a subsidiary of WGI Heavy Minerals (Willis 2003).

Preparation for Market. Almost 100% of the garnet sold is sized and graded. Mining techniques and end use govern sizing. Sizing generally conforms to specific standards (e.g., Standards for Quality Criteria, and Standard Methods of Test, Rating, Certification) established in cooperation with the U.S. Department of Commerce's National Institute of Standards and Technology (NIST) to provide a uniform basis for fair competition. Grading standards for coated abrasive use and micrometer sizing for grades used in glass grinding and metal lapping have exceedingly close tolerances. Wheel grades, polishing grades, and sand blast grades each have different standards and much greater tolerances. Specifications can be found in *Grading of Certain Abrasive Grain on Coated Abrasive Material* (ANSI 1996) and in *Size of Abrasive Grain-Grinding Wheels, Polishing and General Industrial Uses* (ANSI 2001). Specifications are increasingly tied to Occupational Safety and Health Administration (OSHA) regulations and certification standards set by the Coated Abrasives Manufacturers Institute (Harben 2002). In the United States, a material used as an abrasive is required to contain little or no free silica; pass the Toxic Characteristic Leaching Procedure (TCLP); conform to the U.S. military specification *Abrasive Blasting Media Hull Blast Cleaning* (Naval Sea Systems Command [Ship Systems] 1993) for the content of total metals, soluble metals, and radiation; and receive certification from California Environmental Protection Agency's Air Resources Board (Harben 2002).

Practically all garnet grains used today are heat-treated to improve adhesion rather than inherent abrasiveness. This degree of heat exposure is known as RT treatment. Impurities picked up during processing adhere to garnet particle surfaces and destroy cleanliness and capillarity needed to give adhesion for bonding. In the mid-1960s, the coated abrasives industry accepted uniform color standards for cleanliness of the grain surface and presented a color standard most closely approaching the natural red color of abrasive garnet.

There is no exact method for testing the abrasive quality of garnet or any loose abrasive except by practical application. Several rough tests and examinations indicate their abrasive possibilities. Fracture, sharpness and shape of the grain, character of the grain structure, and the presence of inclusions of other minerals, which weaken the grain structure, can be studied under the microscope. Hardness and toughness of grains can be roughly determined by placing a definite grade, such as #60, between two glass microscopic slides and rubbing them together. Skilled technicians can assess the relative scratch hardness of the grains and the amount of breakdown.

NIST developed an abrasive tester primarily for testing the abrasive quality of corundum. It can be adapted for testing the abrasive quality of any loose, abrasive grain. This type of grain is also tested on various production or laboratory machines that evaluate glass (stock) removal on flat plates. This data can be correlated with the anticipated performance of the material to be abraded as an evaluation of actual abrasive performance. In all these methods, actual stock removal is determined by either weighing or measuring. In the coated abrasives industry, test belts are made and stock removal is measured on test blocks. These tests measure stock removal only and are a valuable indicator when other important variables such as bond, backing, coating flex, and grit size are closely controlled.

In judging the abrasive quality of garnet and all other abrasives, stock removal is important but it is not the only factor to be considered. Surface finish is, in most cases, a more important factor. An abrasive used on some materials can be too hard and cause scratches so deep in the substructure that they cannot be removed in subsequent operations. If the abrasive does not have the proper grain shape or becomes dull (does not break down to yield new sharp cutting edges), it will tend to burn or gouge the material being worked.

Uses and Markets. Garnet-coated papers and cloths are used primarily for sanding wood, but also for finishing leather, hard rubber, plastics, glass, and softer metals. Coated abrasives have been improved in recent years, mainly by using resin bonds in place of glue bonds for certain applications. Electrostatic coating is now in general use. Garnet is being replaced in many of these applications by synthetic abrasives such as silicon carbide and fused alumina.

During World War II, when imported corundum became scarce for grinding optical lenses, garnet was the logical substitute

mineral. It had never been processed for this application, however. After development, garnet filled the critical need, and its desirable qualities became widely known. Its use decreased lens scratching, produced a superior finish, and, as a result, improved product quality. Using garnet reduced rejections and decreased polishing time, both important factors in the development of more economical lens grinding. The properties that made garnet a competitive abrasive for this application continue to produce new markets in the glass, plastics, ceramics, and soft metal industries. High-quality garnet powders are used for polishing and finishing cathode-ray tube (CRT) faceplates, liquid crystal display (LCD) screens, semiconductors, and polishing ceramics (Willis 2003). Abrasive powders from garnet make up 10% of the total end use in the United States.

A major nontechnical use of garnet in loose form is blasting and water-jet cutting. Garnet has the advantage of containing no free silica and thus it cannot cause silicosis. Being heavier than quartz, garnet delivers harder blows than quartz grains of equal size. Production of Idaho garnet is sold to aircraft industries on the U.S. West Coast as a blasting agent because of its price and location. Water-jet cutting requires consistent grading, good cutting speed, and durability, all of which garnet grains provide. In the United States, garnet use is primarily as blasting media (35%) and water-jet cutting (30%) (Olson 2005c).

Garnet, in different grain sizes, is also used for the manufacture of grinding wheels, as tumbling media, for nonskid applications, and as filter media. In powder sizes, it is made into lapping and buffing compounds. Water filtration is 15% of the total garnet end use in the United States.

Markets and Prices. In general, every abrasive has an application for which its qualification surpasses others, but in applications where qualifications overlap there is keen competition, based on relative cost, and grinding and finishing abilities. Garnet has maintained its position in the ever-expanding abrasives market through exploration and application of new technology. Because of health issues, garnet has the potential to increase its market share in areas previously supplied by silica sand. Market prices of garnet grains and powders vary widely, depending on garnet type (almandine, pyrope, etc.), purity, particle size, grade control, shipping quantities, and packaging.

Production. In 2004, the United States produced about 10% of the world's garnet. Reported production of crude garnet was 29.7 kt with a value of \$3.2 million. Imports into the United States were 50.4 kt of industrial garnet (Olson 2005c). Table 1 shows crude garnet production in the United States from 1999 to 2003.

Estimated world production for 2004 is 283 kt (Olson 2005c). Australia, India, and China are large producers of garnet. Production from China is on the rise, with one major producer, WuXi Ding-Long Trading-Sinogarnet. Sinogarnet's mines are in Inner Mongolia and produce almandine garnet from a biotite garnet schist containing 45% to 70% garnet (Willis 2003). Markets include Japan, Taiwan, Australia, India, Europe, Canada, the United States, the Middle East, and Africa. Uses include sandblasting, water-jet cutting, glass polishing, and textile and paper abrasives. Other operations in China have been plagued by long domestic transport distances, low quality control, and lack of water for cleaning (Willis 2003).

Staurolite

Staurolite, a complex iron-aluminum silicate, has been commercially recovered from various placer deposits in the southeastern United States, with one at a DuPont operation in Stark, Florida. Hardness—7 to 7.5 on the Mohs scale—is equal or slightly higher than that of quartz. Staurolite is used mostly for pressure blasting.

Latest production data are not disclosed, but 2002 industrial-grade staurolite production decreased 15% in quantity and 6% in value compared to 2001 (Spencer 2003).

Silica

Silica Sand. The use of silica sand as an abrasive has significantly decreased because of the potential health hazard from crystalline silica. In the United States, OSHA has created a permissible exposure limit stipulating the maximum amount of crystalline (free) silica to which workers may be exposed in an 8-hour shift. Garnet, olivine, slag, and fused alumina are being marketed as "safer" alternatives.

Abrasive sand accounted for 3% of the total amount of industrial sand and gravel sold or used in the United States in 2004 (Dolley 2005). The amount used for sandblasting in 2003 was 796 t valued at \$27.3 million with an average value of \$34.33/t. In addition, 55 t of ground sand, used in scouring powders, was sold at an average price of \$54.26/t. An undisclosed amount of silica sand used for sawing and sanding sold at an average price of \$38.25/t in 2003 (Dolley 2003).

Quartz. Crushed and graded quartz is used as the abrasive in flint sandpapers. Almost any deposit of massive white quartz is suitable. Being the cheapest of all the abrasive-coated paper, this product is still sold in fair amounts, mainly in hardware stores and by small jobbers. It is made only in the form of paper, not as cloth. True chalk flint from England and France is used extensively for this purpose in Europe; it has better cutting qualities and longer life than ordinary quartz.

Crushed and ground sand, sandstone, powdered quartz, and silt are sometimes used in hand soaps, scouring compounds, and harsher metal polishes.

Soft Siliceous Powder Abrasives. Some natural, highly siliceous materials occur as a powder or a fine abrasive used only in a powdered form as a mild abrasive. For most of these materials, use as an abrasive is of minor importance compared with their principal applications. The abrasive uses of diatomite, pumice, and tripoli are reviewed here.

Diatomite production in the United States comes primarily from California and Nevada, with small outputs from Oregon and Arizona. Abrasive uses include metal (silver) polishes, dental powders and pastes, and buffing compounds. More significant markets are filtration media, mineral fillers, and absorbents.

Included within the category of pumices are lump pumice and pumicite or volcanic dust, a natural powder. Lump pumice is used by manufacturers of furniture and musical instruments for dressing wood and metal surfaces, by silver platers for preparing metal surfaces, by lithographers for cleaning stone surfaces, by restaurants for scouring grills and cooking utensils, in household cleansers and hand cleaners, and by jeans manufacturers for stonewashing denim (Hoffer 1994). Pumice is also used for rubbing down and polishing fine tools and instruments. Pumicite or ground pumice is mainly used as a cleanser where thin, sharp, and striated grains are particularly suitable. Minor uses for abrasive pumice entail applications in polishing compounds; in polishing powders for bone, celluloid, and hard rubber; in dental use; in electronic circuit board preparation; and in the manufacture of some rubber erasers.

The fine-grained, porous materials—tripoli and rottenstone—are known to the trade as *soft silicas*. In the United States, white or cream tripoli comes from southern Illinois. Buff-to-rose-colored tripoli is mined and processed in Garland County, Arkansas (Malvern Minerals Co.), and similar material, mined in northeast Oklahoma, is milled in southwest Missouri. The colors are imparted by minor iron content. Tripoli from the Oklahoma-Missouri district

(American Tripoli Co.) is mainly used for metal finishing, for lapidary, and as friction products, including scouring agents.

Tripoli is composed of microcrystalline quartz grains that do not have distinct sharp edges and therefore perform a mild abrasive function in toothpaste, industrial soaps, and metal polishing compounds. It is employed to a small extent in the manufacture of some scouring and cleaning powders and for rubbing down painted surfaces such as automobile bodies.

Cream tripoli from southwestern Illinois is differentiated from rose tripoli based on its low iron content, high reflectance, and color, allowing for use in a wide range of filler-and-extender uses. It is also employed in buffing and polishing compounds and is in high demand for use in white coloring operations on high-class work. Chemically precipitated amorphous silicas are also used in polishing and buffing compositions.

Rottenstone, a fine-grained, gray-buff, siliceous-argillaceous limestone, comes from Antes Fort, Lycoming County, Pennsylvania, and is used as a base for automobile polishes.

Five firms in the United States produce and process tripoli (Dolley 2003); two of these companies specifically list abrasive uses for their products. American Tripoli Co. produces crude material in Ottawa County, Oklahoma, and finished material in Newton County, Missouri, which is used in metal finishing, lapidary, and friction products. Malvern Minerals Co. in Garland County, Arkansas, produces crude and finished material from novaculite primarily used as filler and extenders and as a wet-blasting media. Keystone Filler and Manufacturing Co. in Northumberland County, Pennsylvania, processed rottenstone from a fine-grained siliceous shale purchased locally (Dolley 2003).

The end use for tripoli has changed dramatically in the past 30 years because of the regulation of crystalline silica. In 1970 almost 70% of processed tripoli use was as an abrasive. In 2003 only 16% of the production was used for abrasive applications (Dolley 2003). The current primary use (70%) of tripoli is as a filler and extender in paints. The amount of processed tripoli, including amorphous silica and Pennsylvanian rottenstone, used or produced in the United States in 2003 was 68.8 kt, valued at \$17.7 million (Dolley 2003). The average reported unit value of all tripoli sold or used was \$257/t. The average reported unit value for abrasive tripoli used or sold in the United States during 2003 was \$194/t. The consumption and production of tripoli are not expected to change significantly in the future because the markets are well defined and the potential of new end uses is relatively low (Dolley 2003).

Other Soft Abrasives

Ground Feldspar. Ground feldspar is extensively used in scouring and cleaning compounds and for a window cleaner.

Chalk. Chalk (calcium carbonate) is a soft, compact, fine-grained, white limestone composed of the calcareous remains of microscopic marine shells. A small amount of this chalk, mainly from England and France and known in the trade as "whiting," is used as a very mild abrasive for hand polishing nickel, gold, silver, or plated ware, buttons, and similar materials.

China Clay. China clay (kaolin) and some pipe clays have been used successfully in polishing powders. Pipe clay at one time was the standard polish for naval and military tunic buttons.

Bath Brick. Bath brick, used for scouring steel utensils, is made from very fine-grained, quartzose clay found along the banks of the Parrot River in England.

Special Silica Stone

Although in general stones made from bonded artificial abrasive grains have largely replaced natural sharpening stones, there is still

small production of oilstones, whetstones, and deburring media in Arkansas, and whetstones and oilstones in New Hampshire. Arkansas novaculite stones are still preferred by surgeons, carvers, and engravers for sharpening fine-edged tools. It is claimed that these stones give a smoother and longer-lasting edge.

Natural abrasive stones are made from a wide variety of materials, including sandstone, novaculite, mica schist, siliceous argillite, shale, slate, and pumice. The superior cutting quality of some of these stones is due to the well-disseminated, fine-grained inclusions of garnet or other minerals of superior hardness.

Table 1 lists the quantity and value of finished grindstone, oilstone, and whetstone products sold or used by producers in the United States from 1999 to 2003 under the category "special silica stone products." Production in 2003 was 1,070 t valued at \$313,000. Arkansas accounted for most of the total quantity and value. Exports of special silica stone in 2003 were valued at \$7.8 million and categorized as hand-sharpening or polishing stones. The value of imported silica stone was \$6.3 million; a portion of the finished products imported were probably made from crude novaculite produced in the United States and exported for processing (Dolley 2003).

Grinding Pebbles and Tube-Mill Linings

Tube mills, conical mills, and cylindrical batch mills are most often used for the fine grinding of hard ores, minerals, paints, chemicals, ceramic bodies, glazes, enamels, portland cement clinker, and similar materials. Most efficient grinding can be done in mills with iron or steel liners and iron or steel balls, slugs, or rods. Where contamination of the color or chemical purity of the product by metals and metal oxides must be avoided, the grinding surfaces consist of blocks or bricks for the mill linings, and natural pebbles or artificially prepared balls are specified for grinding media. These materials should (1) have high abrasive hardness; (2) have great toughness and freedom from flaws that will result in breaking and chipping; (3) produce a white powder when abraded; and (4) contain no dark-colored metallic impurities such as iron or manganese. Although most of the natural and artificial mill linings and pebbles have a specific gravity close to that of quartz (2.6), pebbles with greater density have obvious advantages. The heavier the pebbles per unit of size, the greater the impact and abrasive grinding forces. Thus, with heavy pebbles, less mill volume is needed for a given mill capacity (throughput). With equal pebble volume, faster grinding can be done. Small balls—having more surface area per kilogram than large balls—grind faster, but with small pebbles the unit weight is low unless high-density pebbles are used.

The favored natural mill-lining material for most purposes is Belgian silex, which is a very hard, tough, more-or-less cellular quartzite resembling French buhrstone. It is imported in rectangular blocks essentially shaped to fit the curve of a mill. During World Wars I and II, when imports were cut off, and to a much lesser extent at other times, domestic substitutes have been used. These have consisted chiefly of quartzite from near Jasper, Minnesota; Iron City, Tennessee; and Baraboo, Wisconsin; and granites from Salisbury, Lillesville, and Faith, North Carolina. Some of these materials are reported to give service equal to that of Belgian silex. Special hard, dense, porcelain blocks are used in some mills for grinding paint, ceramic, and chemical materials.

For grinding media, Danish flint pebbles, when available, have long been standard because of their superior hardness, toughness, and uniformity. These pebbles are found on the shores of Greenland but are marketed through Denmark. Other foreign sources of similar pebbles exist along the seacoasts of Belgium, France (between Le Havre and St. Valéry-sur-Somme), Norway, and England. Seven sizes of Danish pebbles are marketed, ranging from 25.4 to 203 mm.

Table 6. Crude manufactured abrasives produced in the United States and Canada, by type

Type	2002	2003	2004*
Silicon carbide, kt†	30	35	35
Value, 1,000 US\$	15,900	18,500	21,500
Fused aluminum oxide, regular abrasives, kt	20	20	25
Value, 1,000 US\$	5,300	5,800	7,300
Metallic abrasives, kt‡	218	193	194
Value, 1,000 US\$	101,000	90,800	92,000
Total, kt§	268	248	254
Total value, 1,000 US\$	122,200	115,100	120,800

Adapted from Olson 2004, 2005a.

* All 2004 data are estimated.

† Approximately one half of quantity and value consists of material used for refractories and other nonabrasive purposes.

‡ Does not include reported exports.

§ Excludes U.S. and Canadian production and value of aluminum–zirconium oxide.

Domestic substitutes for grinding media are natural pebbles of flint, quartz, and quartzite, and pebbles artificially rounded by tumbling small blocks of quartzite, granite, chalcedonized rhyolite, or other siliceous materials in rotating cylinders. During World War II, natural pebbles were shipped from Encinitas Beach, California (true flint); Jasper, Minnesota (quartzite); the Austin chalk beds in south-central Texas (true flint); Salisbury and Faith, North Carolina (granite); Baraboo, Wisconsin (quartzite); and several other points in the United States. Extensive deposits of quartzite pebbles in southwestern Saskatchewan have been reported. Beach pebbles were reported to be nonuniform in hardness and required careful sorting.

Ceramic pebbles are made from very dense, tough porcelain, alumina, and sillimanite (mullite). A dense, heavy pebble having a specific gravity of 3.7 is made from zircon. For certain purposes, blocks of ore are used as grinding media. This practice has been followed to some extent in the autogenous grinding of some nepheline syenite. Ceramic products and high-alumina grinding media are tending to replace natural materials in these niche markets.

Manufactured (Artificial) Abrasives

The discovery of the electric-furnace method for making silicon carbide by Edward G. Acheson in 1891 began the revolution in the high-grade abrasives industry. Before that time, all abrasives were natural minerals and rocks except for minor chemically prepared materials such as rouge and Vienna lime. Today, artificial abrasives, with a few notable exceptions such as diamond and garnet, dominate the field of high-grade abrasives. Manufactured abrasives are essential to modern industry because they are not only superior to natural abrasives but are also uniform in quality and their properties can be varied to meet differing needs. Modern, high-speed, streamlined production methods require very accurate, specialized tools with a degree of uniformity and dependability that cannot be met with natural abrasives.

Manufactured abrasives may be divided into three main groups: (1) electric-furnace products, (2) chemical precipitates, and (3) miscellaneous additions.

Electric-Furnace Abrasives

Electric-furnace abrasives include silicon carbide, fused aluminum oxide (alumina–titania; alumina–chromium oxide; alumina–zirconia; alumina–zirconia–titania), and boron carbide.

Silicon Carbide. Silicon carbide, with the chemical formula SiC, is commonly known by the trade names Carborundum and Crystolon. It is made by fusing a mixture of high-grade silica sand and carbon in an electric furnace. The preferable form of carbon used is petroleum coke, but anthracite and coke made from coal low in ash have been used. High iron and alumina in the ash are objectionable because they tend to assist in the formation of elemental graphite and metallic silicon during the reaction. High-ash carbons make impure grades of silicon carbides.

Silicon carbide is made by charging a resistance-type electric furnace with pure glass sand and finely ground petroleum coke. The silicon of the sand combines with the carbon from the coke to form silicon carbide. The temperature at the core of the furnace is about 2,200°C. If the temperature is too high, silicon carbide decomposes: The silica is volatilized and the carbon becomes graphitized. The time of a run is about 60 hours (36 hours heating and 24 hours cooling). At the end of the run, the core consists of loosely knitted silicon carbide crystals surrounded by unreacted or partially reacted raw materials. The quality of the product depends largely on the raw materials used and the accuracy of control and operation of the furnace. Several types of products are made in which the toughness of the grains varies. A special surface treatment is given to grains for coated abrasives to increase adhesion of the glue.

The lump material from the furnace is first crushed in jaw crushers and then sequentially processed in roller, ball, or hammer mills. It is passed through a magnetic separator to remove magnetic impurities. The grains are screened mechanically into 20 or more standard sizes from 8 to 240 mesh. The finer flour sizes are prepared by air or water flotation and sedimentation.

Olson (2005a) shows crude manufactured abrasives produced in the United States and Canada during 2000 to 2004. Total production of silicon carbide in 2004 was 35 kt compared to 45 kt in 2000 (Table 6). About half the 2004 total value and quantity is material for metallurgical and other nonabrasive applications (Olson 2004). The average value of a abrasive-grade silicon carbide at the point of manufacture was estimated at \$614/t (Olson 2004). Washington Mills in Hennepin, Illinois, produced abrasive-grade and metallurgical-grade silicon carbide. The United States exports and imports crude and refined silicon carbide. Imports for consumption are estimated at 197 kt for 2004 (Olson 2005a). Imports of crude silicon carbide come from 8 countries, and 21 countries supply refined silicon carbide to the United States. China supplies 57% of the crude and 36% of the ground and refined imports (Olson 2004). The value of crude silicon carbide from China averages \$452/t; the remaining amount of crude silicon carbide imports has an average price of \$389/t. The average price of ground and refined silicon carbide imports is \$1,000/t. China has been excluded from the European Union markets because of import tariffs; therefore, China's main markets for silicon carbide are North America and Japan (Harris 2004). Other major producers are Norway, Japan, Mexico, Brazil, and Venezuela. China (455 kt) and Norway (80 kt) are the top producers of silicon carbide (Olson 2005a).

Fused Aluminum Oxide. Aluminum oxide abrasives are made in electric-arc furnaces. Bauxite, the crude raw material, should have the following typical chemical properties:

Al ₂ O ₃	85.0% to 87.0%
TiO ₂	3.0% to 4.5%
SiO ₂	3.0% to 5.5%
Fe ₂ O ₃	6.0% to 10.3%
Loss on ignition (LOI; plus combined H ₂ O)	1.0% to 2.0%

The ore as mined is crushed and then calcined to remove both free and combined water. The calcined ore (80%) is mixed with iron borings (15%) and ground coke (5%) and charged into the furnace. The coke reduces the impurities, which combine with the iron and sink to the bottom of the furnace.

At the end of the melting and reacting period, the charge is poured into cooled molds and allowed to cool under controlled conditions to obtain desired crystal size. The finished, crystallized alumina typically consists of about 96% Al_2O_3 ; 2.7% TiO_2 ; 0.67% SiO_2 ; 0.11% Fe_2O_3 ; and 0.40% other oxides. Fused aluminum oxide made with bauxite is referred to as brown fused alumina, or BFA. For certain purposes, Bayer-process alumina is used instead of calcined bauxite, making a product with >9% Al_2O_3 called white fused alumina, or WFA. White fused alumina is used entirely for grinding wheels (O'Driscoll 2003).

The cooled mass from the furnace is crushed, screened, and cleaned in about the same way as silicon carbide. Several types of grains are made that vary in toughness, type of fracture, glue adhesion, and other properties. Another form of fused Bayer-process alumina is achieved with the addition of 0.15% to 3.00% chromium oxide. Adding chromium oxide increases the hardness of these abrasives without substantially increasing the toughness. These properties are useful in preparing grinding wheels that produce a cool grind without resulting damage to the metal being ground.

Other heavy-duty fused abrasives have been developed. One is an electric-furnace fusion product made primarily of intimately crystallized mixtures of aluminum oxide and zirconia. Although other proportions have been successful, two mixtures—one containing approximately 25% and the other about 40% zirconia—have found the most widespread commercial applications in niche markets. The 25% zirconia product is used in bonded abrasive applications for foundry markets (\$1.00 to \$2.00/lb) and the 40% zirconia is used for selected bonded and coated abrasives costing \$1.50 to \$3.00/lb. Another fused abrasive is composed of a mixture of alumina, zirconia, and titania, which is fast-cooled or quenched. A favored mixture contains 34% zirconia, 3% titania, and 63% alumina. Fused alumina–zirconia abrasives have extreme durability and are particularly well suited for foundry snagging and steel conditioning.

Uses of fused aluminum oxides included bonded abrasives, coated abrasives, and closed blasting systems where the material can be recycled many times and chemical purity is important, such as in the aircraft industry (O'Driscoll 2003). Bonded and coated abrasive products account for most of the consumption of fused aluminum oxide. Fused aluminum oxide in a micropowder form is used in industrial and electronic applications that require fine surface finishing (Olson 2004).

Table 6 shows data on the production of fused alumina from 2002 to 2004. Data on production of alumina–zirconia abrasives are withheld. Estimated production in 2004 of fused aluminum oxide in the United States and Canada was 30 kt with an estimated value of \$10.7 million (Olson 2005a). Of this total, 25 kt was regular grade (valued at \$7.3 million), and 5 kt was high-purity fused aluminum oxide (valued at \$3.4 million). Imports increased from 164 kt in 2003 to an estimated 213 kt in 2004. Imports of crude fused aluminum oxide were from China, Canada, and Venezuela. Ground and refined imports were from China, Germany, Brazil, Austria, and Canada (Olson 2005a).

Boron Carbide. Boron carbide (B_4C) is an artificial abrasive introduced in 1934 by the Norton Company under the name Norbide. Although considerably harder than silicon carbide, it is far from the hardness of diamond (see Table 2). It is made from B_2O_3

and carbon in the form of petroleum coke in a carbon-resistance or arc furnace at about 2,600°C. The finished product is crushed and ground to make a range of sizes of grains and powders. In grain form, it is used for grinding and lapping operations previously possible only with diamond dust. Pulverized boron carbide can be molded under very high heat and pressure to form extremely wear-resistant products such as pressure-blast nozzle liners, thread guides, extrusion dies, and all types of extremely accurate plug, snap, and ring gages. It is not manufactured into bonded wheels or sharpening stones. Washington Mills was the only producer of boron carbide in the United States in 2004.

Sintered Abrasive

A different family of abrasives is the sintered product. This group differs drastically in method of manufacture from the more conventional fused product. The raw materials are heated in kilns only to the sintering temperature (1,200° to 1,400°C) rather than being carried all the way to the fusion point. Although other basic starting materials have been used, bauxite, with or without additives and still in the green (unfired) state, is formed into predetermined sized and shaped granules by certain granulation techniques or by extrusion through an appropriately shaped orifice. The resultant presized and preshaped granules are then sintered to make the finished abrasive grain. Process steps such as crushing, shaping, and sizing (common to manufacturing fused products) are eliminated in making a sintered product.

Sol-Gel Abrasives

Sol-Gel abrasives are prepared by jelling a form of aluminum oxide known as boehmite, adding various precursors to enhance the properties along with a seed or nucleation agent (various types have been used), evaporating the water from the gel, and producing a hard, solid material. The resulting product is crushed and graded into sizes and fired at 1,200° to 1,500°C. 3M, a diversified technology company, and Saint Gobain, who pioneered the products, hold the patents.

Although most of the raw materials used in the Sol-Gel process are considerably more expensive than those going into regular aluminum oxide abrasives, the performance of the Sol-Gel abrasives—particularly in paper, cloth, and grinding wheel applications—seems to justify the additional cost in a number of uses. In 1991, Sol-Gel abrasives were predicted to dominate the high-quality abrasives market; the market share has not materialized, however, because of high manufacturing costs (Burke 2004). The minimum pricing for Sol-Gel products is \$6 to 8/lb.

Manufactured Diamond

In February 1955, General Electric Co. announced that its laboratories had succeeded in producing diamonds from carbonaceous material subjected to pressures of about 5.5 GPa at very high temperatures for prolonged periods. Crystals up to 1.6 mm long were made in 16 hours, but smaller ones were produced in much shorter times. The pressure capable of maintaining temperatures above 2,760°C at pressures up to about 11 GPa. Costs were reported to be about twice that of comparable natural diamonds, and the sizes were small. Today, production is commercially economical. Diamonds can now be made in a relatively few minutes, and their performance in specific applications, discussed in the Natural Industrial Diamonds section, equals that of natural diamond.

Several types of manufactured diamond, both domestic and foreign, are now on the market, and each has distinct characteristics. Synthetic industrial diamonds are superior to natural diamonds because their properties can be tailored to specific applications and

they can be produced in large quantities. Metal coating of the diamond improves the adherence of the bond to the abrasive in resinoid bonded grinding wheels. Metal-coated (nickel, copper) diamond represents still another commercially available diamond type. Resin-bonded diamond grinding wheels are used in the production of cement carbide tools. Metal bond and electroplated diamond wheels are used in glass cutting and finishing. Polycrystalline diamonds (PCDs) are formed under high pressure and temperatures, resulting in thousands of microcrystallites bonded together. PCDs have self-sharpening properties: the polycrystalline structure allows new sharp edges to be available by releasing an outer layer of dull microcrystallites. Other properties of PCDs are high wear resistance, high shock resistance, good thermal stability, and a homogeneous structure. PCDs are used in drilling bits, wire-drawing dies, and reaming shells. A newly developed method from Apollo Diamond Inc. for growing gem-quality as well as industrial-grade diamonds is chemical vapor deposition (CVD). This technique transforms carbon into plasma that is then precipitated onto a substrate as diamond. This method has been used in the past to cover large surfaces with microscopic diamond crystals, but now Apollo has developed a method to create a single diamond crystal (Olson 2003b). Another advantage of CVD is finer control of impurities over the PCD method. The CVD diamonds can be used to fashion surgical blades that are resistant to dulling (Yarnell 2004).

The use of manufactured diamond has steadily increased. In 1969, domestic production of manufactured industrial diamonds amounted to approximately 13 million carats. By 1981, productivity had soared to approximately 57 million carats. In 2004, two U.S. producers of synthetic diamonds estimated an output of 250 million carats. More than 88% of the industrial diamond market now uses synthetic diamonds because of quality control and customization for specific requirements (Olson 2005b). Nine U.S. firms manufactured PCDs from synthetic diamond grit and powder (Olson 2005b). Recycling has become important as well; an estimated 4.4 million carats were recycled in 2004 from bort, grit, dust, and powder. Additionally, an estimated 275,000 carats of diamond stone were recycled. Lower prices for newly produced industrial diamonds reduced recycling operations from 4.9 million carats in 2003. The United States continues to be the world's leading market for industrial diamonds and remains a significant producer. The Congo (Kinshasa) and Australia, are major producers as well.

Boron Nitride

Boron nitride in cubic form is a manufactured abrasive discovered by General Electric Co. Laboratories in 1957 and trademarked as Borazon. Unlike manufactured diamond, it has no known counterpart in nature. It is made at temperatures and pressures comparable to those required for diamond manufacture. The thermal stability of cubic boron nitride exceeds that of diamond. It is stable at temperatures greater than 1,371°C, whereas diamond reverts to graphite at greater than 816°C. The Knoop hardness (K100) is 7800, well above ordinary abrasives but inferior to diamond.

Borazon is used in industrial applications to shape tools because it can withstand temperatures greater than 2,000°C. Cutting tools and abrasive components, particularly for use with low-carbon ferrous metals, have been developed using cubic boron nitride. In this application the tools behave in a similar manner to PCD tools but can be used on iron and low-carbon alloys without risk of reaction.

Metallic Abrasives

Metallic abrasives include crushed steel, steel shot, angular steel grit, steel wool, brass wool, and copper wool. The following

description of the first three of these products is by Johnson and Schauble (1939):

Crushed steel is made from high-carbon and crucible sheet steel specially treated to impart brittleness. It is then crushed to sizes ranging from 2- to 200-mesh. After screening, each batch is heat-treated and separated into 25 sizes ranging from 20- to 200-mesh. Sizes from 70-mesh upward are screened on silk bolting cloth, and the finer sizes in powder form are used in steel cement, various chemical compounds, and fireworks sparklers.

Steel shot is merely chilled cast iron. Only raw materials of the highest grade, including selected scrap and charcoal iron are used in its manufacture. These are melted in a cupola. During the casting period, the molten metal is separated into small spherical globules by directing high-pressure steam or heated compressed air against the stream of metal. The globules are blown into water and cooled. The shot, made brittle by the rapid cooling, is heat-treated to impart a temper of hardness and graded by mechanical means into 15 sizes that range from 4- to 90-mesh. Coarse material left on the 4-mesh screen is granulated by specially designed crushing equipment and in this form is known as angular steel grit. The crushed material is heat-treated to impart toughness and durability. It is then graded into 15 sizes ranging from 7- to 100-mesh. Steel shot and angular steel grit are used for many abrasive purposes.

Steel wool, made from both ordinary and stainless steel in various degrees of fineness, is used for finishing wood and soft metals such as aluminum, and for scouring and cleaning. It is made in several types of machines by shaving or scraping continuously moving wire with a fixed serrated cutting tool. Brass and copper wool are used chiefly for household cleaning.

Today, most metal abrasives (75%) are used as loose particles propelled at high velocities for blast cleaning or for improving the properties of metal surfaces. Industries using metallic abrasives include foundries, automotive and aircraft manufacturing, and metalworking and steel plants (Olson 2004).

Olson (2005a, 2003b) reported production, shipments, and annual capacities of metallic abrasives in the United States, by product, for 2002 through 2004. Table 6 shows total production of 194 kt valued at \$92 million are reported for 2004. Steel shot and grit accounted for 99% of the total metallic abrasives produced domestically. Seven companies reported production of cut wire shot in 2004, most cut from carbon-steel wire and stainless-steel wire. Other products include shot cut from aluminum, copper, and zinc wire (Olson 2004). The United States increased exports of metallic abrasives by 21% in 2004. More than 90% of these exports were to Canada and Mexico. The United States also imports metallic abrasives from 12 countries; 71% of imports are from Canada (Olson 2004).

Chemical Precipitates

Chemical precipitates, mainly oxides, all have a very fine grain size and are used as final polishing agents.

Iron Oxides. Rouge, a ferric oxide, has its largest use in polishing plate glass, but it is also widely used in powder, paste, coated cloth, and stick form for polishing precious metals, stone, and other materials to give a final high luster. Crocus is similar to rouge in composition, but purplish red in color. Crocus is used in finishing cutlery and some brass work.

Other Precipitates. Chromium oxide, or green rouge, is used chiefly for platinum and stainless steels. Tin oxide is used largely for polishing glass and precious stones. Putty powder is a mixture of tin oxide and oxalic acid used for polishing glass and precious stones. Cerium oxide is a polishing agent for glass and can be substituted for tin oxide in other applications. Magnesia in the soft precipitated form has been noted as a mild polishing powder. The hard-burned variety, artificial periclase, has also been used as an abrasive. Precipitated calcium carbonate is used as a mild abrasive in some dentifrices.

Calcium and Magnesium Oxides (Lime)

Lime (CaO), manufactured by calcination of limestone, and dolomitic lime (CaO•MgO), derived by calcination of dolomite, have important abrasive uses. This has been especially true of those marketed under the names of Vienna lime or Sheffield lime. The so-called Vienna lime (originally from Vienna, Austria), which is used on the American continent in a grease-brick buffing composition, is obtained from certain beds of dolomite at Francis Creek and Manitowoc, Wisconsin. Vienna lime is made by calcining the dolomite, then cleaning and grinding to a specific fineness. It is packed in carefully sealed containers. As soon as the lime becomes hydrated, it ceases to function and attacks the grease composition. This product is used for buffing brass, copper, bronze, steel, pearl, celluloid, and similar materials. Its principal use is for coloring nickel after plating. Vienna lime gives nickel a deep undersurface blue peculiar to the metal. Lime attacks aluminum and thus is not applied with this metal.

Miscellaneous Manufactured Abrasives

Porcelain. The use of porcelain blocks and pebbles for grinding mills has been noted. This porcelain may consist largely of zirconium oxides or silicate, or of mullite converted from andalusite, kyanite, or dumortierite.

Glass. Crushed and screened glass has been used for coated abrasives to make glass paper.

Lampblack. Lampblack, fine soot collected from incompletely burned carbonaceous materials, finds some use for polishing celluloid and bone.

Clay. Clay, burned to a very hard state and finely pulverized, is reported to have been used as an abrasive for polishing metal.

Government, Environment, and Health Considerations

One of the most important issues affecting the abrasives industry in recent years has been the potential effect of crystalline silica on human health. OSHA created a permissible exposure limit that stipulates the maximum amount of crystalline silica to which workers are exposed in an 8-hour work shift (29 C.F.R. 1926.55, 1910.100; U.S. Department of Labor 2002). This legislation has influenced the use of silica sand, diatomite, tripoli, and special silica stone as an abrasive.

Trends and Opportunities

Abrasives are used in almost every manufacturing and industrial sector of the economy and are greatly influenced by the economic and technological trends of these markets. Many natural abrasive materials have been replaced by synthetics, and that trend is likely to continue. Garnet is an exception, particularly in the water-jet cutting market, and abrasive blast cleaning has a bright future for market development. Garnet is replacing silica sand as a sandblasting agent because of the health risks.

With improved technology, surface quality requires less grinding and finishing, meaning less-coarse abrasives are required

(Harris 2000), creating a greater need for finer grades. Demand for industrial diamonds in the United States is likely to continue with growth in the construction sector, particularly with the rebuilding of the nation's highway system (Olson 2003b), where diamonds are used on the cutting edges of saws employed in highway construction and repair work. With the current housing construction boom in North America, the demand for manufactured abrasives used in cutting and finishing wallboard and timber will also continue (Olson 2004). Rising energy costs and falling prices influenced by a flood of imports from China have been, and will continue to be, a challenge to domestic production.

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Construction Sand and Gravel

William Langer

INTRODUCTION

Sand and gravel are among the most familiar minerals in everyday life, and together comprise one of the two principal sources of aggregate. Crushed stone, the other source, is discussed in a separate chapter and is mentioned here only in a general manner, such as when both sand and gravel and crushed stone are being described as aggregate.

This chapter is intended to present a general perspective on the geology of sand and gravel deposits, and how they are explored, mined, and processed for aggregate to meet the needs of the construction industry. The transportation, marketing, specifications, and uses of sand and gravel are discussed only briefly in this chapter (for a more detailed discussion, see the Lightweight Aggregates chapter in this volume).

Most sand and gravel is used as construction aggregate. In many cases, it is preferred over crushed stone for use in portland cement concrete because its smooth, rounded shape allows for easy mixing without addition of excess water and cement. Gravel commonly must be crushed for use in asphaltic concrete where interlocking edges add strength. An average six-room house requires about 82 t of aggregate, and an average school building requires about 14,000 t of aggregate (Langer and Glanzman 1993). Sand and gravel also has numerous applications in an unbound state. The proportional share of aggregate consumed by each person in the United States is about 9 tpy, about 3.8 t of which is sand and gravel.

Definitions

Wide variations exist for the definition of sand and gravel; some terms have different meanings to different users. In addition, some terms have descriptive characteristics that are dependent on local conditions and, as such, serve an important function. The terms used in this chapter generally conform to geologic descriptions.

- Sand and gravel: a mixture of unconsolidated material resulting from the natural disintegration of bedrock and the subsequent transport, abrasion, and deposition of the particles by ice, water, wind, and gravity. Sand and gravel normally occur together and can contain particles ranging in size from clay to boulders.
- Sand: natural granular material resulting from rock disintegration, consisting primarily of particles having a diameter in the range of $1/16$ in. to 2 mm, according to the definition of Bates

and Jackson (1987). Manufactured sand resulting from the production of crushed stone is discussed in the Crushed Stone chapter in this volume.

- Gravel: unconsolidated, natural accumulation of rounded rock fragments resulting from erosion, consisting predominantly of particles larger than sand (diameter greater than 2 mm), such as boulders, cobbles, pebbles, and granules (Bates and Jackson 1987).

Production and Trade, Substitutes, and Resources and Reserves

Sand and gravel is the second largest nonfuel mineral commodity in the United States in both volume and value. About 1.13 billion t of sand and gravel, with a value of \$5.8 billion, was produced by an estimated 4,000 companies from 6,400 operations in 50 states (Bolen 2004). About 25% of the operations produce less than 25,000 tpy of sand and gravel. About 3% of the operations produce more than 1 Mtpy of aggregate and account for nearly 30% of the total sand and gravel production (Bolen 2002). About 10% of the operations account for more than half the annual production. About 53% of the 1.13 billion t of construction sand and gravel produced in 2003 was for unspecified uses. Of the remaining total, about 42% was used as concrete aggregates; 23% for road base and coverings and road stabilization; 15% as construction fill; 12% as asphaltic concrete aggregates and other bituminous mixtures; 3% for concrete products, such as blocks, bricks, and pipes; 1% for plaster and gunite sands; and the remaining 4% for snow and ice control, railroad ballast, roofing granules, filtration, and other miscellaneous uses (Bolen 2004).

Sand and gravel production, expressed as a percentage of total aggregate production, varies from state to state depending on a variety of reasons, including geology, availability, ease of obtaining permits, local or regional specifications, and operator preferences. Generally, in the United States, more crushed stone is produced than sand and gravel (Table 1). More sand and gravel than crushed stone is produced in 24 states.

The amount of foreign trade of construction sand and gravel is minor. During 2001, about 3.06 Mt were exported, and about 3.82 Mt were imported. Most trade is with Canada and Mexico.

Total world production of aggregate (including crushed stone as well as sand and gravel) is estimated at 15 billion tpy. Production in the European Union is about 3 billion tpy, representing about two

Table 1. Sand and gravel production, by state, for 2002

State	Sand and Gravel Value, \$1,000	Sand and Gravel Production, kt	Sand and Gravel as Percentage of Total Aggregate Production	State	Sand and Gravel Value, \$1,000	Sand and Gravel Production, kt	Sand and Gravel as Percentage of Total Aggregate Production
Alabama	60,700	13,500	19.8	Montana	94,300	20,200	86.4
Alaska	67,800	11,500	88.5	Nebraska	41,500	12,300	66.6
Arizona	265,000	47,700	83.7	Nevada	168,000	32,300	77.9
Arkansas	52,500	10,400	24.4	New Hampshire	45,200	8,830	65.0
California	1,160,000	157,000	71.1	New Jersey	91,700	15,400	47.1
Colorado	236,000	44,800	72.3	New Mexico	58,500	11,100	67.7
Connecticut	68,400	11,500	52.0	New York	152,000	28,700	32.4
Delaware	13,500	2,320	100.0	North Carolina	52,400	10,300	13.9
Florida	117,000	26,300	20.0	North Dakota	26,700	10,300	100.0
Georgia	28,100	6,750	8.6	Ohio	249,000	48,100	38.4
Hawaii	6,000	500	6.7	Oklahoma	41,300	10,200	20.6
Idaho	60,200	16,900	78.6	Oregon	114,000	19,500	46.0
Illinois	128,000	28,200	26.7	Pennsylvania	121,000	18,700	16.1
Indiana	122,000	28,100	33.0	Rhode Island	10,100	1,280	49.4
Iowa	65,000	14,200	27.8	South Carolina	31,200	9,510	27.5
Kansas	27,400	9,450	30.5	South Dakota	39,500	10,500	63.9
Kentucky	41,000	10,100	15.5	Tennessee	54,900	9,680	14.7
Louisiana	76,800	16,000	100.0	Texas	384,000	76,900	37.9
Maine	44,600	10,900	72.2	Utah	119,000	30,600	78.4
Maryland	76,000	11,000	32.8	Vermont	18,900	4,240	50.5
Massachusetts	90,600	13,900	48.4	Virginia	60,100	10,800	15.3
Michigan	269,000	75,500	64.8	Washington	238,000	43,900	74.8
Minnesota	179,000	45,300	82.3	West Virginia	8,080	1,560	8.8
Mississippi	77,900	14,900	72.9	Wisconsin	139,000	35,500	52.4
Missouri	40,700	9,480	10.6	Wyoming	47,600	9,570	66.2
				Total	5,710,000	1,120,000	41.7

Source: Bolen 2002; Tepordei 2002.

thirds of the European total (Regueiro et al. 2002). Aggregate production rates plummeted in Eastern Europe following the political reorganization of the early 1990s. More recently, production rates have stabilized, resulting in modest increases in demand in countries with emerging economies. Approximate production in other major aggregate-producing countries, in metric tons per year, follows: China, 4.5 billion; Japan, 550 million; Russia, 432 million; and Canada, 385 million (Regueiro et al. 2002).

Although aggregate resources, like all nonrenewable resources, are finite, the potential worldwide supply of aggregate resources is so large that "finite" loses its urgency in this context. But natural aggregate of suitable quality for an intended use can be in short or nonexistent supply on a regional or local scale because of unfavorable geology, encroachment by incompatible land uses, and the inability to obtain necessary permits.

A number of materials may be used as a substitute for sand and gravel. The most widely used one for gravel is crushed stone; for natural sand, it is manufactured sand. Other substitutes include recycled concrete or asphalt, slag, and shells.

GEOLOGIC ORIGIN AND MODES OF OCCURRENCE

The distribution and size of deposits of sand and gravel are primarily controlled by glacial, fluvial, and marine processes (Langer 1988). Wind is an inconsequential geologic agent when considering gravel. Consequently, sand and gravel is widely distributed and abundant near present and past rivers and streams, in alluvial basins, along marine or lake shorelines, and in previously glaciated

areas (Figures 1 and 2). The debris from in situ weathering of some bedrock can also be a source of sand and gravel.

Glacial Deposits

The most recent episodes of glaciation took place over the last 2.5 million years during which much of the world's temperate zones were alternately covered by glaciers and uncovered during the warmer interglacial periods. A number of ice sheets expanded from Canada into the northern tier of conterminous states and Alaska, at times covering all of New England; almost all of New York; all of Michigan; parts of Wisconsin and Iowa; almost all of Minnesota and North Dakota; and some of New Jersey, Pennsylvania, Ohio, Indiana, Illinois, Missouri, Nebraska, South Dakota, Montana, Idaho, Washington, and Alaska (Mickelson and Colgan 2004; Booth et al. 2004). These ice sheets persisted until about 11,000 years ago, and remnants occur in Alaska, Canada, and the higher portions of some Rocky Mountain states. Extensive ice fields and valley glaciers were found in the high ranges in all of the mountainous western states (Pierce 2004). These glaciated regions generally contain abundant deposits of sand and gravel, although glaciated areas exist where sand and gravel is absent or is covered with sufficient fine material to make discovery or exploitation uneconomical.

As glacial ice melts, rock particles that had been crushed, abraded, and carried by the ice are further transported, abraded, and rounded by meltwater. These deposits are potential sources of sand and gravel that are of great importance for use as aggregate. The particle size in the glacial meltwater deposits ranges from boulders

to sand, silt, and clay, and can change abruptly, both with depth and laterally, especially where the material was deposited under the ice (eskers, for example) or on or near the ice (moraines or kames, for example).

In some areas near the ice margins, large lakes were formed when meltwater was trapped between the ice and higher ground. For example, Lake Agassiz covered an area of about 365,000 sq mi (945,000 sq km) in Manitoba, Ontario, and Saskatchewan in Canada, and North Dakota and Minnesota in the United States; and the Great Lakes were once much larger than at present. Deltas formed where glacial meltwater streams emptied into these and numerous other smaller temporary lakes. These glacial lake deposits are important sources of high-quality aggregates.

Pluvial Lakes

In the Great Basin of the United States, a large number of closed basins exist. During the cooler weather that prevailed in that area during glacial times, precipitation was greater than it is today, and water did not evaporate as rapidly. Many closed basins contained large lakes, such as Lake Bonneville (of which Great Salt Lake in Utah is a remnant) and Lake Lahontan (of which Pyramid Lake and Walker Lake in Nevada are remnants). Fifty or more other lakes have since disappeared. Sand and gravel was deposited along the shorelines of some of these lakes. The old shorelines of former Lake Bonneville are a conspicuous landform at Salt Lake City. These types of beach deposits are a large potential supply of sand and gravel resources.

Marine Beaches and Terraces

During periods of glacial retreat, much of the glacial ice melted and the water returned to the oceans, causing the sea level to rise. Some inland areas of today were once coastal beaches or terraces, such as strandlines along the Atlantic and Gulf coasts. These are important sources of sand and gravel, although the gravel in some of the older deposits has deteriorated due to prolonged weathering.

Marine Offshore Deposits

In Europe, Japan, and elsewhere, marine (offshore) sand and gravel deposits are economically exploited for use as aggregate. Marine sand and gravel deposits are located on the continental shelf of North America along the Atlantic, Pacific, and Gulf coasts. Gravel is most common offshore from Canada, New England, New York, and New Jersey on the Atlantic Coast, and from Canada, Washington, and Oregon on the Pacific Coast. Gravel occurs infrequently in southern coastal areas of the United States.

Some sands obtained from U.S. federal waters have been used for beach renourishment, and sand and gravel has been recovered from dredging projects. Otherwise, marine deposits have generally not been commercially exploited in the United States.

Alluvial Deposits

In many states, alluvial (river) sand and gravel, either in the channels or floodplains of rivers and streams, or in terraces found alongside the rivers or streams, are the principal sources of sand and gravel. Alluvial sand and gravel deposits are products of bedrock erosion and the subsequent transport, abrasion, and deposition of the particles. The availability and quality of the gravel is strongly dependent on occurrence and properties of nearby bedrock sources.

If a river or stream changes gradient and downcuts its channel, the older channel and floodplain deposits may be preserved as river terraces. Repeated downcutting can result in a series of terraces or terrace remnants above the level of the modern stream base, which can be sources of sand and gravel. Older terraces may be exposed to



Figure 1. Generalized distribution of sand and gravel in the conterminous United States

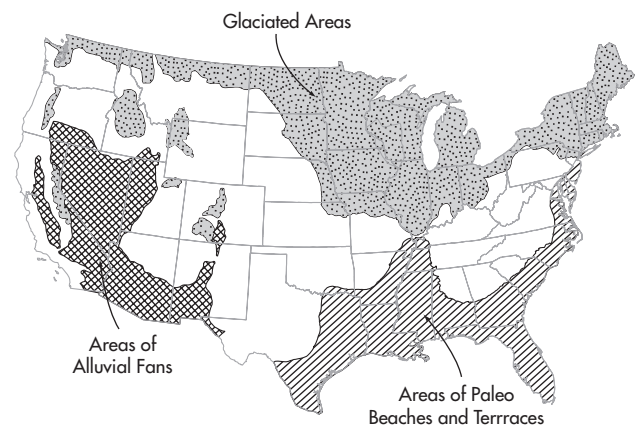


Figure 2. Generalized sand and gravel regions in the conterminous United States

prolonged weathering, thus weakening the material and reducing its suitability as aggregate.

Alluvial Fans

In mountainous arid and semiarid regions of the western United States, rock fragments are eroded and transported during storms down steep-gradient streams to the adjacent basins. Upon reaching the basins, the suddenly reduced sediment capacity of the water causes deposition, resulting in alluvial fans. These deposits commonly contain thick unconsolidated material ranging from large boulders to clay-size particles. Generally, the largest material is deposited adjacent to the mountains and becomes progressively finer toward the downstream edge of the deposits. Over time, fans from adjacent valleys can coalesce to form continuous, thick deposits. Sand and gravel in alluvial fans may be suitable for aggregate, but much of the material is poorly stratified and poorly sorted. In older fans the gravel may be highly weathered and not suitable for aggregate. In addition, fan gravels may be cemented with caliche, a calcium carbonate precipitate in the soil, making them difficult to extract and process.

In Situ Weathered Rock

In some areas physical or chemical weathering can disaggregate rock in place, resulting in a coarse lag material that sometimes is

used as sand and gravel. Rock types that are particularly susceptible to this type of weathering include conglomerate, sandstone, and coarse-grained granitic rocks. In some situations, the lag gravels may contain considerable fine material and require additional processing.

PROPERTIES

Some properties, such as mineralogy, density, and porosity, are inherent in sand and gravel particles. Other properties, such as size, shape, and sorting, are acquired as the result of processing the deposit. The properties discussed in this chapter are the inherent properties.

Sand and gravel is always of secondary origin and commonly reflects the petrology of the local rock types. An exception occurs in glaciated terrains where deposits can contain exotic rocks transported long distances by ice. Sand and gravel deposits may be composed of materials in which a single mineral dominates or may consist of a wide variety of rocks and minerals.

The properties of sand and gravel result from the petrology of the source rocks, the method of transport and deposition, and the subsequent weathering of the aggregate particles (Langer 2001b). Sand and gravel should be durable and strong, which means they should support the intended load and resist mechanical breakdown resulting from the action of mixers, mechanical equipment, and/or traffic. Particles should be sound, which means they should be able to resist weathering, such as repeated freezing and thawing or wetting and drying. Sand and gravel should be composed of clean, uncoated particles of proper size and shape for the intended use. Sand and gravel commonly meets these requirements, because the natural abrasion processes associated with the formation of most sand and gravel deposits tends to eliminate weaker particles.

The quality of the aggregate is defined most often by its conformance to specifications set by the user. Because aggregate commonly is used in highway construction, those specifications are usually set by state departments of transportation. Most states conform to the grading and testing standards of the American Association of State Highway and Transportation Officials (AASHTO) or the American Society for Testing and Materials (ASTM).

Physical Properties

The producer has little control over certain properties of individual particles in a deposit. These are particle size, shape, strength, specific gravity, porosity, and petrology. Size and shape can be modified if the gravel clasts are sufficiently large and can be processed by crushing and screening. If the properties do not meet local specifications, the deposit probably is not economically exploitable.

Particle Size and Size Distribution

Aggregate for most construction applications can be prepared from sand and gravel deposits containing a wide range of particle sizes. Particle-size distribution of sand and gravel deposits can be quite variable, both laterally and vertically. The larger the gravel-to-sand ratio, the better the deposit (Langer and Knepper 1998), except in areas where crushed stone is abundant and natural sand is lacking. Silt and clay occurring either as layers, interstitial material, or as coatings on larger clasts are undesirable. Silt-sized or smaller fine particles generated from crushing gravel are also undesirable.

Particle Shape

Three techniques are commonly used to describe particle shapes of naturally occurring gravel. One technique, commonly used by geologists, compares the lengths of three diameters of the particle and describes them as equidimensional, disk, blade, or rod shaped (Langer and Knepper 1998). Another technique, commonly used by

engineers, utilizes a proportional caliper to determine the ratio of the maximum-to-minimum dimensions. A third technique visually estimates shapes and describes them using terms such as rounded, flaky, and elongate (Marek 1991). Particle shapes tend to be beneficial when the predominant shape is equidimensional and detrimental when the predominant shape is disk, blade, or rod shaped (Langer and Knepper 1998). Particles can also be described based on the angularity of their edges and can be divided into a number of classes from round to angular. The desired roundness or angularity depends on use.

Specific Gravity

Specific gravity is the ratio of the mass of a given volume of aggregate to the mass of an equal volume of water. Very low specific gravity frequently indicates aggregate that is porous, weak, or absorptive; high specific gravity generally indicates high-quality aggregate. Bulk specific gravity is the ratio of the weight of a given volume of material, including all voids, to the weight of an equal volume of water. Apparent specific gravity is the ratio of the weight of a given volume of material, including all impermeable voids, to the weight of an equal volume of water.

Porosity and Pore Structure

Porosity is the percentage of the total volume of a gravel particle occupied by pore spaces. Pore structure is the size, shape, volume, and interconnectedness of the spaces within an aggregate particle. Pores can be impermeable (isolated, enclosed cavities) or permeable (interconnected and connecting to the surface of the particle). Gravel particles with high permeability are not desirable for most applications because they absorb large volumes of water or salt solutions, thus reducing soundness. For bituminous mixtures, high permeability also increases the absorption of binder, thus increasing the cost of the paving mixture (Barksdale 1991).

An approximate inverse correlation exists between aggregate quality and rock porosity. Porosity affects the strength and elastic characteristics of an aggregate, and may influence permeability, absorption, and durability. Rock with water absorption of 2% or less will usually produce good aggregate, whereas otherwise suitable rocks with a water absorption that exceeds 4% may not (Smith and Collis 2001).

Chemical Properties

The chemical properties of sand and gravel vary from deposit to deposit and within clasts, and commonly are identified through petrographic analysis. They are primarily controlled by the mineralogy of the individual particles. Most sand and gravel is considered to be inert, but it may contain minerals that adversely react with portland cement or bitumen and affect the product life.

Weathering and Impurities

Sand and gravel should not be excessively weathered. Weathering of gravel clasts lessens the strength of aggregate and increases the overall cost of mining and processing. Once sand and gravel has been deposited, it is subjected to natural weathering processes. The rate and type of weathering depends on the local climatic conditions, the geometry of the deposit, the relationship to the water table, and the properties of the sand and gravel clasts. Weathering can range from slight discoloration of the clasts, through the introduction of fractures and alteration of minerals, to complete decomposition and disintegration of the clasts. In arid and semi arid climates, sand and gravel may be cemented with caliche, a calcium carbonate, and may be difficult to extract and process. In humid regions, sand and gravel may be cemented or stained with iron or manganese dioxide. Sand and gravel must be free of objectionable

rocks, such as shale, mica schist, coal, and gypsum, and of roots and other organic material.

PROSPECTING, MINING, AND PROCESSING

Sand and gravel must physically be able to be mined and be accessible to transportation systems and to markets. The site must qualify for all necessary land use and environmental permits. The operation must be profitable considering all costs, including acquisition, operation, compliance with regulations, and reclamation (Dryer 1976; Banino 1994). These requirements usually make opening a new operation a complicated process that involves substantial cost and can take many years.

Prospecting Techniques

The U.S. Bureau of Mines Information Circular 6668 (Thoenen 1932) was one of the first comprehensive publications to describe sand and gravel prospecting techniques. The 3rd edition of *Industrial Minerals and Rocks* (Lenhart 1960) and all subsequent editions contain discussions on prospecting for sand and gravel. Dunn and Cutcliffe (1971) include socioeconomic factors as part of the exploration process. A chapter in *The Aggregate Handbook* (Dunn 1991) and a four-part series of articles in *Rock Products* (Timmons 1994, 1995) describe many aspects of both exploration and characterization of aggregate resources.

Exploration for sand and gravel has become more than simply locating a source of suitable material and commonly is based on the principle of the weakest point (Dunn 1991). During exploration, a weakest point exists that should be analyzed before proceeding to other elements of exploration. For example, it may be unwise to intensely study sand and gravel deposits in an area where fragmented land ownership makes acquisition difficult. It would also be unwise to thoroughly address all permitting requirements before determining some estimate of the quality of a deposit. Thus, exploration requires judgment and experience in order to proceed in a logical sequence. Each weak point should be resolved to an acceptable level of risk before proceeding to the next weakest point (Dunn 1991).

When assessing preliminary target areas for sand and gravel exploration, economic and social factors such as markets, transportation options, current land use, zoning regulations, and property ownership should be considered. Public hearings commonly are held before governmental bodies such as county or town boards, and the public and governmental views toward aggregate production must be carefully analyzed (Dunn 1991).

Exploration for sand and gravel deposits within target areas commonly begins with desktop studies utilizing existing data. Detailed geologic maps and cross-sections for large parts of the United States and elsewhere can be used to help locate sand and gravel deposits. Hydrologic reports of alluvial areas frequently contain logs of wells and test holes. In glaciated terrain, geologists commonly can readily identify typical glacial features that are likely to contain sand and gravel by using topographic maps with a contour interval of about 5 m or less, and large scale (about 1:50,000 or larger) aerial photographs. Geologists can also identify stream terraces, floodplains, alluvial fans, and beach deposits in many nonglaciated terrains using the same type of maps or photographs.

In developing areas or other locations where existing large-scale geologic information and other map data are inadequate, remote sensing data (satellite or airborne spectral imagery) and airborne geophysical surveys may be useful for detecting sand and gravel resources. Knepper, Langer, and Miller (1995) reviewed a number of techniques that have been successfully applied in locating

sand and gravel. These include the use of satellite data, in some instances in conjunction with aerial photographs, to delineate gravel-filled paleochannels (USGS 1981), buried gravel deposits (Peterson, Goodrick, and Melhorn 1975), and calcrete for use as roadstone (Henry 1989). Sand and gravel has been identified using satellite or airborne thermal infrared data to detect differences in diurnal (Carr and Webb 1967) and soil-moisture temperatures (Jackson et al. 1978; Schmugge, Jackson, and McKim 1980; Sabins 1984). Knepper, Langer, and Miller (1995) also describe the application of airborne very low frequency (VLF) resistivity surveys to locate exposed gravel deposits (Middleton 1977) and buried gravel deposits (Culley 1973).

Field studies commonly are conducted to check the veracity of desktop analyses and collect new data. These activities may include a comparison of the geomorphology, as observed in the field, with the desktop interpretations of the topographic and aerial photographic analyses. Natural and synthetic exposures are investigated and sampled to determine the extent of the deposit, sand and gravel properties, and subsurface conditions. A geologist may also evaluate the site to identify potential environmental factors and to prepare plans for more detailed site evaluation.

Detailed Evaluation of Deposits

If reconnaissance studies indicate a target area worthy of further investigation, the next step is more detailed field studies. Acquisition of more detailed information increases costs, and it is appropriate to assess the weakest point at this stage of exploration. Economic and social factors, such as current land use, zoning regulations, and property ownership, might be investigated in more detail, particularly because it will be necessary to obtain permission from landowners to access sites for further studies.

Systematic sampling should be conducted to determine the areal extent, thickness, stratigraphic variation, and physical properties of deposits. Test pits, truck-mounted augers, and other truck-mounted drills commonly are used to determine the factors as well as to obtain samples to find out the properties of the sand and gravel. A power hoe can dig test pits or trenches about 4 or 5 m deep. Truck-mounted augers have a capacity to drill to depths of about 60 m. Auger sizes range from about 6 to 60 cm, with the most common sizes between 10 and 15 cm. Deposits of cobble and boulder gravel are difficult for augers to penetrate and may require the use of other drilling equipment.

The spacing of drill holes, test pits, and trenches, and remote sensing patterns are site specific and should be based on the predictability and geologic continuity of the deposit's critical characteristics as determined by qualified personnel experienced in such procedures (Dunn 1991; Timmons 1994). Sample spacing depends on the desired level of detail and needed confidence, and typically ranges from 30 m in highly complex areas to as much as 500 m in large areas of very simple geology. Sampling plans may be modified based on updated knowledge gained during ongoing site characterization.

Electrical resistivity techniques were used to explore for sand and gravel prior to the late 1930s (Patterson 1937). Techniques used today include direct current resistivity (DCR) soundings, time domain electromagnetic (TEM) soundings, ground-penetrating radar (GPR), and seismic refraction.

Properly conducted surface geophysical surveys can provide information on the areal extent and thickness of the deposit, thickness of overburden, stripping ratios, depth to the water table, and critical geologic contacts. They are appropriate for a quick location and correlation of geologic features such as silt and clay lenses. Surveys can be run where closely spaced geological changes might

be undetected by drilling, such as areas of suspected buried channels, and where other elusive, but important, geologic conditions may exist.

Geophysical surveys can be conducted to provide subsurface detail in areas where digging test pits, augering, or drilling are encumbered because of limited access. Landowners may prohibit invasive exploration activities, such as drilling or digging test pits, or restrict vehicular access to existing roads. Augering, drilling, or digging test pits might be unacceptable in some areas such as active cropland or forested land. Auger trucks or drill rigs may be unable to reach sample areas if the ground surface is soft, muddy, or covered with water. The geologic properties of the target deposit may confound augering—for example, where deposits contain cobble-sized or larger clasts. Additional problems related to drilling are described by Timmons (1995).

Geophysical surveys can be of value when performed early in the field exploration program in combination with limited subsurface investigations. Such surveys, when conducted prior to intensive drilling, can be used to help locate auger or drill holes and can reduce the number of test drilling sites. Geophysical surveys can provide continuity between sampling sites in order to upgrade the confidence of reserve calculations from probable reserves to proved reserves.

An experienced field geologist can determine whether or not a geophysical survey is warranted and which methods should be used. The spacing of geophysical survey patterns is site specific and should be based on geologic characteristics of the site and the predictability of continuity of the deposit's critical characteristics as determined by personnel specially trained in such procedures (Dunn 1991; Timmons 1994). Survey plans commonly are modified during site characterization based on knowledge gained during the sampling process.

Ellefson, Lucius, and Fitterman (1998) tested the effectiveness of DCR, TEM, GPR, and seismic refraction using S-waves to characterize sand and gravel. Haeni (1995) similarly tested DCR and seismic refraction using P-waves. In most cases, useful geologic information, such as sediment thickness, was obtained with all methods. Shortcomings include the presence of clay-rich soil limiting the effectiveness of GPR and the difficulties of P-wave seismic studies used below the water table.

The results of geophysical surveys are limited because it is not possible to translate geophysical data without correlative evidence normally provided by borings. In addition, geophysical surveys generally provide a very broad guide to the characteristics of a sand and gravel deposit that must be refined by other means. Actual subsurface information is desirable so that geophysicists have an idea of what to expect when measuring resistivities. The presence of conductive fluids in pores and of synthetic conductors such as fence posts and pipes can create erroneous results.

All critical variations in the geologic characteristics of a sand and gravel deposit should be recorded. Geologic mapping systematically documents field observations and is a valuable tool for planning drilling and sampling locations (Dunn 1991), assessing geophysical needs, establishing background data, and identifying potential environmental impacts associated with aggregate development. Geologic maps, cross-sections, and accompanying reports of potential sand and gravel operation sites commonly show the location and outline of the deposit, location of sampling sites and geophysical surveys, thickness of the deposit, and descriptions of materials throughout the deposit. Supplemental maps and reports can also describe related issues such as the thickness of overburden, depth to ground water, and geologic hazards. In many states, such reports must be prepared by a licensed professional geologist.

The difficulty of calculating volumes of deposits has been greatly simplified with the use of specialized mining and quarrying software, the geographic information system (GIS), and computer-aided design (CAD) software. Usable volumes exclude areas of setbacks, access roads and other infrastructure, maintenance facilities, and so forth. Information obtained during geologic mapping and sampling can be entered directly into these programs, and resource volumes can be calculated using various algorithms. For people who choose not to use computers, other methods exist to calculate volumes of deposits (Peters 1987).

Gross reserve tonnage is calculated by multiplying the unit weight of sand and gravel by the estimated usable volume. The unit weights of sand and gravel varies widely from deposit to deposit and is sometimes arbitrarily considered to be 1.78 t/m³. The in-place density of deposits can be determined more accurately by weighing the contents of an excavated known volume.

Net reserve tonnage is the percentage of the gross reserve that can be made into usable products. Excluded are overburden, fines and other waste, and uncrushable oversized boulders.

There are numerous methods for appraising sand and gravel pits depending on the purpose of the appraisal and the status of the pit (Paschall 1998; Evans 1995), but for industrial minerals such as sand and gravel, economic and legal issues usually are far more important than the geologic aspects of a deposit. Companies perform detailed reserve estimates and appraisals for a variety of reasons, including sale or purchase of undeveloped resources or reserves, acquisitions and mergers, valuation of a mining property, accounting, financing, taxation, condemnation, mineral conservation, and for internal planning. Customers or investors can precipitate an analysis of reserves by demanding proof of the existence and quality of reserves before committing to long-term purchase agreements.

Mining

Site preparation starts with grubbing and stripping sufficient overburden to access the resource. Often required by regulation, topsoil commonly is separated from the overburden and stockpiled for reclamation activities. Overburden may be used to construct berms, be stockpiled, or sold. Soil or overburden should not be stockpiled over parts of the deposit where future extraction is expected, and final need for reclamation should be considered. Site preparation also includes construction of access roads, fences, berms, haul roads, drainage ditches, culverts, settlement ponds, processing and maintenance facilities, and other plant infrastructure.

Sand and gravel is mined from open pits and dredged from underwater bodies. In upland areas, such as high terraces and some glaciofluvial deposits, sand and gravel may occur as unsaturated deposits. Where sand and gravel mining does not penetrate the water table, the aggregate can be extracted by using conventional earth-moving equipment.

In some areas, such as low terraces and glaciofluvial deposits, the pit may extend into the water table. In some geologic settings, wet pits can be dewatered by collecting the groundwater in drains on the pit floor and pumping the water out of the pit, or by isolating the pit from the groundwater through the use of slurry walls. In some situations where the sand and gravel pits penetrate the water table, such as floodplains or low terraces, the pit may be allowed to fill with water, and the operator may extract the material by using wet mining techniques such as draglines, clamshells, bucket and ladder, or hydraulic dredges.

Sand and gravel can be excavated directly from stream channels or from the edge of stream channels. During times other than flooding, aggregate can be skimmed from bars in channels or from

active floodplains. Stream channels may be temporarily or permanently diverted to allow for aggregate extraction using conventional earth-moving equipment in the natural streambed. A variety of methods can be used to divert the channel, including the construction of a new diversion channel, split-channel mining, and the construction of harvest pits (Colorado Division of Minerals and Geology 1998). In arid areas, some stream channels or washes only occasionally have stream flow, and sand and gravel can be mined from the channels using conventional excavation equipment.

Processing

After extraction, sand and gravel occasionally is used as-is, which is called bank-run or pit-run gravel; most frequently, it is processed before use. Processing may be as simple as a portable crusher and screens or can be a highly automated, sophisticated procedure. There are numerous ways to configure equipment depending on the characteristics of the sand and gravel deposit and its final use. Figure 3 is a flow diagram showing the generalized processing steps.

Material to be processed commonly is transported from the pit face to the processing plant by conveyor or haul truck. The material may be processed to remove lumps of clay, which can plug processing equipment and contaminate the final product. Deposits containing boulders may be fed through a “grizzly” screen to remove boulders too large to go through the crusher. The material is stored in a surge pile. A gate at the bottom of the surge pile releases a controlled amount of sand and gravel to a screen where the sand is separated from the gravel.

Gravel follows one path through the process; sand follows another. If the gravel is larger than about 1 to 1.5 in. (2.5 to 3.81 cm), it is crushed and screened to separate properly crushed particles that go through the screen (“throughs”) from those that go over the screen and back into the crusher (“oversized”). Throughs pass over a series of screens to divide the gravel into specific particle sizes. Gravel may be washed to remove fine particles. Conveyors move the sized gravel to separate stockpiles awaiting sale. Sand is sent to a classifier where it is tailored for its final use (such as asphalt, portland cement concrete, or masonry sand). Waste fines are sent to a settling pond.

Procedures must be followed carefully when stockpiling and handling the final product. The processing of aggregate requires significant effort and cost to prepare a product that meets exacting specifications for grading, freedom from contaminants, and other requirements. Mishandling of aggregate can result in significant degradation of the product (Rollings and Rollings 1996). When aggregate falls too far from conveyors onto coned stockpiles, when it is dumped from trucks down a slope, or when equipment pushes it over long distances, the material can separate from a well-blended product into individual size fractions. Improper handling can also result in contamination of the aggregate with foreign material from underneath the stockpile.

Upon sale, the stockpiled material may be sold as a single-size product, or two or more materials may be blended to make a new, graded product. For example, sand and properly sized gravel may be mixed in specific proportions to be used with cement to make concrete.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Regulations

Sand and gravel mining is permitted or controlled at the federal, state, and local levels of government by numerous governmental agencies (Arbogast 2002). All states are subject to federal law, whether land within state boundaries is federal, state, or privately

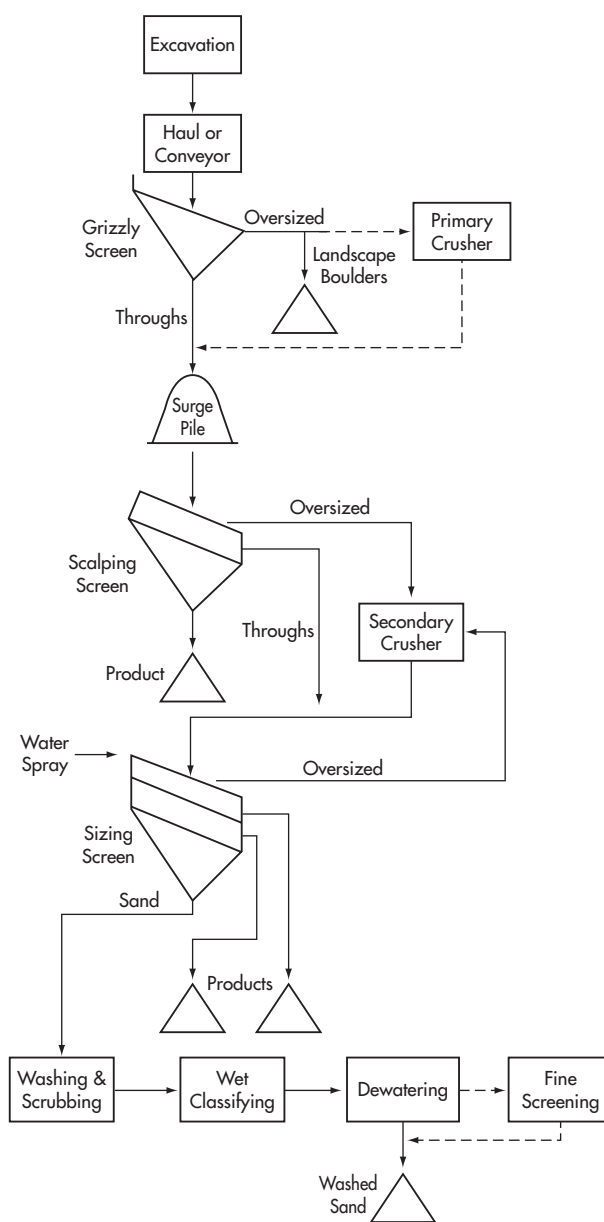


Figure 3. Diagram showing typical sand and gravel processing

owned. Indian tribal lands are considered sovereign and are subject to federal law, but without state jurisdiction or taxation.

Approximately one third of all land in the United States, most of it in the westernmost conterminous states and Alaska, is owned by the federal government. The agencies managing most of those lands are

- Bureau of Indian Affairs
- Bureau of Land Management
- Bureau of Reclamation
- National Park Service
- U.S. Army Corps of Engineers
- U.S. Fish and Wildlife Service
- U.S. Forest Service

The General Mining Act of 1872 encouraged exploration of federal lands for mineral resources, including common minerals. In 1955 Congress removed common construction materials (termed “salable minerals,” including sand and gravel) from the mining law and made them available through a contract or bidding process at the discretion of the land management agency (Arbogast 2002).

The Water Quality Act of 1965 and the Federal Water Pollution Control Act Amendments of 1972 (retitled the federal Clean Water Act) were enacted to provide efficient programs of water pollution control. Every major point source (a confined conveyance such as a pipe, drain, or ditch) from which pollution is discharged into U.S. waters requires a joint federal–state permit (Arbogast 2002).

The Air Quality Act of 1967 (amended by the Clean Air Amendments of 1970) gives states and local governments the responsibility to develop and implement plans to address airborne pollution at its source. Sand and gravel mining activities that are covered include dust and exhaust emissions (Arbogast 2002).

Other federal regulations indirectly control the production of aggregate resources through numerous acts, including the Fish and Wildlife Resource Management Act, the Fish and Wildlife Coordination Act, the Migratory Bird Treaty Act, the Endangered Species Act, including the Rivers and Harbors Act, the Coastal Zone Management Act, and the National Environmental Policy Act. The operation of sand and gravel mining is controlled at the federal level by the Mine Safety and Health Administration (MSHA).

Each of the 50 states has a different process to obtain permission to extract minerals. Some states issue permits for aggregate mining; others leave that authority with local agencies. The result is inconsistent policies among states and between the states and the federal agencies. Commonly, state agencies enforce federal regulations such as air quality, water quality, diversion or impoundment of surface water, and withdrawal of groundwater.

In a review of various state mining laws, Arbogast (2002) found that state laws related to mining vary greatly. At least 37 states regulate non-coal surface mining on a statewide basis. Thirty-five states require some sort of bond or security from the operator. At least 26 states provide for public comment at permit review. Some states have no legislation to regulate sand and gravel mining. In other states, sand and gravel mining is regulated at the local level.

The federal government encouraged state and local governments to create zoning codes through the Standard State Zoning Enabling Act of 1922. The authority of governments to enforce zoning regulations was upheld by the Supreme Court in 1926 in the landmark case of *Village of Euclid, Ohio v. Ambler Realty*. Since then, every state has enacted zoning legislation. Many, but not all, states transfer zoning authority to county or municipal authorities. Some rural areas in the United States, however, remain unzoned.

The United States is made up of more than 3,000 counties and many more local governmental authorities. Counties and other local governments may or may not have final permitting authority for sand and gravel mining. Even where local governments do not have this authority, they commonly influence the final land-use decision by controlling land-use activities such as ground disturbance, grading, noise, traffic, aesthetics, storm water, erosion and sedimentation, land use, building codes, hours of operation, and regulation of utilities. Approval of sand and gravel mining is frequently contingent on these issues (Arbogast 2002).

Environmental Considerations

Two reference documents dedicated to the aggregate industry that address environmental impacts from aggregate mining are by Barksdale (1991) and Smith and Collis (2001). Five comprehensive

collections of individual papers that describe many issues related to aggregate development are the International Association of Engineering Geology (1984), Kelk (1992), Lüttig (1994), Bobrowsky (1998), and Kuula-Väisänen and Uusinoka (2001). These papers, as well as information from other journals, are summarized by Langer (2001a). Langer, Drew, and Sachs (2004) describe potential environmental impacts from aggregate extraction and methods to control those impacts. A study of these reports provides an understanding of the many different environmental impacts related to aggregate mining and also gives a historical perspective of the issues.

Sand and gravel deposits commonly occur in areas that are also favorable for other land uses. Frequently, urban growth occurs without any consideration of the resource below or any analysis of the impact of its loss. Prime aggregate resources are precluded from development if permanent structures such as roads, parking lots, houses, or other buildings are built over them. The value of the improvements probably will permanently prevent any further development of aggregate at those locations. Such a situation is referred to as “sterilization” of the resource. New aggregate operations may have to be located long distances from the markets, and the additional expense of the longer transport of resources must be passed on to consumers. Also, the new deposit may be of inferior quality compared with the original source, yet it may be used to avoid the expense of importing high-quality material from a more distant source. Any savings for aggregate may be offset by increased processing costs or decreased durability of the final product.

In addition to encroaching on aggregate resources, urban growth often threatens established aggregate operations. Some residents in the vicinity of pits and quarries object to the noise, dust, and truck traffic associated with the aggregate operation. Many citizens do not support mining, in part because they do not recognize the dependence of society on aggregate. Personal use of aggregate is very little, if any, and individuals may not recognize aggregate mining as a necessary land use, even though the need for the commodity is constant. For these and other reasons, citizens commonly prefer that stone and sand and gravel not be mined nearby (Langer and Glanzman 1993). This “not in my backyard” syndrome may restrict aggregate development. Furthermore, governments require permits, impose regulations, or establish land-use zones, some of which may preclude mining.

Poulin, Pakalnis, and Sinding (1994) concluded that sterilization, permits, and regulations restrict development or expansion of aggregate production in established areas more than any actual limitations of suitable resource availability. The failure to plan for the protection and extraction of aggregate resources often results in increased consumer cost, environmental damage, and an adversarial relation between the aggregate industry and the community.

Because sand and gravel mining is an extractive industry, it cannot be obtained from the landscape without causing environmental impacts, which are commonly engineering related. These impacts, which include conversion of land use, changes to the visual scene, loss of habitat, erosion, sedimentation, noise, and dust, generally receive the greatest public attention. Many of these impacts, however, are restricted to the mining site, start when extraction begins, occur only as long as extraction and processing take place, and are easy to predict and control using standard engineering techniques.

The extraction of sand and gravel from river and stream terraces, floodplains, and channels commonly attracts additional attention because it may conflict with other resources such as fisheries, aesthetic and recreational functions, or with the need for stable river channels. The floodplains and channels of many rivers and

streams can accommodate the removal of some portion of sand and gravel without creating adverse environmental impacts, provided that the mining activities are kept within the limits set by the natural system. The principal cause of impacts from in-stream and near-stream mining is the modification of natural characteristics beyond what the system can tolerate.

Reclamation

Mining sand and gravel resources creates economic wealth, and the facilities made from aggregate improve the quality of human life. Reclaiming the mine site and associated areas may also create additional wealth and improve the quality of life. Reclamation is a major step in environmental stewardship.

Arbogast, Knepper, and Langer (2000) provide a review of the literature for actual and proposed reclamation sites. In the expanding suburban areas of today, mined-out aggregate pits and quarries are converted into second uses, such as wildlife habitat, recreational areas, agricultural areas, parks, school grounds, high-quality lake-front housing sites, and a myriad of other land uses. A plan for reclaiming the disturbed land and its ecosystem should be a part of every plan to mine natural aggregate.

There is a growing appreciation for the reversionary value of sand and gravel operations. Reclamation is becoming a major factor in sustaining the environment and in creating habitat biodiversity. And the need for specific postmining land uses such as water storage is becoming an important consideration in mining. For example, local municipalities have condemned alluvial land and leased the land to aggregate operations for gravel extraction, with the end goal of creating water storage reservoirs. The postmining land uses are being offered as justification for gravel extraction permits.

OUTLOOK AND FUTURE TRENDS

The U.S. Geological Survey (USGS) calculates future sand and gravel production using a conservative value of 0.5% increase per year. At this rate, sand and gravel production would exceed 1.25 billion tpy by 2025. Even with an increasing market, the USGS anticipates an increasing gap between crushed stone and sand and gravel production with a move toward crushed stone (Tepordei 1997).

In the last few decades, the process to permit new sand and gravel reserves has become increasingly difficult, lengthy, and expensive. Regulations, more than actual resource availability, restrict development or expansion of aggregate in established areas (Poulin, Palkanis, and Sindig 1994). This trend, fueled by increased citizen opposition to disruptive land-use practices, is likely to continue. One area of particular concern is the in-stream mining of sand and gravel because of its potential for widespread environmental impacts; opinions differ on which impacts are the result of mining or other land uses.

The industry trend is toward large businesses with large operations and large output. Acquisitions of such companies are expected to continue, especially as a means to obtain their permitted reserves. Increased costs, combined with local opposition to aggregate operations in populated areas, will likely force the location of new operations into more remote localities. These large centralized plants will utilize rail, barge, or ship transport and will service one or more urban distribution centers. The automation of processing plants and bulk material handling systems will allow for larger production rates at reduced costs.

Imports from Canada and Mexico are likely to increase, but with strong environmental controls to offset the concern of exporting environmental problems from the United States to Canada and Mexico.

Integrated software for permitting, reserve calculations, mine design, mine operation, stockpile management, scalehouse operations, and reclamation have become available at reasonable costs. Machine guidance systems are available that use global positioning satellites to determine the position of excavating equipment with centimeter-level accuracy.

Silicosis is a potential environmental health issue that faces the sand and gravel industry. This disabling, sometimes fatal lung disease afflicts workers that are overexposed to respirable crystalline silica. Silicosis is an occupational disease that is not known to affect the general population. Possible measures to address the issue, in addition to dust control, include employee training on silica hazards, periodic medical exams of potentially silica-exposed workers, and exposure monitoring (Bailey and Sharpe 2003).

There is a slow but inexorable move toward implementation of sustainable resource management principles and best management practices by sand and gravel producers, particularly large U.S. and multinational companies. Sustainable aggregate resource management can be achieved in a practical sense by adopting the following simple principles (after Plant and Haslam 1999).

Planning, project design, approvals assessment, and site conditions should

- Maximize the economic value of the resource, by extracting as much material as possible from the disturbed area and for the most economically valuable use it can accommodate
- Minimize waste of the resource, by a voiding high grading (picking the best parts of the resource and spoiling the ability to extract the remainder) and by finding uses and markets for all of the disturbed material (e.g., turning crusher fines into "manufactured sand," thus reducing the need for natural sand sources in more environmentally sensitive areas; and blending of lower-quality with higher-quality material as long as product specifications can be met)
- Minimize social and environmental impacts, by planning that protects important resources from urban encroachment and protects growing communities from the nuisance impacts of poorly designed, poorly located, and poorly managed aggregate operations; by using best-practice designs and operations to control the effects of blasting, noise, dust, sediment erosion, and visual scarring in extractive and transport operations; and by providing for conservation of natural areas by management of buffer areas that maintain or enhance vegetation, wildlife habitats, and corridors
- Maximize rehabilitation of disturbed areas, by allowing for reclamation as part of the quarry/pit design process before extraction begins; by starting rehabilitation from day one; and by being flexible enough to allow advances in technology and for changing local needs
- Maximize community engagement, by involving the local community in planning activities through open visit days and community awareness and educational activities. (This may lead to a measure of community acceptance and a "social license to operate," which can be just as important as the official legal permits.)

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Crushed Stone

William Langer

INTRODUCTION

Crushed stone is one of the most familiar natural resources used in everyday life and is one of the two principal sources of aggregate. Sand and gravel, the other aggregate source, is discussed in a separate chapter and is only mentioned here when describing both crushed stone and sand and gravel as aggregate.

The purpose of this chapter is to provide a general perspective on the geology of potential sources of crushed stone and on how that material is mined and processed to meet the needs of the construction industry. The transportation, marketing, specifications, and uses of crushed stone are discussed in the Aggregates chapter in this volume.

Most crushed stone is used as construction aggregate, commonly in the form of asphalt or concrete. In many cases it is required for use in asphaltic concrete, because the angular surfaces provide the needed intergranular strength. One km of a four-lane interstate highway requires nearly 50,000 t of aggregate (Langer and Glanzman 1993). The proportional share of aggregate consumed by each person in the United States is about 9 tpy, about 5.2 t of which is crushed stone.

Definition

Crushed stone commonly is produced by drilling, blasting, excavating, and crushing bedrock, although it may involve crushing large boulders or cobblestones. Crushed stone tends to have angular edges, and substantially all of its surfaces have resulted from the crushing operation. It differs from sand and gravel, which tends to be rounded and is naturally occurring.

Unusual Considerations Specific to Crushed Stone

Over six times more aggregate operations exist in the United States than all other types of mines combined (excluding coal). Consequently, crushed stone and sand and gravel operations are a much more common component of the landscape than other mining operations.

The value of most metallic minerals and high-value industrial minerals rests on their properties or combinations of properties, such as hardness, strength, flexibility, electrical properties, and resistance to acids. These minerals have a high "unit value" and commonly can be economically transported significant distances to their market areas. In contrast, aggregate has a high "place value" because it is a high-bulk, low unit value commodity that is expensive to transport

to the market (Bates 1969), so its location (place) is preeminent. Aggregate operations frequently are located near population centers.

Potential sources of crushed stone are undeveloped areas of near-surface bedrock, which often are elevated above surrounding areas and highly visible. These unspoiled bedrock areas frequently are cherished as public "open space," even though the land may be privately owned.

The prevalence of aggregate operations, their proximity to population centers, their visibility, and their inherent disruptive appearance make proposed crushed stone operations ready candidates for citizen opposition. Quarries commonly have a life span greater than 40 years, thus adding to the concerns of nearby residents.

PRODUCTION AND TRADE, SUBSTITUTES, RESOURCES, AND RESERVES

Crushed stone is the largest nonfuel mineral commodity in the United States in terms of volume and value. During 2004, about 1.6 billion t of crushed stone, with a value of nearly \$9.7 billion was produced by an estimated 1,200 companies from about 3,200 surface and underground quarries (Tepordei 2005). Surface quarries are spread out over 47 states, whereas most underground quarries are in the central United States (Tepordei 2002). About 12% of the crushed stone operations produce less than 25,000 tpy of crushed stone. About 14% of the operations produce more than 1 Mtpy of aggregate and account for more than half of the total crushed stone production (Tepordei 2004). The uses of crushed stone are discussed in the Aggregates chapter in this volume.

The aggregate industry does not adhere to a scientific rock classification when describing or reporting production of crushed stone. For example, *limestone* commonly refers to limestone, dolomite, and marble. The coarse-crystalline igneous or metamorphic rocks, whether light colored (such as granite or gneiss) or dark colored (such as gabbro), commonly are referred to as *granite*. The term *traprock* is generally used to describe any fine-grained, dark-colored extrusive igneous rock such as diabase, basalt, or andesite. Following that terminology, limestone made up about 71% of crushed stone production for the year 2000. Granite comprises 15% of crushed stone. Traprock comprises 7%. Other miscellaneous stone, including sandstone and quartzite, account for the remaining 7% (Tepordei 2004).

Crushed stone production, expressed as a percentage of total aggregate production, varies from state to state, depending on a

Table 1. Crushed stone production for the year 2002 by state

State	Crushed Stone Value, \$1,000	Crushed Stone Production, kt	Crushed Stone as Percentage of Total Aggregate Production	State	Crushed Stone Value, \$1,000	Crushed Stone Production, kt	Crushed Stone as Percentage of Total Aggregate Production
Alabama 34	8,000	54,700	80.2	Montana	13,300	3,190	13.6
Alaska	8,400	1,500	11.5	Nebraska	45,200	6,170	33.4
Arizona	56,500	9,280	16.3	Nevada	46,100	9,190	22.1
Arkansas	165,000	32,200	75.6	New Hampshire	20,900	4,760	35.0
California	421,000	63,700	28.9	New Jersey	123,000	17,300	52.9
Colorado	111,000	17,200	27.7	New Mexico	33,300	5,300	32.3
Connecticut	90,900	10,600	48.0	New York	405,000	59,900	67.6
Delaware	—	—	0.0	North Carolina	456,000	63,800	86.1
Florida	600,000	105,000	80.0	North Dakota	withheld	withheld	assumed >1.0
Georgia	445,000	72,100	91.4	Ohio	350,000	77,000	61.6
Hawaii	69,200	7,000	93.3	Oklahoma	172,000	39,200	79.4
Idaho	20,100	4,600	21.4	Oregon	112,000	22,900	54.0
Illinois	450,000	77,600	73.3	Pennsylvania	567,000	97,800	83.9
Indiana	277,000	57,000	67.0	Rhode Island	7,740	1,310	50.6
Iowa	200,000	36,900	72.2	South Carolina	154,000	25,100	72.5
Kansas 10	7,000	21,500	69.5	South Dakota	28,100	5,920	36.1
Kentucky	309,000	55,100	84.5	Tennessee	336,000	56,000	85.3
Louisiana	withheld*	withheld	assumed >1.0	Texas	639,000	126,000	62.1
Maine	24,600	4,190	27.8	Utah	41,500	8,450	21.6
Maryland	137,000	22,500	67.2	Vermont	20,800	4,150	49.5
Massachusetts	125,000	14,800	51.6	Virginia	396,000	60,000	84.7
Michigan	155,000	41,100	35.2	Washington	90,400	14,800	25.2
Minnesota	58,100	9,730	17.7	West Virginia	70,600	16,100	91.2
Mississippi	58,100	5,530	27.1	Wisconsin	135,000	32,200	47.6
Missouri	407,000	79,600	89.4	Wyoming	23,300	4,880	33.8
				United States	8,990,000	1,570,000	58.3

Source: Tepordei 2002; Bolen 2002.

* Withheld to avoid disclosing company proprietary data.

variety of reasons including geology, availability, ease of obtaining permits, local or regional specifications, and operator preferences. Some 26 states produce more crushed stone than sand and gravel. In the United States in general, more crushed stone is produced than sand and gravel (Table 1).

The amount of foreign trade in crushed stone is minor. During 2002, about 2.6 Mt were exported, and about 14.3 Mt were imported. Most trade is with Canada and Mexico.

Total world production of aggregate (including crushed stone as well as sand and gravel) is estimated at 15 billion tpy. Production in the European Union is about 3 billion tpy, representing about two thirds of the European total (Regueiro et al. 2002). Aggregate production rates plummeted in Eastern Europe following the political reorganization of the early 1990s. More recently, production rates have stabilized, resulting in modest increases in demand in countries with emerging economies. Approximate production in other major aggregate-producing countries, in tons per year, is China, 4.5 billion; Japan, 550 million; Russia, 432 million; and Canada, 385 million (Regueiro et al. 2002).

Although crushed stone resources, like all nonrenewable resources, are finite, the potential supply of crushed stone resources on a worldwide scale is so large that "finite" is meaningless. But sources of crushed stone of suitable quality for an intended use can be in short or nonexistent supply on a regional or local scale

because of unfavorable geology, encroachment by incompatible land uses, and inability to obtain the necessary production permits.

A number of materials may be used as a substitute for crushed stone. The most widely used one is sand and gravel. Other common substitutes include recycled concrete or asphalt and slag. An expanded discussion of substitutes can be found in the Aggregates chapter in this volume.

GEOLOGIC ORIGIN AND DISTRIBUTION

Origin

Sedimentary rocks form by consolidation of loose sediment by biochemical, chemical, or mechanical processes. Biologically or chemically deposited carbonate sedimentary rocks form from the remains of living things, such as corals, clams, and other marine organisms that have the ability to secrete calcium carbonate, or they chemically precipitate directly from the water. Carbonate sedimentary rocks commonly used as crushed stone include limestone (calcium carbonate) and dolomite (calcium-magnesium carbonate).

Mechanically deposited (clastic) sedimentary rocks are classified according to the sizes of contained particles. Rock that consists mostly of pebbles and larger fragments is conglomerate; rock that consists mostly of sand-sized particles is sandstone; and rock that consists primarily of silt- or clay-sized particles is siltstone or shale, respectively. Of the clastic sedimentary rocks, hard and

dense sandstone, and to a much lesser amount siltstone and conglomerate, are commonly used for crushed stone.

Igneous rocks form from cooled magma and are classified by their origin and composition. Intrusive igneous rocks solidified at depths within the earth and developed large mineral crystals owing to the slow cooling associated with deep burial. Examples of extrusive igneous rocks with large crystals include granite (light colored) and gabbro (dark colored). Volcanic igneous rocks were extruded onto the earth's surface where they cooled and solidified relatively rapidly. Rapid cooling promoted the formation of only small or microscopic crystals. Examples include rhyolite (light colored) and basalt (dark colored). Many igneous rocks such as those mentioned are hard, tough, and dense, and make excellent crushed stone.

Metamorphic rocks form when existing rocks are subjected to heat and pressure within the earth. Metamorphic rocks that are hard, tough, and dense can be used as aggregate. These include gneiss, marble, hornfels, amphibolite, and quartzite. Some metamorphic rocks, such as highly foliated schist, have planar foliation caused by crystallization of parallel phyllosilicate minerals (micas). This foliation produces planes of weakness that are undesirable in crushed stone. In some parts of the Southwest, the Dakotas, and Wyoming, metamorphic rocks referred to as *clinker* are formed by the heat from in situ coal combustion. In some places clinker is used as aggregate.

Distribution of Major Rock Types

Limestone (using industry terminology) is widely distributed throughout the United States (Figure 1), although its suitability for crushed stone varies greatly. Limestone occurs in the mid-continent from the Great Plains eastward to the western flank of the Appalachian Mountains; the Coastal Plains of Florida, Mississippi, Alabama, Georgia, and South Carolina; the Balcones Escarpment in Texas; the Black Hills of South Dakota and Wyoming; the Great Plains in Kansas and Nebraska; all the western states, including the Rocky Mountains and areas to the west; Alaska; and Hawaii. During 2002, every state in the United States, except Delaware and New Hampshire, produced crushed limestone (Langer 1988).

Granite is widely distributed throughout the United States (Figure 2). It occurs in the Appalachian and Adirondack mountains, northern Minnesota and Wisconsin, the Black Hills of South Dakota and Wyoming, southeastern Missouri, central Arkansas, southern Oklahoma, central and southwestern Texas, all the western states including the Rocky Mountains and areas to the west, and Alaska (Langer 1988). During 2002, 35 states produced crushed granite.

Extensive amounts of traprock occur in the western United States from the eastern flanks of the Rocky Mountains to the west coast (Figure 3). In the eastern United States, traprock generally is restricted to the Triassic/Jurassic basins in the Appalachian Province, primarily in the Connecticut River valley of Connecticut and Massachusetts; the Palisades of New Jersey and New York; the Piedmont of Pennsylvania, Maryland, and northern Virginia; and in Georgia and Alabama (Langer 1988). During 2002, 24 states produced crushed traprock.

PROPERTIES

The properties of crushed stone result from the origin and mineralogy of the source rock and its subsequent alteration and weathering. Some important properties of a rock are the type, size, shape, orientation, and proportions of mineral grains; the type of contacts between the mineral grains; the layering of minerals; and the presence and interconnectedness of voids (Dolar-Mantuani 1983; Langer 2001b). These are all characteristics related to the origin

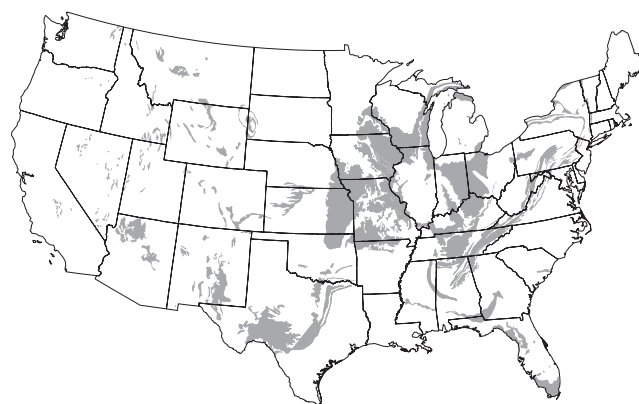


Figure 1. Generalized distribution of limestone in the conterminous United States

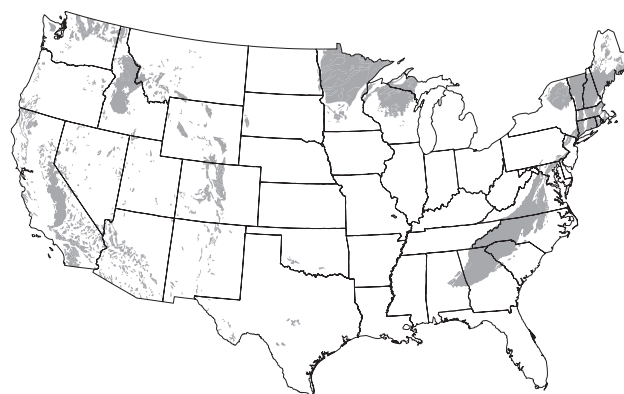


Figure 2. Generalized distribution of granite in the conterminous United States

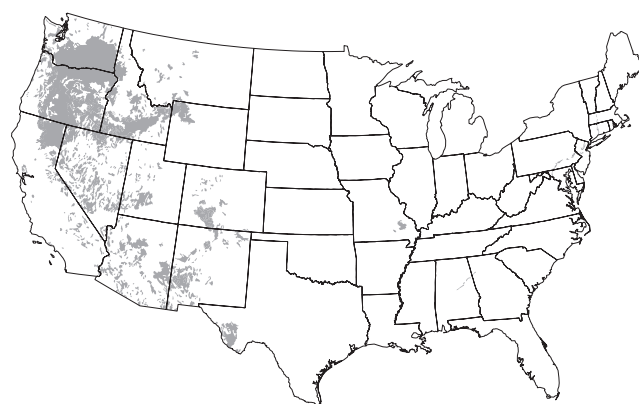


Figure 3. Generalized distribution of traprock in the conterminous United States

and subsequent weathering or alteration of the rock and can be observed and described by traditional geologic methods.

The important properties of the minerals that comprise the rock are hardness and cleavage. Hardness of a mineral commonly is measured by geologists using the Mohs hardness scale, which

refers to the ability of one mineral to scratch the other. Cleavage is the ability of a mineral to break along a fixed crystal plane and varies from “perfect,” as illustrated by the mineral mica, to “none” as found in the mineral quartz.

The quality of crushed stone is most often defined by its conformance to specifications set by the user. Because most crushed stone is used in highway construction, those specifications commonly are set by state departments of transportation. Most states conform to the grading and testing standards set by the American Association of State Highway and Transportation Officials (AASHTO) or the American Society for Testing and Materials (ASTM). An expanded discussion of specifications and testing methods for crushed stone can be found in the Aggregates chapter in this volume.

Physical Properties

When crushed, the stone particles should be strong, which means they should resist abrasion; hard, which means they should resist loads; tough, which means they should resist impact; and sound, which means they should be able to withstand stresses caused by repeated freezing and thawing or wetting and drying (Langer and Knepper 1998; Langer 2001b).

Limestone and dolomite generally make good sources of crushed stone, although some limestone and dolomite may be soft, absorptive, and friable, which results in poor-quality aggregate. Typical compressive strengths for unweathered carbonate rocks range from 2,000 to 37,000 psi (Winkler 1973). The main factors responsible for strength of carbonate rocks are their interlocking grain fabric and their mineralogy. Strength of carbonate rocks generally increases over geologic time because of recrystallization and associated decreasing porosity. Consequently, geologically older carbonate rocks tend to be stronger than younger rocks (Bell 1993). Siliceous limestone and dolomite tend to have higher abrasion resistance than their nonsiliceous counterparts. The low hardness of minerals in younger limestone and dolomite give those rocks low abrasion resistance. Siliceous rocks such as chert have high resistance to abrasion.

Hard, well-cemented, or indurated, quartz-rich sandstone commonly makes an excellent source of crushed stone, although some sandstone may be soft, absorptive, and friable, which results in poor-quality aggregate. Typical compressive strengths for unweathered sandstone range from 5,000 to 36,000 psi (Winkler 1973). The main factors affecting the strength of clastic sedimentary rocks are porosity and the nature and amount of cementation of the grains. Development of mineral orientation in the sediments can result in planes of weakness in the rock. The abrasion resistance of sandstones largely depends on the nature of the cement between the grains.

Hard, tough, and dense, extrusive volcanic rocks commonly make an excellent crushed stone. Typical compressive strengths for unweathered basalt range from 16,000 to 49,000 psi (Winkler 1973). Some volcanic rocks may be unsuitable for aggregate if they are flow-banded, strongly jointed, vesicular, or brecciated. The presence of vesicles tends to reduce resistance to abrasion. If the vesicles are filled, the mineral content of infillings influences the resistance of rocks to abrasion. Pyroclastic volcanic materials such as ash and tuff may be unsuitable for some uses.

Intrusive igneous rocks commonly are hard and strong. Typical compressive strengths for unweathered granitic rocks range from 14,000 to 45,000 psi (Winkler 1973). The high strength results from mineralogy (large amounts of quartz and feldspars), small grain size, and intense grain intergrowth. The main factors that reduce the strength of igneous rocks are large crystal size, a high

proportion of soft minerals such as mica, and weathering or alteration. Weathering may increase the proportion of soft material and may result in destruction of intergranular bonding.

Metamorphic rocks commonly used as aggregate include gneiss, quartzite, and hornfels. These rocks tend to be hard and strong because of interlocking grains and low porosity. Granular quartzite and hornfels have a high abrasion resistance caused by their strong mineral contents. Quartzite is so tough that it commonly causes excessive wear on crushing equipment. The principal factors causing reduced strength of metamorphic rocks are increases in grain size, porosity, proportion of soft minerals, and, in particular, loss of intergranular bonding resulting from the development of strong mineral orientation (schistosity or foliation). Strong mineral orientation can also create a rock with high strength in one direction and low strength in another.

Properties of rock particles that affect soundness are the size, abundance, and continuity of pores, channels, and fractures, together with the degree of water saturation (McLaughlin et al. 1960). Porosity affects the strength and elastic characteristics of rock, and may affect permeability, absorption, and durability. It is generally accepted that there is an approximate inverse correlation between quality, as it pertains to soundness, and rock porosity. Rock with water absorption of 2% or less will usually produce good crushed stone, whereas otherwise suitable rocks with a water absorption that exceeds 4% may not (Smith and Collis 2001).

One of the most important physical properties of rock particles that affect freezing–thawing is the size of the pores. When water turns to ice, it increases in volume by about 9%, thus creating pressure within the pores of a stone. The critical pore size for freeze–thaw durability appears to be about 5 μm (Larsen and Cady 1969). Larger pore diameters allow drainage and escape of water from the frontal ice advance line.

Specific gravity is a general term used to express the relationship of the weight of a substance to the weight of an equal volume of water. Bulk specific gravity is the ratio of the weight of a given volume of material, including all voids, to the weight of an equal volume of water. Apparent specific gravity is the ratio of the weight of a given volume of material, including all impermeable voids, to the weight of an equal volume of water. High specific gravity generally indicates high-quality aggregate. Very low specific gravity frequently indicates aggregate that is porous, weak, or absorptive, although contractors generally favor the lightest stone that will pass specification, because in applications such as concrete or asphalt, aggregate is purchased by the ton while the final product is sold by the yard. Specific gravity of crushed stone is important in some applications that require heavyweight applications.

Other factors contributing to low soundness include the presence of weak, cleavable, absorptive, or swelling particles. Examples of low-soundness rocks include some shales, sandstones, limestones, clayey rocks, some very coarse crystalline rocks, and porous cherts (Neville 1973; Gillott 1980). Weathered rock types, such as weathered igneous rocks where secondary clay minerals are produced, can also be unsound (Fookes 1980). Because the physical properties of the rocks, not their composition, control frost susceptibility, not all the types of rocks mentioned have soundness problems.

Weathering and Impurities

Crushed stone should show no visible signs of weathering. Conduits in the bedrock provide for the passage of water, which in turn accelerates the weathering process. The presence of weathered bedrock increases the overall cost of separating suitable from unsuitable material and affects the blasting and extractive techniques used. The

rate and type of weathering depends on the climatic conditions, the geometry of the deposit, the relationship to the water table, and the properties of the rock. Weathering can range from slight discoloration, through the introduction of fractures and alteration of minerals, to complete decomposition and disintegration of the rock.

Chemical Properties

The chemical properties of crushed stone vary among rock types and are controlled by the mineralogy of the individual particles. Crushed stone generally is considered to be inert, but it may contain certain types of silica minerals that adversely react with the alkaline fluids in cement concrete and affect the life of concrete. Carbonate rock is soluble in weak acids. Certain zeolites release sodium and potassium, thus changing the pore water chemistry. Sulfides oxidize (rust), and salts dissolve or impede setting of concrete. The Aggregates, and Cement and Cement Raw Materials chapters in this volume contain expanded discussions of the physical and chemical properties of aggregates and how they affect their use.

CRUSHED STONE INDUSTRY

Crushed stone must physically be able to be mined and be accessible to transportation systems and to markets. The site must qualify for all necessary land use and environmental permits. The operation must be profitable, considering all costs, including acquisition, operation, compliance with regulations, and reclamation (Drye 1976; Banino 1994). These requirements make opening a new operation a complicated, risky process that involves substantial cost and can take many years.

Prospecting Techniques

The Stone Industries (Bowles 1939) is one of the first comprehensive publications on the stone industry that describes prospecting techniques for potential sources of crushed stone. Exploration for sources of crushed stone has become more than simply locating a source of suitable material and commonly is based on the principle of the "weakest point" (Dunn 1991). During exploration, a weakest point exists that should be analyzed before proceeding to other elements of exploration. For example, it may be unwise to intensely study a potential source of crushed stone in an area where fragmented land ownership makes a new operation highly unlikely. Conversely, it would be equally unwise to thoroughly address all permitting requirements before some estimate of the quality of the rock is determined. Thus, exploration requires judgment and experience and should proceed in a logical sequence. Each weak point should be resolved to an acceptable level of risk before proceeding to the next weakest point (Dunn 1991).

Assessing preliminary target areas for sources of crushed stone exploration should consider favorable geologic terrains as well as economic and social factors such as markets, transportation options, current land use, zoning regulations, and property ownership. Public hearings commonly are held before governmental bodies such as county or town boards, and the public and governmental views toward aggregate production must be carefully analyzed (Dunn 1991).

Exploration for potential sources of crushed stone within the target areas commonly begins with desktop studies utilizing existing data. Detailed geologic maps and cross-sections exist for large parts of the United States and elsewhere, and many of these can be used to help locate potential sources of crushed stone. Other sources of information include test holes and engineering tests of core from highway and other construction projects.

In areas where existing large-scale geologic information and other data are inadequate, or as a supplement to other information,

aerial photography (about 1:50,000 scale or larger), remote sensing (satellite or airborne spectral imagery), and airborne geophysical surveys may be useful for detecting and identifying bedrock outcrops (Knepper, Langer, and Miller 1995).

Preliminary field studies commonly are conducted to check the veracity of desktop analysis and to collect new data. Natural and synthetic exposures are investigated and sampled to determine variations in mineralogy, layering, fractures, weathering, and other rock properties. A geologist may also evaluate the site to identify potential environmental factors and to prepare plans for more detailed site evaluation.

If reconnaissance studies indicate a target area worthy of further investigation, the next steps are more detailed field studies. Acquisition of more detailed information increases costs, and it is appropriate to assess the weakest point at this stage of exploration. For example, economic and social factors, such as current land use, zoning regulations, and property ownership, as well as environmental factors, might be investigated in more detail, particularly because it will be necessary to obtain permission from landowners to access sites for further studies.

Systematic sampling must be conducted to determine the areal extent, thickness, stratigraphic variation, and physical properties of the rock. A variety of truck-mounted drills commonly are used to determine these factors as well as to obtain samples to determine the properties of the rock (Saint Don, Prueher, and Barnwell 2004). Core drilling is the most common type of exploration and should be of a size (after splitting) that allows for testing of the largest product to be mined. The core should be logged and split for testing. The remaining material should be archived as a permanent record.

The spacing of drill holes are site specific and should be based on the predictability and geologic continuity of critical characteristics of the deposit as determined by personnel specially trained in such procedures (Dunn 1991; Timmons 1994). Sample spacing depends on the desired level of detail and confidence of measurements, and typically ranges from 30 m in highly complicated areas to as much as 500 m in large areas of very simple geology. Sampling plans commonly are modified during site characterization based on knowledge gained during the sampling process.

Sedimentary and metamorphic rocks can be highly variable in quality and thickness. A single fault can trigger displacements and change the dips of beds. Many intrusive igneous rocks are difficult to characterize because of subtle changes in mineralogy and the presence of fault or fracture zones. Relatively flat-lying extrusive igneous and homogeneous sedimentary rocks sometimes can be characterized with less robust sampling. In dipping sedimentary rocks, drilling should be as close to perpendicular to the bedding as possible and should have some stratigraphic overlap between holes.

Test holes commonly are measured to determine the depth to the water table. Other observation wells may also be drilled to monitor groundwater conditions.

Seismic geophysical methods have been applied to the investigation of stone resources for more than 65 years (Patterson 1937). Those techniques, as well as other properly conducted surface geophysical surveys, can provide information on the thickness of overburden and can be used to help locate drill holes, provide continuity between drill holes, locate large openings in bedrock, and identify major changes in bedrock types. The surveys can be run in areas where rapid geological changes might be undetected by drilling such as areas of suspected fault zones, areas of steeply dipping bedrock, and areas of other elusive, but important, geologic conditions. The locations and results of the geophysical surveys commonly are included on the geologic maps and accompanying reports prepared for potential crushed stone operation sites.

Table 2. Specific gravities of selected common rocks

Rock Type	Specific Gravity	Rock Type	Specific Gravity
Andesite	2.4 to 2.8	Granite	2.6 to 2.8
Basalt	2.7 to 3.2	Limestone	1.9 to 2.8
Dolomite	2.7 to 2.8	Marble	2.6 to 2.9
Gabbro	2.9 to 3.1	Sandstone	2.0 to 3.2

Source: Adapted from Dunn 1991 and Marek 1991.

Five methods of geophysical surveys can be used to evaluate bedrock sources of crushed stone: seismic, radar, gravity, magnetic, and electrical. None of these techniques is particularly useful for characterizing rocks. They do have engineering applications, however, that can be applied to quarrying. Seismic studies can be used to estimate rippability of stone, to identify weathering zones, and to locate the water table. Radar is routinely used to detect voids and may have application in cavernous limestone areas. Gravity can be used for a qualitative estimate of cavities, joints, or other discontinuities of highly contrasting bedrock. Most rocks considered for use as aggregate do not contain magnetic minerals, but if they do, magnetic surveys may prove useful. Electrical surveys may help identify changes in water content or in some situations identify electrical properties of some rocks.

An experienced field geologist can determine whether or not a geophysical survey is warranted and which methods should be used. The spacing of geophysical survey patterns are site specific and should be based on geologic characteristics of the site and the predictability of continuity of the deposit's critical characteristics as determined by personnel specially trained in such procedures (Dunn 1991; Timmons 1994). Survey plans commonly are modified during site characterization based on knowledge gained during the sampling process.

The results of geophysical surveys are limited because it is not possible to translate geophysical data without correlative evidence normally provided by borings. In addition, geophysical surveys generally provide a very broad guide to the site characteristics and must be refined by other means. Actual subsurface information is desirable so that geophysicists have an idea of how to interpret the results of the surveys.

The geology of a potential crushed stone source must be sufficiently known so that all critical variations in the characteristics of the bedrock and overburden are understood. Geologic mapping is a way of systematizing field observations and is a valuable tool for planning drilling and sampling locations (Dunn 1991), assessing geophysical needs, establishing background data, and identifying potential environmental impacts associated with aggregate development. Geologic maps, accompanying cross sections, and geologic reports of potential sources of crushed stone vary depending on the rock type, but commonly show the location and outline of the rock, the location of sampling sites and geophysical surveys, measurements of the thickness and attitude of rock units, and descriptions of rock properties at depth. Supplemental maps and reports can also describe related issues such as the thickness of overburden, altitude of the water table, geologic hazards, and so forth. In many states, such reports must be prepared by a licensed professional geologist.

The difficulty of calculating volumes of deposits has been greatly eased with the use of specialized mining and quarrying software, geographic information systems (GISs), and computer-aided design (CAD) software. Usable volumes exclude areas of setbacks, access roads and other infrastructure, maintenance facilities, and so

forth. Information obtained during geologic mapping and sampling can be entered directly into these programs, and the programs can calculate resource volumes using various algorithms.

Regardless of how volumes are determined, the *in situ tonnage* of rock is calculated by multiplying the weight of rock per unit volume by the estimated volume. If the weight of the rock is expressed as specific gravity (Table 2), the weight of rock per unit volume can be calculated by multiplying the specific gravity by the weight of water per unit volume. For example: the unit weight of water is 62.4 lb/ft³ (1 t/m³). Assume the specific gravity of basalt is 3.0. The unit weight of basalt is $(62.4 \text{ lb/ft}^3 \times 3.0) = 187.2 \text{ lb/ft}^3$.

The *usable tonnage* of rock is the *in situ tonnage* less the uncoveredable material from waste rock, buffer zones, quarry slopes, haul roads, facility sites, and so forth.

There are numerous methods for appraising crushed stone quarries depending on the purpose of the appraisal and the status of the quarry (Evans 1995; Paschall 1998), but for industrial minerals such as crushed stone, economic and legal issues may be as important as the geologic aspects of a deposit. Companies perform detailed reserve estimates and appraisals for a variety of reasons, including sale or purchase of undeveloped resources or reserves, acquisitions and mergers, valuation of a mining property, accounting, financing, taxation, condemnation, mineral conservation, and for internal planning. Customers can precipitate an analysis of reserves by demanding proof of the existence and quality of reserves before committing to long-term purchase agreements.

Mining

Site preparation commonly starts with grubbing followed by stripping of sufficient overburden to access the resource. Topsoil commonly is separated from the overburden and stockpiled for reclamation activities. Overburden may also be used to construct berms or to be stockpiled or sold. Soil or overburden should not be stockpiled where future extraction is expected, and the final need for reclamation should be considered. Site preparation also includes construction of access roads, fences, berms, haul roads, drainage ditches, culverts, settlement ponds, processing and maintenance facilities, and other plant infrastructure. Quarrying commonly progresses downward on several different levels or "benches," which are formed by drilling, blasting, and excavating rock.

The technology of rock blasting is highly developed. Holes are drilled into the rock and are partially filled with explosives. The top portion of the hole is filled with nonexplosive material (usually sand or crushed stone, sometimes separated from the explosives with a manufactured plug) that is referred to as *stemming*. The explosive in each hole is initiated with detonators or blasting caps. Digital timing, detonator design, or other technology creates delay periods between blasts in individual holes. The total blast commonly lasts only a fraction of a second and consists of many smaller individual blasts separated by delays of a few thousandths of a second. When the explosive is detonated, large volumes of gases are instantly produced, fracturing the rock. The stemming material keeps the expanding gases in the rock in order to maximize the effect. The delay periods between charges ensure that each hole will have to break only the rock immediately in front of it. For example, if two rows of blast holes are parallel to the quarry face, the front row of holes will be detonated first, fracturing and displacing that rock. The back row of holes will then be detonated and will not have to break the rock already displaced by the first round of blasts. In addition, each single blast hole in each row of holes will be detonated separately to reduce ground vibrations from the blast, which may be important when the quarry is near structures.

After the rock is blasted, it is loaded onto trucks or conveyors using conventional earth-moving equipment such as front loaders and track hoes. The blasted material is then transported to the processing facility.

Processing

Processing may be as simple as a portable crusher and screens or can be a highly automated, sophisticated procedure. There are numerous ways to configure equipment, depending on the characteristics of the rock being crushed and its final use. Figure 4 is a flow diagram showing the generalized processing steps.

Rock rubble from the quarry face is dumped into a primary crusher where the large rock fragments are broken into smaller sizes. In some operations, the rubble goes over a large screen (referred to as a “grizzly”) located before the primary crusher. Large material, referred to as the “overs,” is rejected by the grizzly, and smaller material, referred to as “throughs,” goes into the crusher. In other operations, large material is selectively avoided by the loader operator, and the grizzly is located after the primary crusher. The overs are either put back into the primary crusher and broken into smaller pieces, or they are set aside for sale as riprap or armor stone.

The material that comes out of the crusher is moved by a conveyor to a surge pile. A gate at the bottom of the surge pile releases the rock rubble at a constant feed rate to a secondary crusher where it is broken into smaller sizes. Crushing to the proper size usually occurs in stages, because rapid size reduction, accomplished by applying large forces, commonly results in the production of excessive fines (Rollings and Rollings 1996). The crushed stone is screened to sort into size ranges. Particles that are too large go back through the crushing and screening process. After crushing, the material may be washed to remove fines, depending on the type of material being processed and on the final product. After screening, sorting, and washing (if necessary), conveyors move the material to stockpiles.

Procedures must be followed carefully for stockpiling and handling the final product. The processing of aggregate resources requires significant effort and cost to prepare a product that meets exacting specifications regarding grading, freedom from contaminants, and other requirements. Mishandling of aggregate can result in significant degradation of the product (Rollings and Rollings 1996). When aggregate falls from conveyors onto coned stockpiles, when it is dumped from trucks down a slope, or when equipment pushes it over long distances, the material can separate from a well-blended product into individual sizes. Improper handling can also result in contamination of the aggregate with foreign material from underneath the stockpile.

Depending on the crushing and screening process, stockpiled material may consist of a single size of rock clasts or a range of particle sizes. For example, the crushing and screening can be designed to produce a well-graded base course material that ranges from coarse to fine particles, or to produce a single-sized product such as 4 to 2 cm stone. See the chapter on aggregates in this volume for a discussion on transportation, marketing, and uses of crushed stone.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Regulations

Crushed stone quarrying is permitted or controlled at the federal, state, and local levels of government by numerous governmental agencies. All states are subject to federal law, whether land within state boundaries is federal, state, or privately owned. Indian tribal lands are considered sovereign and are subject to federal law, but without state jurisdiction or taxation.

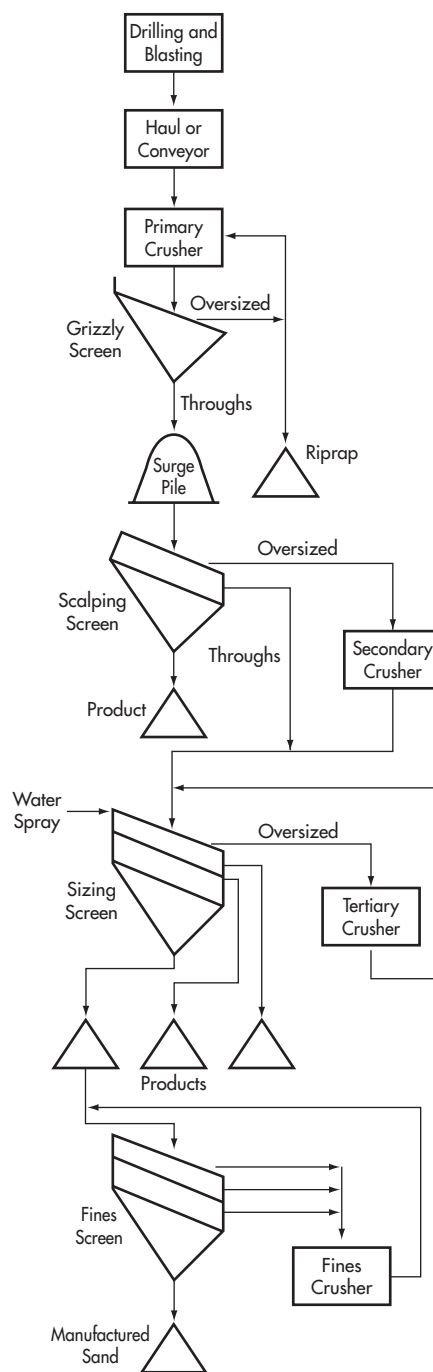


Figure 4. Diagram of crushed stone processing

Approximately one third of all land in the United States, most of it in the westernmost conterminous states and Alaska, is owned by the federal government. The agencies managing most of those lands are:

- Bureau of Indian Affairs
- Bureau of Land Management
- Bureau of Reclamation
- National Park Service

- U.S. Army Corps of Engineers
- U.S. Fish and Wildlife Service
- U.S. Forest Service

The General Mining Act of 1872 encouraged exploration of federal lands for mineral resources, including common minerals. In 1955 Congress removed common construction materials (termed "saleable minerals," including crushed stone) from the mining law and made them available through a contract or bidding process at the discretion of the land management agency (Arbogast 2002).

The Water Quality Act of 1965 and the Federal Water Pollution Control Act Amendments of 1972 (retitled the Clean Water Act) were enacted to provide efficient water pollution control. Every major point source (a confined conveyance such as a pipe, drain, or ditch) from which pollution is discharged into U.S. waters requires a joint federal-state permit (Arbogast 2002). Crushed stone quarrying activities that are covered include quarry runoff and discharges from settlement ponds and quarry dewatering.

The Air Quality Act of 1967 (amended by the Clean Air Act Amendments of 1970) gives states and local governments the responsibility to develop and implement plans to address airborne pollution at its source. Crushed stone quarrying activities that are covered include dust and exhaust emissions (Arbogast 2002).

Other federal regulations indirectly control the production of aggregate resources through numerous acts, including the Fish and Wildlife Resource Management Act, the Fish and Wildlife Coordination Act, the Migratory Bird Treaty Act, the Endangered Species Act (including the Rivers and Harbors Act), the Coastal Zone Management Act, and the National Environmental Policy Act. The operation of crushed stone quarrying is controlled at the federal level by the Mine Safety and Health Administration (MSHA).

Each of the 50 states has a different process for obtaining permission to extract minerals. Some states issue permits for aggregate mining; others leave that authority with local agencies. The result is inconsistent policies among states and between the states and federal agencies. Commonly, state agencies enforce federal regulations such as air quality, water quality, diversion or impoundment of surface water, withdrawal of groundwater, and water quality.

In a review of various state mining laws, Arbogast (2002) found that at least 37 states regulate non-coal surface mining on a statewide basis. Thirty-five states require some sort of bond or security from the operator. At least 26 states provide for public comment at permit review. Some states have no legislation to regulate crushed stone quarrying. In some states, crushed stone quarrying is regulated at the local level.

Through the Standard State Zoning Enabling Act of 1922, the federal government encouraged state and local governments to create zoning codes. The authority of governments to enforce zoning regulations was upheld by the Supreme Court in 1926 in the landmark case of *Village of Euclid, Ohio v. Ambler Realty*. Since then, every state has enacted zoning legislation. Many, but not all, states transfer zoning authority to county or municipal authorities. Some rural areas in the United States, however, remain unzoned.

The United States is made up of more than 3,000 counties and many more local governmental authorities. Counties and other local governments may or may not have final permitting authority for crushed stone quarrying. Even where local governments do not have this authority, they commonly influence the final land-use decision by controlling land-use activities such as ground disturbance, grading, noise, traffic, aesthetics, storm water, erosion and sedimentation, land use, building codes, hours of operation, and regulation of utilities. Approval of crushed stone quarrying is frequently contingent on these issues (Arbogast 2002).

Environmental Considerations

Two reference documents dedicated to the aggregate industry that address environmental impacts from aggregate mining are by Barksdale (1991) and Smith and Collis (2001). Five comprehensive collections of individual papers that describe many issues related to aggregate development are by the International Association of Engineering Geology (1984); Kelk (1992); Lüttig (1994); Bobrowsky (1998); and Kuntz, Väisänen, and Uusinoka (2001). This information on the environmental impacts of aggregate mining, plus references from other journals, is summarized by Langer (2001a) and Langer, Drew, and Sachs (2004). A study of reports in these papers provides an understanding of the many different environmental impacts related to aggregate mining and gives a historical perspective of the issues.

Potential environmental impacts—such as visual changes, noise, dust, runoff, sedimentation, and impacts to groundwater and surface water—may occur with any type of aggregate operation. Most environmental impacts associated with crushed stone operations are relatively benign because aggregates are environmentally inert materials and their processing commonly does not involve the use of hazardous chemicals. Furthermore, environmentally sound and safe aggregate operations effectively manage physical disturbances, protect ground- and surface waters, control noise and dust, use safe blasting procedures, and have long-term operation and closure plans that recognize habitat and community needs.

Some of the most frequent concerns associated with crushed stone operations are the noise, dust, and ground vibrations associated with blasting, which may be daily or as infrequently as once or twice a year. A small amount of energy from a blast is released as vibrations through and along the surface of the earth and through the air. Extensive research by the former U.S. Bureau of Mines resulted in ground vibration standards that have become industry standards for safe blasting. Levels of ground vibration from blasting for residential structures that can limit damage to the type that develops in all homes, independent of blasting, range from 0.5 to 1.0 in./sec (1.27 to 2.54 cm/sec) peak particle velocity (Stagg et al. 1984). Some energy from a quarry blast escapes into the atmosphere and causes audible noise as well as subaudible airblast, which is also referred to as air concussion. Airblast is most noticeable within a structure, particularly when windows and doors are closed, and frequently is mistaken as ground vibrations. U.S. Bureau of Mines research demonstrated that airblasts with an intensity of 134 dB (2 Hz) produce wall vibrations equivalent to that from a 0.5-in./sec (1.27-cm/sec) ground vibration (Siskind et al. 1980). Airblasts are less likely to crack walls than ground vibration because of the differences between the mechanics of vibrations from airblasts versus those from ground shaking.

Blast design parameters, which include maximum instantaneous charge; delay timing; hole diameter, spacing, and orientation; amount and type of stemming; and burden (the material between the face of the quarry and the first row of blast holes) can be altered to limit levels of ground vibration and airblast. Alternative rock-breaking techniques, such as ripping with heavy equipment or hydraulic fracturing, can be considered. Blasting times can be scheduled to coincide with periods of high activity rather than when people are relaxing in their homes.

Reclamation

The primary goal of reclamation is to return the land to a beneficial second use. Reclaimed pits or quarries have been converted to diverse uses, including lakefront property, recreational areas, wildlife areas, botanic gardens, golf courses, agricultural areas,

industrial and commercial properties, office parks, and landfills. Reclamation frequently is planned before mining begins, although less often with crushed stone operations than with sand and gravel operations because of the long period of time between opening and closing of stone quarries. Arbogast, Krepper, and Langer (2000) describe many reclamation options.

OUTLOOK AND FUTURE TRENDS

The U.S. Geological Survey (USGS) calculates future crushed stone production using a conservative value of 1.0% increase per year. At this rate, crushed stone production would be nearly 2 billion tpy by 2025. The USGS anticipates an increasing gap between crushed stone and sand and gravel production with a move toward crushed stone (Tepordei 1997).

Over the last few decades, the process to permit new crushed stone reserves has become increasingly difficult, lengthy, and expensive. Regulations, more than actual resource availability, restrict development or expansion of aggregate operations in established areas (Poulin, Pakalnis, and Sindig 1994). This trend, fueled by increased citizen opposition to disruptive land-use practices, is likely to continue.

The industry trend is toward large businesses with large operations and large output. Acquisitions of such businesses are expected to continue, especially as a means to obtain their permitted reserves. Increased costs, combined with local opposition to aggregate operations in populated areas, will likely force the location of new operations into more remote localities. Large centralized plants may take greater advantage of rail, barge, or freighter transport and will service one or more urban distribution centers. The automation of processing plants and bulk material handling systems will allow for higher production rates at reduced costs.

Imports of crushed stone from coastal Canada and Mexico to Atlantic, Pacific, and Gulf coastal ports are likely to increase, but with strong environmental controls to offset the concern of exporting environmental problems from the United States to Canada and Mexico.

Integrated software for permitting, reserve calculations, mine design, mine operation, blast-hole designs, blasting seismic records, stockpile management, scalehouse operations, and reclamation have become available at reasonable costs. Machine guidance systems are available that use global positioning satellites to determine the position of excavating equipment with centimeter-level accuracy.

Naturally occurring asbestos in mineral deposits, including some types of crushed stone, and the release of asbestos fibers into the air are potential environmental health concerns that face the crushed stone industry (Bailey 2004). Issues relevant to the industry are how to identify, measure, and prevent exposure to asbestos-form minerals. Crystalline silica is another potential environmental health issue that the aggregate industry faces, especially in crushed stone. Possible measures to address these issues, in addition to dust control, include employee training on asbestos and silica hazards, periodic medical exams of potentially exposed workers, and exposure monitoring (Bailey and Sharpe 2003).

There is a slow but inexorable move toward implementation of sustainable resource management principles (Langer, Guisti, and Barelli 2003) and best management practices by sand and gravel producers, particularly by large U.S. and multinational companies. Sustainable aggregate resource management can be achieved in a practical sense by adopting the following simple principles (after Plant and Haslam 1999).

Planning, project design, approvals assessment, and site conditions should

- Maximize the economic value of the resource: by extracting as much material as possible from the disturbed area and for the most economically valuable use it can accommodate
- Minimize waste of the resource: by avoiding high grading (picking the best parts of the resource and spoiling the ability to extract the remainder) and by finding uses and markets for all of the disturbed material (e.g., turning crusher fines into “manufactured sand,” thus reducing the need for natural sand sources in more environmentally sensitive areas; and blending of lower-quality with higher-quality material while meeting product specifications)
- Minimize social and environmental impacts: by planning to protect important resources from urban encroachment and protect growing communities from the nuisance impacts of poorly designed, poorly located, and poorly managed aggregate operations; by using best-practice designs and operations to control the effects of blasting, noise, dust, sediment erosion, and visual scarring in extractive and transport operations; and by providing for conservation of natural values by management of buffer areas that maintain or enhance vegetation, wildlife habitats, and corridors
- Maximize rehabilitation of disturbed areas: by allowing for reclamation as part of the quarry/pit design process before extraction begins; by starting rehabilitation from Day One; and by being flexible enough to allow for advances in technology and for changing local needs
- Maximize community engagement: by involving the local community in planning activities through open visit days and community awareness and educational activities (this may lead to a measure of community acceptance and a “social license to operate,” which can be just as important as the official, legal permits)

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Lightweight Aggregates

Alfred L. Bush, Dennis P. Bryan, and Daniel R. Hack

INTRODUCTION

Lightweight aggregates are those minerals, natural rock materials, products, and by-products of manufacturing processes used as bulk fillers in lightweight structural concrete, concrete masonry units, precast concrete structural products, road-surfacing materials, plaster aggregates, and insulating fill. Other uses include architectural wall covers, suspended ceilings, lightweight structural fill, soil conditioners, and other agricultural uses (Mason 1994).

Separate commodity chapters elsewhere in this volume discuss aggregates in general, as well as individual commodities that comprise lightweight aggregates, such as common clays and shale, crushed stone, perlite, pumice, scoria, vermiculite, and volcanic cinders. In addition, Chandra and Berndtson (2003) is an excellent reference book on this topic.

LIGHTWEIGHT AGGREGATE TYPES

Most lightweight aggregates are mineral raw materials; the remainder are waste or synthetic products (Mason 1994). Lightweight aggregate materials are generally classified into four groups:

1. Natural lightweight aggregate materials—prepared by crushing and sizing natural rock materials such as pumice, scoria, tuff, breccia, and volcanic cinders.
2. Manufactured structural lightweight aggregates—prepared by pyroprocessing shale, clay, or slate in rotary kilns or on traveling grate sintering machines.
3. By-product lightweight aggregates—prepared by crushing and sizing foamed and granulated slag, organic cinders, and coke breeze. Other by-product lightweight aggregates in use include coal combustion by-products (fly ash and bottom ash), flue gas desulfurization by-products resulting from manufacturing processes, or other waste products. This group, with the exception of slag, has continued to decline in popularity and is not discussed here.
4. Manufactured insulating ultra-lightweight aggregates—prepared by pyroprocessing ground vermiculite and perlite (Mason 1994).

This chapter covers the use of both natural lightweight aggregates and manufactured insulating ultra-lightweight aggregates and focuses on the production and use of manufactured structural lightweight aggregates. Organic products such as rice hulls, straw, and peat have been used as lightweight aggregate, but they are quantitatively insignificant and are not discussed here.

STRUCTURAL LIGHTWEIGHT AGGREGATES

Lightweight aggregates—both natural and manufactured, and suitable for structural uses—should have low bulk density yet suitable strength characteristics to pass on to the end product. For the most part these end uses are concrete products such as portland cement concrete or concrete masonry units, both of which are used extensively in structures of various kinds. Heat treatment usually results in relatively thick pore walls (compared to void diameter) that give the aggregates suitable compressive strengths. The porosity of all these aggregates results from heat treatment, either naturally or artificially induced. A porous but relatively impermeable texture not only makes these materials lightweight but also makes them both thermal and acoustic insulators, desirable for bulk use in floor and roof fill and with an added advantage of saving weight in concrete (Bush 2001).

Higher strength and increased weight go together. Compressive strength, for example, ranges from about 1,200 psi (8.3×10^6 Pa) for 60 lb/ft³ (960 kg/m³) pumice aggregate concrete to more than 6,000 psi (42×10^6 Pa) for 120 lb/ft³ (1,920 kg/m³) expanded (sintered) shale concrete. In this broad range, lightweight aggregate concretes can be used for bridge decks; concrete walls and floors; concrete frames using precast, prestressed, or post-tensioned girders; precast tilt-up panels; poured barge and ship hulls; and lightweight concrete masonry units. In bulk form, the aggregates are also sometimes used as railroad ballast, as highway and embankment fill, and in the surface course of bituminous paving mixtures (Bush 2001).

The distinction between normal-weight and lightweight aggregates is about 75 lb/ft³ (1,200 kg/m³) for loose-graded coarse aggregate (between approximately ¾ in. and #4 sieve size). Most lightweight aggregates used for structural purposes are in the range of 35 to 60 lb/ft³ (560 to 960 kg/m³); those used for nonload-bearing purposes (ultra-lightweight aggregates) are in the range of 5 to 20 lb/ft³ (80 to 320 kg/m³). In contrast, most normal-weight aggregates such as crushed stone, and sand and gravel, are in the range of 70 to 110 lb/ft³ (1,150 to 1,700 kg/m³) (Bush 2001). Low-density lightweight aggregates are used primarily for insulation, and they have relatively low compressive strength. The middle-density aggregates are used for insulation and for fill. Those at the upper end develop excellent compressive strength and are used in many structural applications (Mason 1994). Dry weights for various lightweight aggregates are given in Table 1.

Table 1. Dry weights for various lightweight aggregates

Aggregate Type and Size Designation	Dry Loose Weight, maximum, kg/m ³ (lb/ft ³)
Structural lightweight aggregate	
Fine aggregate, 4.75 mm (No. 4) to 0	1,120 (70)
Coarse aggregate, 9.75 to 2.36 mm (3/8 in. to No.8)	880 (55)
Combined fine and coarse aggregate	1,040 (65)
Vermiculite	160 (10)
Perlite	196 (12)

Table 2. Grading requirements for lightweight aggregates (in percentages, by weight, passing sieves with square openings)*

Size Designation	25.0 mm	19.0 mm	12.5 mm	9.5 mm	4.75 mm	2.36 mm	1.18 mm	0.29 mm	0.149 mm
Lightweight Aggregates for Structural Concrete (ASTM C330-04)									
Fine aggregate									
4.75 to 0 mm				100	85–100		40–80	10–35	5–25
Coarse aggregate									
25.0 to 4.75 mm	95–100		25–60		0–10				
19.0 to 4.75 mm	100	90–100		10–50	0–15				
12.5 to 4.75 mm		100	90–100	40–80	0–20	0–10			
9.5 to 2.36 mm			100	80–100	5–40	0–20	0–10		
Combined fine and coarse aggregate									
12.5 to 0 mm		100	95–100		50–80			5–20	2–15
9.5 to 0 mm			100	90–100	65–90	35–65		10–25	5–15
Lightweight Aggregates for Concrete Masonry Units (ASTM C331-04)									
Fine aggregate									
4.75 to 0 mm				100	85–100		40–80	10–35	5–25
Coarse aggregate									
12.5 to 4.75 mm		100	90–100	40–80	0–20	0–10			
9.5 to 2.36 mm			100	80–100	5–40	0–20	0–10		
Combined fine and coarse aggregate									
12.5 to 0 mm		100	95–100		50–80			5–20	2–15
9.5 to 0 mm			100	90–100	65–90	35–65		10–25	5–15

* Blank spaces in this table indicate no specification given for this size range.

Most structural lightweight aggregate can make concrete weighing from 100 lb/ft³ (1,575 kg/m³) to 125 lb/ft³ (2,000 kg/m³). Exfoliated vermiculite and expanded perlite are sometimes referred to as *super* or *ultra-lightweights*. Insulating concrete (nonload-bearing) weighing as little as 15 lb/ft³ (240 kg/m³) can be made with these aggregates.

The principal properties desired in materials used as lightweight aggregates vary according to end use, but normally include the following (Mason 1994):

- Light weight—reduces dead load (weight in place) and facilitates the physical handling of the materials
- Strength—maintains the structural integrity of the end product, such as in concrete products
- Thermal and acoustical properties—normally the result of air spaces, voids, or pores in the lightweight aggregate materials
- High fire resistance—low probability of physical breakdown at temperatures below the melting point of the aggregate
- Toughness—minimum tendency to crack or break if nailed or stressed in construction use

Other properties that are sometimes considered desirable, depending on the application, include the following:

- Low water absorption
- Resistance to freezing and thawing
- Low shrinkage characteristics and minimum thermal expansion

- Good bonding with cement
- Chemical inertness
- Good elastic properties
- Abrasion resistance

The actual specifications and tolerances vary according to the end use or final product in which the lightweight aggregate is consumed. The American Society for Testing and Materials (ASTM) compiles specifications for various lightweight aggregate materials by use and standards can be consulted as required. Grading requirements for lightweight aggregates, based on ASTM C 330-04 and ASTM C 331-04, are given in Table 2. Grading requirements for lightweight aggregates for insulating concrete, based on ASTM C332-99, are given in Table 3. ASTM standards C330-04 (*Standard Specification for Lightweight Aggregates for Structural Concrete*), C331-04 (*Standard Specification for Lightweight Aggregates for Concrete Masonry Units*), and C332-99 (*Standard Specification for Lightweight Aggregates for Insulating Concrete*) are the most relevant for most lightweight aggregate materials (Mason 1994; J.P. Ries, personal communication). In addition, an ASTM special publication (Klieger and Lamond 1994) covers the significance of tests and properties of concrete-making materials.

Natural lightweight aggregates are mostly bulky, have low unit value, and normally serve local and regional markets. Some structural lightweight aggregates, however, are economically

Table 3. Grading requirements for lightweight aggregates for insulating concrete (ASTM C332-99) (in percentages, by weight, passing sieves with square openings)[†]

Size Designation	19.0 mm	12.5 mm	9.5 mm	4.75 mm	2.36 mm	1.18 mm	600 µm	600 µm	600 µm
Group I (Ultra-Lightweight)									
Perlite				100	85–100	40–85	20–60	5–25	0–10
Vermiculite—coarse [†]			100	98–100	60–100	30–85	2–45	1–20	0–10
Vermiculite—fine					100	85–100	35–85	2–40	0–10
Group II									
Fine aggregate									
4.75 to 0 mm			100	85–100		40–80		10–35	5–25
Coarse aggregate									
12.5 to 4.75 mm	100	90–100	40–80	0–20	0–10				
9.5 to 2.36 mm		100	90–100	5–40	0–20				
4.75 to 2.36 mm			100	90–100	0–20				
Combined fine aggregate and coarse aggregate									
12.5 to 0 mm	100	95–100		50–80				5–20	2–15
9.5 to 0 mm	100	90–100	65–90	35–65			10–25	5–15	

* Blank spaces in this table indicate no specification given for this size range.

† Adjustment needed in water content and air entrainment to get comparable oven-dry unit weights for the two gradings.

Table 4. Domestic production of lightweight aggregate, 1990–2002, kt

Type of Aggregate	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
Clay [†]													
USBM–USGS	3,804	3,599	3,400	3,530	3,753	4,170	4,060	3,997	4,170	3,935	3,850	3,869	4,010
ESCSI [‡]	4,063	3,702	3,764	3,814	4,187	4,490	4,612	4,806	5,087	5,336	5,284	5,044	4,647
Slag [§]													
Air-cooled	13,741	10,889	12,711	10,477	10,700	12,000	12,175	10,100	10,300	8.9	8.9	8.1	7.4
Expanded ^{**}	1,315	2,404	1,737	1,864	1,600	1,810	1,680	1,760	1,920	1.9	2.3	2.3	3.7 ^{††}
Volcanic cinders and scoria	3,560	2,039	2,000 ^{††}	2,088	1,994	1,880	2,070	2,240	2,510	2,060	1,840	2,130	1,910
Pumice and pumicite ^{§§}	443	401	461	469	490	529	612	577	872	1,000	1,050	920	956
Perlite ^{***}	576	514	541	569	644	700	684	706	685	711	672	588	521
Vermiculite ^{†††}	209	180	190	190	180	171	>147 ^{††}	>147 ^{††}	147	152	150 ^{††}	115 ^{††}	110 ^{††}

Adapted from USBM and USGS *Minerals Yearbooks* and *Mineral Commodity Summaries*; *Industrial Minerals*; *Mining Engineering*.

* All data are for material sold or used.

† Common clay, in some cases, may include minor amounts of ball clay.

‡ Data from Expanded Shale, Clay, and Slate Institute (ESCSI); total North American production (Canada varies from 1% to 10%; 1% for 2002); J.P. Ries, personal communication.

§ Data based on sales through 1998 reported in kilotons; from 1999 on, in megatons.

** 1990–2001 data include both granulated (major component) and expanded slag, to conceal company proprietary information; 1999–2002 data in megatons.

†† Granulated slag. Expanded (mostly pelletized) slag not included; production about 200,000 t.

††† Estimated.

§§ Data revised from USGS *Minerals Yearbook* and *Mineral Commodity Summaries*.

***Unexpanded, data revised from USGS *Minerals Yearbooks*.

††††Unexfoliated, data revised from USGS *Minerals Yearbooks*.

shipped long distances because the density of these aggregates are one half to one third the density of locally available normal-weight aggregates such as crushed stone, sand, and gravel, and any comparison between lightweight and normal-weight aggregates should be made on a volume basis. For example, lightweight aggregate may be four times as expensive per ton as local normal-weight aggregate but can yield two to three times its volume. One ton of lightweight aggregate will normally make two to three times as much concrete end product as 1 t of normal-weight aggregate.

Products such as pumice or expanded slag may be used in substantial quantities in some localities and may not even be available (at competitive prices) in others. Perlite and vermiculite depos-

its are limited in location but serve national markets because of their relatively high market value and because their ores are shipped before pyroprocessing and physical expansion. Most pyroprocessing and expansion plants reflect specialty uses in regional and national markets. The more specialized uses command higher market prices that lead to extensive geographic distribution and use (Mason 1994).

Table 4 summarizes the annual output of lightweight aggregate in the United States for the period 1990 to 2002 by quantity, and Table 5 summarizes the stated values of lightweight aggregate production for the same period. Note that there is a qualification on the data for vermiculite (see the section on expanded vermiculite

Table 5. Value of domestic lightweight aggregate production, 1990–2002 (values in thousands of 1996 dollars, 1990–1998; in millions of dollars, 1999–2002; italicized values are unit price per metric ton)

Type of Aggregate	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
Clay													
USBM-USGS	7.60	8.34	8.34*	8.34*	10.43	10.43*	12.11	14.63	15.20	16.59	13.40	13.62	13.69
	28,918	30,014	28,348	36,095	39,100	50,500	51,200	56,400	63,400	65.2	51.6	52.7	54.9
ESCSI†	25.75	26.42	27.10	27.39	28.50	29.23	29.99	30.75	31.54	32.35	33.18	34.03	34.9
	104,622	97,807	102,004	105,991	119,330	131,243	138,914	147,785	160,444	172.6	175.3	171.6	162.2
Slag													
Air-cooled	77,863	66,393	74,526	61,685	62,400	68,200	67,500	67,800	83,100	58.3	59.0	56.0	55.0
Expanded‡	26,448	43,484	37,000	41,943	51,100	53,700	52,400	53,800	64,400	62.2	62.0	56.0	210.0§
Volcanic cinders and scoria	3.51	6.29	6.50	6.43	5.87	6.38	6.52	6.65	6.18	6.31	7.45	6.39	7.38
	12,600*	12,828	13,000*	13,435	11,700	12,000	13,500	14,900	15,500	13.0	13.7	14.7	14.1
Pumice and pumicite	24.13	22.90	30.99	25.68	24.08	24.99	24.19	27.90	16.30	19.80	18.00	21.44	20.69
	10,688	9,190	14,900	12,000	11,800	13,200	14,800	16,100	14,200	19.8	18.9	19.7	19.8
Perlite**	169.91	169.71	200.98	196.11	193.40	193.30	204.17	204.29	159.89	202.46	206.99	212.83	216.62
	88,014	90,625	101,695	111,000	123,000	127,000	137,000	143,000	148,000	146.0*	146.0*	146.0	146.0*
Vermiculite††	268.03	283.82	327.86	333.57	335.38	303.08	335.56	318.71††	313.53††	316.00††	322.42††	342.86††	390.43††
	39,400	38,600	45,900	46,700	43,600	39,400	45,300	49,400*††§§	53,300*††	55.3*††	53.2*††	48.0*††	44.9*††

Adapted from USBM and USGS *Minerals Yearbooks*, except where noted.

* Estimated.

† ESCSI, J.P. Ries, personal communication.

‡ Includes both granulated and expanded slag, to conceal company proprietary data. After 2001, includes imported slag, ground and granulated in the United States.

§ Value of expanded slag (mostly pelletized, and about 200,000 t of foamed slag).

** Expanded perlite sold and used.

†† Expanded vermiculite sold and used.

‡‡ Based on limited USGS data.

§§ Based on Table 1 data.

Table 6. Average unit value of lightweight aggregate materials at production plants (values per metric ton)

Material Type	1990*	2002†
Exfoliated vermiculite	\$230.00	\$390.00
Crude vermiculite (concentrate)	142.00‡	133.00
Expanded perlite	209.00	217.00
Crude perlite (ore)	34.24	36.45
Expanded clay, shale, and slate	40.00§	34.90**
Clay and shale (raw)	11.50	6.43
Expanded slag	13.00	35.00††
Pumice and pumicite	24.00	20.71
Volcanic cinders and scoria	5.60‡‡	7.39

* From Mason (1994), except estimated values.

† Adapted from USGS *Minerals Yearbook and Mineral Commodity Summaries*, except as noted.

‡ Compare with 1998 data, Table 4 in Mason (1994).

§ Compare with ESCSI data: \$25.75.

** ESCSI data.

†† Value estimated by T. Wagaman, personal communication.

‡‡ Estimated.

under Ultra-Lightweight Aggregates in this chapter). Table 6 contrasts the average unit value of lightweight aggregate materials at production plants in 1990 and 2002. In recent years, significant price increases for expanded perlite and exfoliated vermiculite gave them a large share of the market in terms of value (approximately 32% in 2002) despite contributing only about 5% of the tonnage. Expanded shale, clay, and slate are widely used. In 2002 they accounted for about 39% of the total quantity and 27% of the value.

NATURAL LIGHTWEIGHT AGGREGATES

The “classic” types of natural lightweight aggregates are pumice and volcanic cinder. Aggregate for lightweight concrete is produced by mining, crushing, and screening to appropriate size. Other types of natural lightweight aggregates are also volcanic rocks such as tuffs, breccias, or pumiceous rhyolites and are found in recent volcanic terranes throughout the western United States.

Some lightweight material in use may be a manufactured product derived from an ore or raw material that is a natural mineral resource. For example, raw materials for lightweight aggregates can be iron ore and flux stone (the components of blast furnace slag); coal (the raw material from which cinders are derived); and shale, clay, and slate (which expand at elevated temperatures; Mason 1994). Even though these may originate as natural products, because heating results in dramatic physical changes, they are considered a manufactured lightweight aggregate.

Various volcanic rocks worldwide are suitable for use as lightweight aggregates; all are extrusive ejecta that range in composition from mafic to silicic. Scoria and volcanic cinder (both mafic) and pumice (silicic) make moderate-to-low strength structural aggregates; expanded perlite is an ultra-lightweight material. Water content in basalt is little different from that in scoria and cinder, but the difference between water in rhyolite and that in silicic glassy rocks is significant. An excess of water allows perlite to be thermally expanded. In a general way, viscosity of extruded rock melt varies directly with the SiO₂, Na₂O, and K₂O content and inversely with the Fe₂O₃, FeO, CaO, and MgO content; the mafic rocks are more fluid and the silicic rocks are more likely to retain gases.

Pumice

Pumice is used both as structural lightweight aggregate and sometimes as ultra-lightweight aggregate. It is lighter colored, of lower density, and more highly cellular than scoria and cinder. Naturally

occurring lightweight aggregate raw materials such as pumice and volcanic cinders are normally mined by open-pit or quarry methods, depending on the degree of consolidation of the raw materials. Mining costs are similar to those for sand and gravel except where substantial blasting and crushing are required. In the latter case, production costs parallel those for crushed stone (Mason 1994). Pumicite, a fine, glassy volcanic ash that historically has been used for similar applications as pumice, is usually discussed as part of the pumice family in the literature. It has not, to the authors' knowledge, been used to any extent as a lightweight aggregate in construction applications and therefore is not discussed here.

Pumice selling prices are approximately two to three times those of sand, gravel, and crushed stone, and have ranged from \$9.35/t (1986) to \$20.71/t (2002). A 20-city average price for gravel and crushed stone (19×9.5 mm) is \$9.68/t and \$6.88/t, respectively, as reported in December 2003 (*Engineering News-Record* 2003). Prices for domestic output of pumice for 1990 through 1997 ranged from \$22.60/t (1991) to \$30.98/t (1992) and averaged \$25.66/t. From 1998 through 2002, prices ranged from \$16.30/t (1998) to \$21.44/t (2001) and averaged \$19.50/t; for the entire 14-year period, the average was \$22.32/t.

Domestic output of pumice has increased steadily in recent years, from a low of 356 kt in 1987 to a high of 1,050 kt in 2000. It has hovered in the 900- to 1,000-kt range since 1999.

Pumice occurs throughout the western United States from the Rocky Mountains to the Pacific Ocean. Domestic producers increased in number from 8 in 1990 to nearly double that by 2000; and in 2002, at least 15 mines were operated in the United States, with Oregon being the leading pumice producer, followed by Arizona, New Mexico, California, and Idaho. Bulk densities range from 500 kg/m³ for pumice to 1,040 kg/m³ for pumicite.

U.S. production of pumice (sold or used) fell in 2003 because of decreased demand from the abrasives, building block, horticultural, and landscaping markets. The amount of pumice sold for building block decreased by about 10%, from 730,000 t to 654,000 t. The only major market that had increased sales was for concrete admixture and aggregate, which nearly doubled from 24,000 t to 42,000 t in 2002. The most important market for pumice remained building block, which consumed about 76.4% of the total domestically produced pumice sold or used in the United States. The average prices reported for pumice varied greatly by use. The overall average price was \$25.20/t in 2002, an increase of \$4.51/t (from \$20.69/t) in 2001. The price change was the result of a significant increase in the average price reported for the grades of pumice used in abrasives, and smaller increases in the prices for building block, horticulture, and landscaping. Average prices were \$312/t for abrasives; \$39/t for miscellaneous uses; \$27/t for concrete admixture and aggregate; \$25/t for horticulture and landscaping; and \$12/t for building block (Bolen 2003b; W.P. Bolen, personal communication).

Volcanic Cinders and Scoria

Scoria and volcanic cinder are cellular, frothy products of explosive volcanism erupted as tephra (blocks, bombs, lapilli, and gravel) or lava flows from mafic magmas. Scoria, which contains variable amounts of air holes (vesicles), is a lighter equivalent, usually of basalt. Much of the material is forcefully ejected from the vent, vesiculating in the air as the volcanic gases (mostly water) expand, and are entrapped by the rapid cooling of the relatively fluid lava. Scoria also develops where the gases are entrapped by rapid cooling at the surface of the flows; it may then be broken into blocks and irregular fragments by continued movement of the flows. There is a fairly wide range in vesicle size (particularly in the ejecta, most of which

have dense fused surfaces) and in the thickness of the cell walls, which results in a considerable variation in the density of the rocks.

The distinction between scoria and volcanic cinder is an arbitrary one of size; cinder is material less than about 2.5 cm (1 in.) in the largest dimension. Characteristically, mafic ejecta are fairly heavy and are not thrown long distances from the vent; they form cinder cones around the vent that are generally a few hundred to several thousand feet in diameter and several hundred feet in height. In contrast, mafic lava flows (basalt or basaltic andesite) tend to be fluid, several hundred feet to tens or even hundreds of miles in lateral extent, and a few feet to several tens of feet thick. The flows are seldom abundantly scoriaceous throughout; most of the vesicular zones are confined to the upper few feet of the flow and are highly variable in their development (Bush 1973).

Mafic vesicular volcanic rocks are widely distributed throughout the western United States, including Hawaii and Alaska, but are missing from the central and eastern states. Deposits of scoria and cinder are known in every state west of the 104th meridian, and production has been recorded from all states except Alaska. The largest producers are Arizona, Oregon, California, Hawaii, and New Mexico, but no one state is consistently largest; in 2002 New Mexico was the largest producer. The ranking in production does not always reflect the relative amounts of scoria and cinder available, in part because production is determined by competition and the size of the market within an economic range of the deposits and in part because, until recent years, the reporting of production included pumice and pumicite. In the states west of 104°, nearly all the metropolitan districts with a core city of at least 50,000 people and most cities of at least 25,000 are within about 100 miles of deposits of scoria or cinder, but not all can be served economically from them.

Cinder and scoria production is reported as part of crushed stone production by the U.S. Geological Survey (USGS), and production reports by the industry, though voluntary, are comprehensive. Because of the small size and intermittent operations of some of the enterprises, accurate production figures are sometimes lacking but, overall, are reliably representative.

Other Volcanic Rocks

Other natural lightweight aggregates in the western United States include variations on the volcanic rocks previously discussed. For instance, pumice is usually very silicic and could be considered a rhyolite if not containing abundant air voids. The air-void density often varies during emplacement, resulting in variable rock densities. Pumiceous rhyolites are currently used as a semi-lightweight aggregate in some western states and have been described by Bryan (1987). Specific gravities of pumice are generally <1.0 (indicating that it floats in water); specific gravities of pumiceous rhyolites that are used in concrete masonry units and structural concrete range from 1.8 to 2.3. Most western rhyolites are usually from 2.5 to 2.7. Pumice and the lower-density rhyolites are generally glassy.

Other volcanic rocks that have sometimes been evaluated in the western United States for potential lightweight applications are welded tuffs, rhyolites of volcanic domes, perlite rocks, and any recent volcanic rocks high in glass content.

Tuffaceous rocks are products usually of explosive volcanism, differing in chemical composition but characterized by lighter weight caused by the collapse of pumice vesicles as the ejecta lithify. Bryan (1987) described their geology, occurrence, and usage in the southwestern United States.

It should be emphasized that the lower-density volcanic rocks are concentrated in the western United States where Tertiary and recent volcanism is present. The eastern portion of the country

lacks young volcanism. Volcanic rocks in the East are generally much older and have been altered and metamorphosed to such a degree that no inherent lightweight characteristics such as glass or voids remain.

MANUFACTURED LIGHTWEIGHT AGGREGATE

Expanded Clay, Shale, and Slate

Many varieties of clays, shales, and slates of diverse origins expand somewhat on heating to about 1,100°C (2,000°F). Basically, all clays, shales, and slates are chemically and, to some extent, mineralogically similar; they differ mostly in their physical characteristics. These lightweight aggregates are used only for their physical properties, and it is their chemical similarity that makes all of them amenable to thermal expansion. See Table 67 in Bush (1973), which presents several representative chemical analyses for the argillaceous rocks that have been tested for use as lightweight aggregate. The range in composition is wide for each of the three materials, and all three ranges largely overlap. Unfortunately, the rocks that expand suitably, that expand inadequately, or that do not expand at all fall in these same ranges.

The basic requirement for expansion of an argillaceous rock is a source of gas within the raw material, but full suitability requires several other physical characteristics. Sufficient gas must form to cause a full bloat in the temperature range where the material is pyroplastic (melted enough to be viscous) so that the gas can be trapped; there must be enough vitrification at a high enough viscosity so that most of the gas can be held in small, evenly distributed pores; and the temperature range between softening and liquefaction must be large enough (about 38°C, or 100°F) that the bloating can be controlled in large-scale commercial production. Economical production is had at kiln or sinter temperatures between 1,000° and 1,200°C (1,830° and 2,200°F), although temperatures can be as low as 870°C (1,600°F) or as high as 1,300°C (2,400°F).

There is little agreement on the relative importance of the number of possible sources for the gas within the raw material. Conventional wisdom in the early days of the industry held that the argillaceous rocks had to have significant organic content, although the amount varied with the practitioner. Laboratory investigation of the evolved gases, however, showed that many materials with very little total carbon expanded better than those with appreciable amounts (Austin, Nunes, and Sullivan 1942; Sullivan, Austin, and Rogers 1942)—to perhaps 1.5%—and that CO₂, SO₂, and H₂O all played a part in the bloating. Riley's (1951) research indicated that thermal destruction of hematite, pyrite, and dolomite provided both CO₂ and SO₂ in amounts sufficient for bloating without recourse to organic carbon. Ehlers and Richardson (1958) emphasized the role of CO₂ derived by the heating of calcite, dolomite, and ankerite in argillaceous rocks, and by subsequent, more-effective entrapment in illite than in kaolinite (kaolinite fuses at a higher temperature than illite). They deemphasized the role of iron in gas liberation, considering its possible significance only where hematite exceeded 5% of the rock.

This history of investigations suggests (1) that opinion as to what causes bloating diverges considerably, (2) that no single factor is most important, and (3) that insufficient consideration has been given to the possible effects of the suggested reactions operating simultaneously, at least as far as the production of gas is concerned (Bush 1973).

Riley (1951) investigated the combinations of constituents that apparently acted as fluxes and affected pyroplastic conditions at the appropriate temperatures for gas formation and retention, and was able to define a range of compositions that included most of the bloatable materials and excluded most of the nonbloatable materi-

als (SiO₂, 52% to 80%; Al₂O₃, 11% to 25%; and combined fluxes, 10% to 25%). Additional investigations since 1951 have shown that this bloating range is less reliable than it first seemed, but it is a useful guideline. White (1960) showed that the range had to be extended in the direction of higher Al₂O₃ and lower flux contents, whereas Sweeney and Hamlin (1965) had to extend the range to a higher flux content. At the same time, materials previously considered to be nonbloatable were included in the bloating range. Conley et al. (1948), Klinefelter and Hamlin (1957), and Hamlin and Templin (1962) described laboratory methods for evaluating raw materials. The ultimate evaluation is how the material expands in a commercial operation; for this determination to be made, several tons of material may need to be run (Bush 1973).

Distinguishing between favorable and unfavorable rocks in the field is difficult because there are no really positive field criteria. Many different argillaceous rocks have been found to be suitable. Darker colored clays, shales, and slates (green, gray, black) are more suitable than light-colored (particularly red) ones; unweathered materials are more suitable than weathered ones; common or brick clay is more suitable both physically and economically than flint or ball clay. Thinly fissile shales and slates tend to expand unidimensionally, which is undesirable. Lateral variation along the sedimentary deposits is such that units unsuitable at one point may be eminently suitable a few hundred yards to a few miles away.

In addition to materials that can be made to expand, argillaceous rocks can be ground, mixed with combustible materials (such as ground coal), and sintered to produce lightweight aggregates. The mass becomes pyroplastic, or cohesive, and voids are left as the combustibles are burned out. Some bloating may occur, but it is incidental to the sintering. Because some clayey rocks that do not bloat can be used for lightweight aggregate, classifying any argillaceous rock as unfit is unwise unless it has been tested and found unsuitable. It must be noted, however, that as of early 2004, no lightweight aggregate was being produced by the sintering process (J.P. Ries, personal communication).

Air-Cooled, Granulated, and Expanded Slag

Of these three types of slag, past U.S. Bureau of Mines (USBM) and USGS production (Table 4) shows that air-cooled slag is the largest category by weight. The lightest air-cooled slag is as heavy as the heaviest lightweight aggregate; it is closer to a normal-weight, sand-and-gravel aggregate. Air-cooled slag is mostly used for road metal, road base and fill, portland cement concrete, and asphaltic concrete, and as railroad ballast (van Oss 2003).

The data for expanded slag cover foamed and pelletized slag, but the dominant data component in this category through 2001 was granulated blast furnace slag (GBFS), a material that has little use as lightweight aggregate. GBFS was put in the expanded slag category to protect proprietary data for both slag types. Granulated slag is formed by quench-cooling molten slag through a water stream to produce sand-sized grains of a calcium-silicate glass. This material, when very finely ground (even finer than portland cement), has moderate hydraulic cementitious properties but the cementitious properties become very strong when the material interacts with free hydrated lime, such as that which is released through the hydration of portland cement.

Expanded slag (foamed slag and pelletized slag) is, like GBFS, cooled quickly with water, and then the foamed slag is crushed and screened. The objective in making expanded slag using large amounts of steam is to create innumerable vesicles in the product. These vesicles make the slag lightweight and allow it to bond well with cement in lightweight concrete applications, the main use for expanded slag. Owing to the inclusion of more complete data in

2002, USGS was able to reveal data for GBFS separately for that year; but this required the withholding of expanded slag data for proprietary reasons. In a footnote, USGS noted that the tonnage of expanded slag sold in 2002 was <0.1 reporting unit (i.e., <100,000 t; van Oss 2003). It is likely that this magnitude of expanded slag sales has not changed significantly in a decade or more.

Data on blast furnace slag pertain to sales of processed material and not to production. Overall production of blast furnace slag is related entirely to the iron and steel market and hence to the output of crude or pig iron, yet the actual slag output is not routinely measured and so data on slag production are virtually unavailable.

ULTRA-LIGHTWEIGHT AGGREGATES (MANUFACTURED LOW DENSITY)

Expanded Perlite

Most perlite applications require the expanded form of the mineral. Run-of-mine perlite is crushed and ground before thermal treatment. Run-of-mine material is normally reduced in size by a jaw crusher. Depending on the end use, it may then be further reduced by cone crushers and then air classified (McMichael 1989). Domestic crude perlite is produced primarily in the western United States. In 2002, New Mexico and Oregon accounted for about 85% of domestic production. The remaining production comes from Arizona, California, Nevada, Idaho, and Utah (Bolen 2003a). The largest foreign producer of perlite is the Greek firm S&B Industrial Minerals SA, with its main deposit on the island of Milos and other deposits on Kos, on Sardinia in Italy, and near Biga in Turkey (Burke 2004).

Expanded Vermiculite

Flakes of raw vermiculite concentrate are mica-like in appearance and contain water molecules within their internal structure. When the flakes are heated rapidly at 900°C (1,650°F) or higher, the water flashes into steam and the flakes expand into accordion-like particles. The color, which can range from black and various shades of brown to yellow for the raw flakes, changes to gold or bronze on expansion. This expansion process is called exfoliation, and the resulting lightweight material is chemically inert, fire resistant, and odorless. Vermiculite provides good thermal insulation in lightweight plaster and concrete. It can absorb such liquids as fertilizers, herbicides, and insecticides, which can then be transported as free-flowing solids (Harben and Kuzvart 1996). In 2002, the two U.S. producers of vermiculite concentrate were Virginia Vermiculite Ltd., with operations near Woodruff, South Carolina, and in Louisa County, Virginia; and W.R. Grace & Co., with its operation at Enoree, South Carolina (Potter 2003).

A USGS study analyzed the mineralogy of vermiculite-rich samples collected from 62 U.S. vermiculite mines and deposits (Van Gosen et al. 2002). The purpose of the study was to determine if amphibole asbestos minerals similar to those found in the Libby, Montana, vermiculite deposit were present in other U.S. vermiculite deposits. The results of this survey suggested that fibrous amphiboles, in more than trace amounts, may not be common in the ore zones of some types of vermiculite deposits. But initial results also suggested that vermiculite deposits that can contain fibrous amphiboles occur in geologic settings similar to the Libby vermiculite deposits—within zoned, alkalic-calcic, quartz-poor plutons, especially plutons with characteristics of carbonatite intrusions. Additionally, vermiculite deposits found where masses of ultramafic rocks are cut by granite or pegmatite can contain amphibole fibers. The results of this mineralogical survey were preliminary, and additional sampling is planned. These relations may help guide priorities for sampling, reclamation, permitting, and monitoring of

active and inactive vermiculite mines. Additional comments on the occurrence of vermiculite can be found in the chapter on vermiculite in this volume.

Some discrepancies exist in the data for vermiculite given in Tables 4 and 5 for 1996 through 2002. This is due in part to differences in the data reported for production and for values in the *Minerals Engineering* information compared to data given by the USBM and USGS. The data from the latter bureaus are constrained by the prohibition against publishing proprietary company data when three or fewer companies are the source of the data. This is the most common reason for the estimated figures in the tables.

OTHER MATERIALS USED AS LIGHTWEIGHT AGGREGATE

Diatomite has reportedly been used as lightweight aggregate, but this use has not been verified; therefore, diatomite is not discussed here. Organic products such as rice hulls, straw, and peat have also reportedly been used in the past as a lightweight aggregate, but they are considered insignificant and are also not discussed.

Coal cinders contribute to the production of ash, more in the southwestern United States than in other parts of the country. Municipal waste combustion produces bottom ash (all solid materials that pass through the furnace unburned, such as tramp metal, plastics, glass, rocks, and dirt). Most coal-consuming end waste processes produce fly ash rather than cinders, so fly ash production continues to increase with both the increased use of pulverized coal in electric power generation and with waste incineration. Approximately 600 kt of fly ash are produced annually, but utilization is only about 13% (Kiser and Zannes 2002). The production of lightweight aggregate from fly ash has potential as a significant market, but improvement in the technology is needed to spur use as a lightweight-aggregate raw material.

Incinerating municipal waste leaves a residue that is a minor source of lightweight aggregate. In 2004 there were 89 waste-to-energy plants in 29 states that handled about 13% (29 Mt) of the approximately 200 Mt of solid waste generated in the United States. In 2003, Kiser and Zannes (2004) estimated that about 600,000 t of ash per year was used as aggregate in road material and as landfill cover.

Most states have now adopted legislated recycling goals. Under the Resource Conservation and Recovery Act (RCRA), passed in 1976 and reauthorized in 1993, the U.S. Environmental Protection Agency (EPA) issued regulations that govern the disposal of fly ash and bottom ash in landfills. Additional pressures have made it necessary to develop alternate means of disposal and alternate uses, and in the ensuing years, many new plants have come onstream to process municipal solid waste and sewage into a lightweight aggregate. The process combines pulverized municipal solid waste (recyclable and oversized material removed) with a mixture of milled clay and liquid nonhazardous waste (sewage sludge) to form a pellet. The pellet is processed through a three-stage kiln. First, the pellet is pyrolyzed (chemically altered by heat), which allows combustible gases to escape. These gases bloat the pellet into a lightweight aggregate but also provide some of the required fuel for the kiln. In the second stage, oxidation removes most of the pellet's carbon, enhancing the lightweight property of the aggregate and supplying some of the energy requirements of the process. In the third stage, the pellet is vitrified.

This process has been in development for about 12 years. It is projected to be self-sustaining with respect to its energy requirements. Income is expected from solid waste disposal fees, use of nonhazardous liquids, and the sale of recovered recyclables. The aggregate is expected to be marketed for approximately \$33/t.

Table 7. Perlite uses in the United States, 1990 and 2002, %

Uses*	1990	2002
Filter aid	16	9
Plaster aggregate	2	1
Concrete aggregate	2	1
Horticultural products	9	13
Low temperature (insulation)	1	1
Formed products	56	62
Masonry and cavity-fill insulation	3	1
Fillers	5	9
Laundries†	—	1
Other uses	7	5

Source: Bolen 1991, 2003a.

* May exceed 100% because of rounding.

† Included with other uses in 1990.

Questions abound, however, about whether this process will pass present air emissions standards and if the lightweight product will be accepted in the marketplace. In 1988 a pilot plant was operated as a test facility near Brisbane, Australia, and many technical process problems were encountered. This process has also been tested in Germany (Bigner 1992; Gershman and Miller 1992).

PRODUCTION AND CONSUMPTION

Table 4 summarizes the annual output of lightweight aggregates in the United States for 1990 through 2002 by quantity, and Table 5 summarizes the stated values of lightweight aggregate production for the same period. Because complete data for 2003 are not available, they are not included in Tables 4 and 5. Where any data were available, however, they are discussed in the text. Table 6 compares the average unit value of lightweight aggregate materials at production plants in 1990 and 2002. From 1990 to 2002, significant price increases for expanded perlite (Table 7) and exfoliated vermiculite gave them a large share of the market in terms of value (approximately 32% in 2002) despite contributing only about 5% of the tonnage. Expanded shale, clay, and slate are widely used and in 2002 they accounted for about 39% of the quantity and 27% of the value of the market.

Natural lightweight aggregates are mostly bulky and of low unit value and normally serve local and regional markets. Some structural lightweight aggregates, however, are economically shipped long distances because the density of these aggregates are one half to one third the density of locally available normal-weight aggregates such as crushed stone, sand, and gravel, and any comparisons should be made on a volume basis. For example, lightweight aggregate may be four times as expensive per ton as local normal-weight aggregate but may yield two to three times its volume. One ton of lightweight aggregate will normally make two to three times as much concrete end product as 1 t of normal-weight aggregate (Gershman and Miller 1992).

Products such as pumice or expanded slag may be used in substantial quantities in some localities and may not even be available (at competitive prices) in others. Perlite and vermiculite deposits are limited in location but serve national markets because of their relatively high market value and because their ores are shipped prior to pyroprocessing and physical expansion. Most of these pyroprocessing and expansion plants reflect specialty uses in regional and national markets. The more specialized uses command higher market prices that lead to extensive geographic distribution and use (Mason 1994).

Expanded clays, shales, and slates make up about 50% by weight of the lightweight aggregates used annually in the United States, with the remainder divided among volcanic cinders and scoria, expanded blast-furnace pelletized slag (excluding air-cooled and nonpelletized granulated types), fly ash, vermiculite, and perlite. Vermiculite and perlite are the most used ultra-lightweight materials, but less than 25% is used as construction aggregate. They are used in about equal amounts. Pumice constitutes the remaining third of that market (Bush 2001).

About 8.1 Mt of rock were used in 2002 for structural lightweight aggregates, and perhaps as much as 0.55 Mt were used for ultra-lightweight aggregates for nonload-bearing concretes, blocks, plaster insulation board, fillers, filters, agricultural aids, and loose fill insulation.

Because the lightweight aggregate industry is largely dependent on the overall construction industry, production follows the level of activity in home, building, highway, and bridge deck construction. Energy costs are a dominant factor wherever raw materials need to be heated for expansion.

Details on the production and sales value of pumice and pumice are given in the section on natural lightweight aggregates in this chapter.

Consumption of expanded clay, shale, and slate increased from about 1.09 Mt in the early 1970s to 4.0 Mt in 2002 and has hovered in the 3.9 to 4.0 Mt range since 1995. Sales generally reflect the state of the construction industry, and the use of lightweight aggregates in concrete block, structural concrete, and highway surfacing. In 2002 the average value of crude ore was \$13.69/t, and the average prices of expanded clays, shales, and slates ranged from \$30/t to \$50/t at the plant, depending on gradation and aggregate type (J.P. Ries, personal communication). Tables 5 and 6 show typical values for lightweight aggregate raw materials (ores) and the expanded products at the production plant.

Prices more than doubled in 10 years from \$11/t to \$20/t in the early 1980s (McCarl 1983), up to \$33/t to \$57/t (depending on gradation and aggregate type) in 1990 (J. Konczak, personal communication). As shown in Tables 5 and 6, cost trends for raw materials between 1990 and 2002 have been variable. Exfoliated vermiculite and expanded slag showed significant price increases (170% and 270%, respectively), vermiculite concentrate and perlite (both crude and expanded) remained virtually static, and raw clay and shale have decreased 44%.

The sales tonnages in the 1980s (1.1 to 1.7 Mtpy) reported by Mason (1994) for expanded slag reflected USBM data for expanded slag combined with granulated slag and were dominantly of the latter, which, when pelletized, was the only slag-based material produced in 2002 used as a lightweight aggregate. Sales of processed slag are almost entirely from stockpiles, some of which may be very old, and are related to construction-sector demand. This demand has also influenced the type of cooling applied to newly formed slags, to the degree that a blast furnace is equipped for cooling options. For both standard and lightweight aggregate markets, slags must compete with natural aggregates (including crushed stone) in a market that is highly sensitive to transportation costs. High transportation costs and, especially, the ease of formation of air-cooled slags (these are cooled under ambient temperature conditions) have long favored the production of air-cooled slag.

Ground GBFS (worth about \$60/t) finds a ready market as an admixture in blended and masonry cements and, especially, as a partial substitute for portland cement in concrete:

"...the growing market and high unit price have led to the addition of granulators at some existing U.S. blast furnaces. At [three]...facilities in Indiana, pelletizers have

also been added, ...which implies that U.S. output and sales of pelletized slag will likely increase from current very low levels beginning in 2003 or 2004" (van Oss 2003).

Unground GBFS is worth about \$30/t, and \$60/t ground; pelletized GBFS is worth roughly \$20/t, so the processing economics in handling the molten and then cooled material are similar.

A major factor in the expanded plus granulated combination is that for the past few years, sales of GBFS ground in the United States from imported unground blast furnace slag were not included. Beginning mid-2003, USGS tried to find all the locations where this material was being handled (including those grinding imported materials). More complete data collection allowed USGS to directly report the granulated slag sales for 2002 (see Table 4), but the 2002 data for expanded slag continued to be withheld for proprietary reasons.

The unit value (about \$13/t in 1990) in Mason (1994; Table 6) for expanded slag increased to about \$35/t in 2002 (T. Wagaman, personal communication); most of the price shifts reported in the intervening years for this (combined) slag category reflect shifts in the data for the granulated slag component.

According to an industry expert, "In terms of the future—granulated sales should at least hold steady and likely will increase. Imports of this material will increase" (H.G. van Oss, personal communication). Expanded (pelletized) slag sales are likely to increase, with the introduction of two pelletizers by Inland Steel Corporation in 2003 (in East Chicago, Indiana).

INDUSTRY STRUCTURE MINING AND PRODUCTION TECHNIQUES

Natural Lightweight

Overall, the industry is characterized by many producers of raw material that do not manufacture the finished product. Among the natural lightweight aggregates, many producers of raw pumice also produce the final product—concrete masonry units, for example—or grind a product that is shipped directly to distributors; others ship unprocessed material to independent processors. Volcanic cinders and scoria are mostly used by the raw material producer to make concrete masonry units close to the quarry site, but some is shipped to independent producers. Rhyolite tuff is used as dimension stone and as aggregate; therefore it may be shipped to independent applicators far from the quarry site.

Mining and processing of pumice and volcanic cinder is simple and straightforward. They are extracted, crushed, and screened, similar in most respects to an ordinary sand-and-gravel deposit. In most cases, the younger materials are fairly unconsolidated and do not require ripping. Older pumice and cinder may be consolidated and do require ripping. Most processed pumice does not require washing for end use; specialty uses may require some washing. Pumiceous rhyolite or tuffaceous rocks are mined in a common quarry operation and thus requires blasting.

Many cinder deposits in the West are also used as a substitute for, or in competition with, ordinary-weight aggregates such as sand and gravel or crushed stone. Often cinder is the cheapest and most easily available material for road surfaces in some of the volcanic terranes in the western United States.

MANUFACTURED LIGHTWEIGHTS

Expanded Clay, Shale, and Slate

The manufactured lightweight aggregates are expanded clay, shale, and, to a lesser amount, slate. In the eastern and western parts of the United States, expansion is commonly done near the quarry site by the raw material producer; in the central part of the country, particu-

larly where transportation by water is available, raw material may be mined hundreds of miles from the expander and sold to independent producers located near the eventual market.

Shale, clay, and slate are normally mined by open-pit and quarry methods, and then dried in large sheds or open stockpiles to control water content in the raw feed before high-temperature pyroprocessing in either rotary kilns or sintering machines. The resulting clinker may then be screened or crushed before screening to yield proper gradation mixes for final use as an aggregate in concrete masonry units, structural concrete, or other applications. The specific gravity of the expanded shale, clay, and slate can be controlled to some degree by the type of kiln or sintering grate used to process the raw material (Mason 1994).

Most producers of expanded shale, clay, and slate find long-run economic survival precarious if they do not engage in substantial raw material testing, geologic and mining studies, and marketing research investigations before selecting the location of a new plant (Conley et al. 1948; Shildeler 1961).

Production costs for expanded shale, clay, and slate have increased in general along with the cost of energy, raw materials, and supplies. In recent years the additional cost associated with the installation of air pollution control equipment (baghouses) has had an effect on operational costs. The cost of labor is considerably higher today in proportion to other cost centers. More direct cost increases were felt as more power was required per unit of production than in the past. Conservation efforts continue to lower the costs of energy-related items, such as refractories and electric power. Most plants continue to use coal or petroleum products as a primary source of fuel (Mason 1994).

Several producers are now using alternate fuels to fire kilns. Some of the alternate fuels are better known as *waste-derived fuels* and solvents from various industrial processes. Waste-derived fuels can be excellent, low-cost fuels, as long as air-emissions parameters can be met. In some cases the producer using these fuels receives an income stream from the generator of the fuel. This has caused some market distortions but has kept production costs stable while providing a reasonable method of disposing large quantities of waste that does not threaten human health (Singletary 1991; Kelly 1992; Kiser and Zannes 2002).

Expanded clay and shale are the most used and the most valued lightweight aggregate materials for structural applications. As with most aggregates, normal or lightweight, mining is by open-pit methods, using drilling and blasting where necessary. Mason (1994) pointed out the need to dry quarried material before processing with either of the two expansion methods: rotary kiln or traveling grate sintering machine. According to the ESCSI (J.P. Reis, personal communication), there has been no sintered production since 1996. The raw feed enters the kiln at the high end, if the kiln is inclined, to take advantage of gravity flow down through the kiln. Usually there is a preheating section, using waste heat from the burning (bloating) zone, and the feed then traverses the burning zone rapidly to avoid agglomeration and sticking to the lining of the kiln. It then goes through a cooling section and is discharged, further cooled, and stockpiled. Crushing and size grading precede the kiln, and grading follows the expansion. Usually the bloated material is graded into coarse ($3/4$ to $3/8$ in.), intermediate ($3/8$ to $3/16$ in.), and fine ($<3/16$ in.) sizes and is then mixed to satisfy the specifications for end uses. Additional detail can be found in the chapters on structural clay products and common clays and shale in this volume.

Slag

By-product lightweight aggregates are expanded (foamed) and pelletized GBFS. Slag producers are not usually the distributors and

are rarely the end-market distributors; they are iron and steel producers who can take advantage of a market for their unavoidable by-product. Fly ash and bottom ash result mostly from coal combustion and significantly from incineration of other materials—to a large extent, municipal waste. Their use is primarily local, except for the amount used to serve the cement industry, which finds the ash's pozzolanic properties attractive as an admixture to portland cement.

Expanded Perlite and Vermiculite

A very important segment of the manufactured lightweight aggregate market is the ultra-lightweights: expanded perlite and expanded vermiculite. Comparatively little use is made of the raw materials in the unexpanded form; both have to be processed at high temperatures to achieve expansion.

Perlite is not a commodity dominated by a single producer. There are too many well-distributed deposits of economic size to capture the market. Of the fewer than 20 producers in 2003, only a few had more than one mine and most of them had their own expansion facilities, although there was some shipment of crude ore to independent expanders.

The history of the vermiculite industry is quite different. Early in the 1920s, a very large vermiculite deposit was discovered near Libby, Montana, and it became the dominant source in the United States for more than 50 years. As a result, a vertically organized business structure developed, with many company-owned or franchised expanders throughout the country. Additional sources came into the market from South Carolina in the late 1940s and thereafter, serving mainly the eastern part of the country, but still as part of the single business structure. The U.S. market attracted imports of crude vermiculite ore after World War II (a available data was first reported in 1950) and sales were made to independent expanders, mostly in the Gulf Coast and eastern seaboard metropolitan areas.

Active mining and milling of vermiculite ore at Libby ceased in 1990, and all shipments of stockpiled ore concentrate ended in 1994. Health problems were factors in that decision, and subsequent publicity led to a marked decrease nationwide in the sales of exfoliated vermiculite. From 1993, vermiculite sold and used decreased from about 190 t to an estimated 175 t in 2000, and then dropped precipitously to 115 t in 2002. The 1994 volume of *Industrial Minerals and Rocks* listed 41 expansion plants in the United States, with 24 producers. The nationwide concern about asbestos led to a survey by the EPA to identify the sites of all exfoliation plants, both past and present (D.H. Thornton, personal communication). Despite the decrease in volume, by 2003 there were, or had been, at least 245 exfoliation plants, operated by about 139 companies. One company operated, franchised, or leased 52 plants. There was one exfoliator in Hawaii and one in Puerto Rico; none is recorded in Alaska (K.C. Land, personal communication).

Since 1990, there has been a very marked decrease in the number of company-owned and franchised expanders, coupled with the availability of crude ore from additional sources in Virginia and South Carolina. Additional comments can be found in the chapter on vermiculite in this volume. New imports from mainland China entered the market in the 1990s and are serving independent expanders, largely along the West Coast but also reaching into the central United States from Gulf Coast ports.

Expanded perlite is subject to two factors of perhaps equal importance. The ore must be carefully and selectively graded, with end usage clearly in mind before "popping," and the ore has to be passed through the hot zone in the furnace under closely controlled time and temperature conditions. Crushing and sizing are done by jaw crushers (primary stage), followed by drying and crushing by

cone crushers (secondary stage), additional drying, and additional crushing (third stage), followed by classification using vibratory screens and forced air. The preexpansion of the raw ore to about 1% surface moisture can alleviate a number of problems in the expansion process. Other ways to crush the ore, depending on its structure, include impact, rod, and hammer mills; roller crushers; and gyro discs. After storage by size, a mix appropriate to the expander's usage is blended and then shipped to the popping plant.

The popper may be one of two major, contrasting types—vertical (or semi-inclined) or horizontal (stationary or rotary, cocurrent or countercurrent)—or a third type, the TORBED (toroidal fluidized bed) process (Clark 1984), which has not found wide acceptance and is mentioned here only to be inclusive. The most commonly used expander is the vertical furnace, particularly for coarser-grade perlite used in horticulture; for finer grades, either can be used efficiently. In the vertical furnace, raw ore is dropped from the top or added through side ports, usually with some preheating. The amount of preheating and the residence time in the hot zone are carefully controlled so that the ore is at its most optimum condition for expansion. In the hot zone, the residence time is usually limited to a few seconds to prevent overexpansion, which can lead to bursting the perlite bubbles. Expulsion from the furnace may be by forced air, by fan suction from or near the top of the furnace, or by simply riding the current of rising hot gases. In the rotating horizontal furnace, the ore enters at the hot zone and spiral baffles in the rotating cylinder propel it the length of the furnace. This allows for a slower cooling rate of the expanded ore (an often desired element in the processing). The horizontal furnace may actually be inclined to allow gravity to help transport the perlite, and the flow can be either cocurrent or countercurrent, taking advantage of the radiant heat from the cooling zone to preheat the incoming air (in a jacket around the furnace) on its way to the combustion zone.

The chapter on perlite in this volume covers expansion and product processing, testing, and specifications in considerable detail, and the reader is referred to it for further information. In 1994, the Perlite Institute published a handbook on test methods and related standards for perlite, and it is an invaluable reference. The institute's Web site (www.perlite.org) lists many publications on the specific details of horticultural, structural, and insulatory applications.

Expanded vermiculite is made at about 900°C (approximately 1,650°F), although the appropriate temperature varies with the ore from deposit to deposit, depending on the degree of alteration from the parent biotite or phlogopite. Almost all expansion is done in vertical furnaces, although for the finer grades a horizontal rotary furnace can operate efficiently.

Milling and beneficiation are almost universally done now by wet methods (flotation). The need to effectively offset the association of asbestiform (tremolite) minerals with vermiculite at the Raily Creek deposit on Vermiculite Mountain near Libby, Montana, and the dust-producing dry beneficiation methods used there until 1970, led to a complete replacement by the wet process. Wet beneficiation requires a drying stage at an additional screening station before the concentrate can be crushed and sized. The Vermiculite chapter in this volume compares beneficiation methods and flowsheets, and also discusses testing, specifications, and particle-size ranges of the preexpansion concentrate required by exfoliation plant operations destined for different products.

There has been little change in vermiculite processing technology since the publication of the 6th edition of *Industrial Minerals and Rocks* in 1994; the Vermiculite chapter in this volume covers the technology so thoroughly that the information is not repeated here.

FINISHED PRODUCTS AND SPECIFICATIONS

Concrete Masonry Units

Concrete masonry units (block) are the predominant concrete product using lightweight aggregates, both natural and manufactured. In the West, most block plants use natural lightweights to at least some degree, if the block plant is within a favorable shipping distance from the source. In the eastern United States, manufactured lightweights predominate. Usually the aggregate is shipped to the plant closest to the market. Often, shipping is by rail if the plant is within a few hundred miles.

The standard block is what is referred to as an 8-8-16, reflecting the dimension in inches, and it contains two hollow cores. The blocks are manufactured in machines that accept a mix of cement, aggregate, and water that is vibrated for consolidation into molds. The resulting texture of a block is more porous than poured concrete. Other size blocks are also manufactured with various dimensions for specialty applications or for architectural needs. For instance, *split-face block* is a larger block that is mechanically broken to expose the inside of the block and to create a rougher texture. To create a certain architectural look, the blocks are often colored, and certain aggregates are chosen also for their color.

Concrete block strengths primarily depend on the cement content and the physical properties of the aggregate used. Often a lightweight coarse aggregate is a major ingredient, with the finer size being ordinary-weight sand; this ensures a lighter block but also one that has strength suitable for structural applications. Block strengths can exceed 4,000 psi (27,600 kPa). Block is used in various applications ranging from fences to high-rise construction.

Blocks are laid in horizontal courses and mortared together to create structures. Probably the main reason for using a lightweight aggregate in block is productivity. A mason can lay more 25-lb block in a day than 35-lb block. For most applications, the hollow cores are subsequently grouted solid with a sanded concrete mix. In addition, steel rebar is generally placed in the cores for added strength. Local building codes and the design of the individual structure govern the strength and other characteristics of the block. The standard specification for concrete masonry units is ASTM C331-04, *Standard Specification for Lightweight Aggregates for Concrete Masonry Units*. This specification outlines in detail the required weights for lightweight aggregates and also gives gradation, shrinkage, and other criteria on limits for deleterious materials and the durability of the finished product. It should be understood, though, that even if some aggregates do not meet these weight requirements, they can be considered a semilightweight and used in block. Local building codes and individual job specifications govern the physical properties of the end product. Often, it is more economical to use a close source of semilightweight aggregate, such as volcanic rocks in the western United States, than it is to use a manufactured lightweight aggregate that is located several hundreds of miles from the project.

Lightweight Structural Concrete

Lightweight structural concrete is usually batched like any other ready-mix concrete in central plants or on-site plants that deposit the wet mix into a ready-mix truck, which transports it to the job site. Ready-mix concrete is more fluid than mix for concrete masonry units but essentially consists of cement, aggregate, and water. A mix design takes into account criteria for strength and weight of the finished product. Often the lightweight material is only a portion of the coarse fraction of the aggregate used in the mix, with ordinary-weight sand making up the fine fraction. In certain western U.S. locations, where semilightweight natural aggregates are available, the entire mix is lighter-weight aggregate.

Lightweight aggregate primarily reduces weight in structures. Reducing weight reduces construction costs, because structural members can be smaller when holding less weight. Lightweight is especially called for in suspended concrete floor slabs aboveground and in structural columns for high-rise buildings.

The generally accepted specification governing lightweight aggregate is ASTM C330-04, *Standard Specification for Lightweight Aggregates for Structural Concrete*. This specification outlines in detail the required weights for lightweight aggregates and also gives gradation, shrinkage, and other criteria on limits for deleterious materials and the durability of the finished product. Other state and federal specifications may be applicable depending on the concrete usage and the structure's owner.

The Aggregates chapter in this volume contains a more detailed discussion of aggregate usage in portland cement concrete.

Insulating and Fire-Resistant Materials

Lightweight aggregates by their nature also enhance the insulating and fire resistance of a structure when incorporated in concrete products. The air voids in a typical lightweight aggregate act as an insulator. Typical lightweight aggregates increase the R value (the resistance value of structural components such as floors, ceilings, and walls; the higher the value, the more insulation value). ASTM C330-04 applies to two general types: (1) those prepared by expanding, pelletizing, or sintering (blast furnace slag, clay, shale, or slate, fly ash, and diatomite); and (2) those prepared by processing natural materials (pumice, scoria, or tuff). ASTM C331-04 covers these types and adds aggregates consisting of end products of coal or coke combustion. ASTM C332-99 outlines the necessary insulating and grading requirements for lightweight aggregates for the ultra-lightweights such as expanded perlite and vermiculite; the two types are described in ASTM C330-04. Generally speaking, the lighter the weight, the better the insulating and fire-resistant properties of the material.

Other Products

New developments in lightweight aggregates in construction have been robust, and this trend will continue as supplies of "conventional" aggregate tighten. A relatively recent innovation is the use of lightweight fill in certain applications where heavier materials would contribute to settlement. Such a use is in the San Francisco area, where the notorious "Bay Muds" are bottomless. Thousands of tons of pumice from northern California are used as fill to support highway structures crossing these muds. Other construction-related innovations include using expanded shales on pavement surfaces for skid resistance.

Numerous applications for lightweight aggregate materials exist outside the construction industry, especially for expanded perlite and vermiculite. These are discussed in their respective chapters in this volume. One often-cited and unusual agricultural use in the 1980s was for bedding on a crocodile farm on the south coast of Natal, South Africa. Female crocodiles apparently became upset because there was no vermiculite—which was being used as a substitute for river sand to nest crocodile eggs—because a shipment of the material was delayed (Griffiths 1989).

ECONOMIC FACTORS

Price Trends

Prices for manufactured lightweight aggregates have risen dramatically in the past 10 years because of general inflation and higher energy costs. Fuel and transportation costs continue to rise. Other energy costs such as electricity for electric power are continuing to increase more rapidly than inflation. Cost of refractories is significant because prices reflect higher energy costs in manufacture.

Similar increases have been influencing the costs of expanded perlite and exfoliated vermiculite. Prices of lightweight aggregates will continue to reflect the rising cost of energy, and prices are likely to parallel energy costs.

Transportation

All forms of surface transport are used in moving lightweight aggregates. Truck transport is especially important in the delivery of expanded aggregates either in bulk or in containers. Economics of lightweight aggregate haulage are very similar to transportation of crushed stone and other aggregates. Because of the higher value of lightweight, however, some additional haulage can be tolerated with proportionately less delivered price impact. Transportation costs are likely to amount to 15% to 35% of the delivered price for most structural lightweight. The effect of transportation costs on delivered prices of vermiculite and perlite is naturally less because of the higher unit value.

A good rule of thumb is that distance of movement of aggregate materials is likely to be directly proportional to unit price and inversely proportional to unit weight and bulk. Perlite and vermiculite ore is air transported by rail from mines to delivery points throughout the United States and by ocean freighter throughout the world. Some vermiculite ores come to the United States by ship from South Africa, and rail haulage from the western United States to the East Coast is common. Exfoliated or expanded products, however, are not likely to be distributed outside local and regional markets because of their great bulk.

Rail transportation of other lightweight aggregates is largely regional; it is normally limited by the proximity of competing producers. Trucking may be local or regional depending on the availability of rail transport and relative costs. Trucks are normally most economical for hauls of 80 km or less; railroads are best suited for hauls in the 160 to 480 km range. The transportation method used is dictated by access to other competitive modes and by haulage costs. The object is to keep delivered price down to maximize returns to the producer.

Marketing

Most producers of natural and manufactured lightweight aggregates maintain their own sales staff and technical service representatives; some producers market products through brokers. Products are sold on the basis of specifications and cost-in-place of the final material. Often the ability to reduce dead loads (the weight of concrete in structures) by using lighter aggregates (in the concrete) will reduce the cost of structural steel. Insulation properties of ultra-lightweight aggregates in concrete and masonry units may enable the construction of thinner walls or reduce the need for other insulation. These factors often permit savings in building construction despite higher unit prices for lightweight aggregate. Product yield commonly can be improved by using manufactured lightweight. Surface textures and uniformity are commonly superior to naturally occurring or by-product aggregates.

By-product materials are normally handled by wholesale and retail dealers. The actual producers often handle slag sales, but cinders, fly ash, coke breeze, and other by-products are usually sold through brokers.

Producers of vermiculite and perlite ores generally license or franchise brokers for the exfoliated or expanded product. The raw material supplier gives trademarks, promotional materials, specifications, and other sales aids to the licensed or franchised dealer. The dealer pyroprocesses the ore and packages the product in bags or ships in bulk. The dealer acts as wholesaler in the distribution to large users and retail building material outlets.

Marketing research studies are usually important in the location of a new lightweight aggregate plant. The actual and potential use of lightweight aggregate materials in the intended market must be measured or estimated from planned and prospective construction trends. The proximity of competitors and transportation costs in the market area must be carefully studied to determine the economic feasibility of a new production plant.

Lightweight aggregate producers that do not maintain a marketing research department are advised not to initiate a new plant location without some market analysis. The choice of a consultant or specialized marketing research firm should be based on both the cost of the service and past experience in similar or related evaluations.

GOVERNMENT, ENVIRONMENTAL, AND HEALTH CONSIDERATIONS

Taxes, depreciation, and depletion allowances for lightweight aggregate producers are similar to those for producers of other construction materials. Zoning and land-use regulations are restrictive in urban and other heavily populated areas, and they are closely related to the situations encountered by producers of crushed stone or sand and gravel. The more limited occurrence of lightweight aggregate raw material deposits and the smaller number of producers, however, generally lead to the location of plants at greater distances from the more heavily populated market centers. Thus, lightweight aggregate producers tend to have fewer problems with zoning and land-use regulation. Where plants are simply pyroprocessing raw materials mined at distant locations or handling by-products, they are in the same category as heavy industry and are located in industrial areas.

As of mid-2005, there have been no significant reductions in government regulations on air and water pollution. Environmental standards continue to present challenges to the industry. If environmental standards are relaxed, there will be some cost savings, but not necessarily any significant reduction in production costs. The same observation can be made for safety and health regulations. Once implemented, the additional costs must be included in operating costs. Any relaxation in government regulations could, of course, hold down future cost increases.

Severe health problems associated with mining and milling of the vermiculite ore body at the Rainy Creek deposit near Libby, Montana, resulted in closure of the mine in 1990. The vermiculite deposit contains the asbestiform minerals tremolite, winchite, and richterite in the gangue; they were removed by dry concentration methods until 1970, when the process was replaced by wet concentration. Stockpiled ore shipments ended in 1994. Withdrawal of Libby vermiculite from the market and the attendant publicity about health problems had a major depressing effect on the vermiculite industry (see Tables 4 and 5). Sole domestic raw ore production has been from one deposit in Virginia and a number of deposits in South Carolina. Imports of ore increased from South Africa (ore from Palabora is reported to be free of asbestiform minerals), which, in turn stimulated imports from China and Brazil; China imported mostly to the West Coast, other imports were mostly to ports in the Gulf of Mexico, along the Mississippi River, and to the southeastern U.S. coast.

FUTURE OUTLOOK

Increase in the output of structural lightweight (suggested by the production figures in Table 4) is related to construction activity, which has been vigorous for several years. Even though gains in market share against conventional crushed stone and gravel for comparable applications have not been as robust as expected, structural lightweight should be expected to sharply gain in popularity

as aggregate supplies tighten. Lightweight should have a promising future because construction professionals will inevitably look more seriously at material replacements as mining for conventional aggregates gets more difficult and expensive. The costs of producing structural lightweight aggregates are related to the costs of energy and raw materials. Transportation costs of the finished aggregate have always had an effect on the price of the various lightweight materials available in the marketplace.

In the future, total consumption of lightweight aggregates will be more closely tied to the construction industry as lightweights are used as replacements in conventional applications, rather than being a function of specialty markets.

Mason (1994) indicated that demand for natural lightweights (specifically, pumice and volcanic cinders) appeared to be increasing over demand for manufactured lightweights, primarily because of their price benefits. Since then, however, industry consensus has tended to ward the opposite—more recently, field practitioners of concrete technology have preferred manufactured lightweights because the water content is much easier to control. Although demand for insulating materials has increased with rising energy costs, a persistent trend since the 1990s, overall perlite and vermiculite consumption have continued to sharply decrease (Bolen 2003a; Potter 2003). The decrease can be attributed, at least in part, to new developments in insulation that are beginning to replace older materials such as perlite. This will have an impact on markets for lightweight aggregates.

Tightening supplies of conventional aggregate, new innovations in manufactured lightweights, and further increases in energy prices should stimulate growth in demand for lightweight aggregates. Growth in demand for commodities used in manufactured lightweights, such as expanded clay, could exceed 4% per year, based on current trends (see Table 4). Demand for commodities used in natural lightweights, such as perlite, should continue to decline as manufactured lightweights gain popularity.

Because the final products of the lightweight aggregate industry have traditionally been energy-efficient buildings, the future of the sector will doubtless be closely linked to energy conservation trends. Insulation qualities of lightweight aggregates will continue to generate markets for these materials, but structural applications may gain prominence as new developments in insulation detract from the importance of lightweight aggregates in energy-efficient buildings.

ACKNOWLEDGMENTS

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Asbestos

Robert L. Virta

INTRODUCTION

Asbestos is the generic name given to six fibrous minerals that have been widely used in commercial products. An industry term rather than a mineralogical term, it is applied to mineral particles that possess high tensile strengths, large length-to-width ratios, flexibility, and resistance to chemical and thermal degradation. Asbestos also exhibits high electric resistance, and many forms can easily be woven in textiles. Asbestos particles generally comprise bundles of fibrils, which are the smallest crystalline units of asbestos. These fibrils typically are less than 50 to 70 nm in width and can be several hundred nanometers in length. Fibrils compose the fibers seen under the light microscope and in hand specimens of asbestos. In regulatory discussions, the terms *fiber* and *fibril* are often used interchangeably.

The six types of asbestos that have been recognized in commercial use are: actinolite asbestos, amosite, anthophyllite asbestos, chrysotile, crocidolite, and tremolite asbestos (Table 1). Chrysotile is the asbestiform variety of serpentine; the other five are amphiboles. Crocidolite and amosite are the asbestiform analogues of riebeckite and grunerite, respectively (Campbell et al. 1977; Ross, Kuntze, and Clifton 1984; Skinner, Ross, and Frondel 1988). Magnesioriebeckite from Bolivia has been used commercially although it was marketed as crocidolite. Other varieties of amphibole asbestos, including richterite and potassian winchite, have been recognized but not used commercially (Wylie and Huggins 1980; Hodgson 1986). Chrysotile historically has been the most commonly used form of asbestos, followed by crocidolite, amosite, and then anthophyllite asbestos. Relatively small amounts of tremolite asbestos and actinolite asbestos have been produced and used.

PRODUCTION AND TRADE

Production

Asbestos has been mined for more than 4,000 years with evidence of its use as early as 2500 BC (Gross and Braun 1984). A small asbestos industry appeared in the early 1800s when the Italians established a textile manufacturing industry (Alleman and Mossman 1997). Use of asbestos did not increase significantly until after 1880 when large chrysotile deposits in Canada and Russia, and amosite and crocidolite deposits in South Africa, were discovered. The development of these deposits provided a large and steady supply of asbestos, allowing the asbestos industry to expand (Sinclair 1959; Selikoff and Lee 1978). This expansion, first observed in the

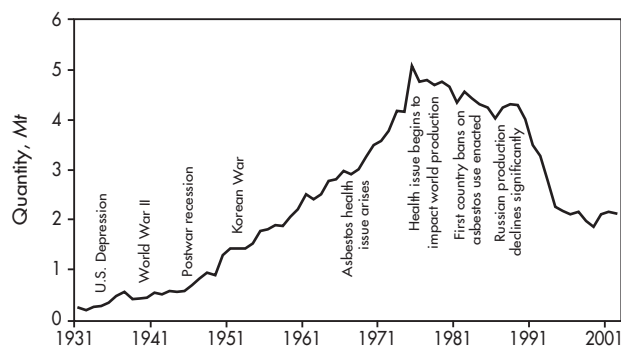
Table 1. Types of asbestos

Type	End Member Formulae
Actinolite asbestos	
Calcium magnesium silicate with varying amounts of iron	$\text{Ca}_2(\text{Mg}, \text{Fe}^{+2})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
Amosite (grunerite asbestos)	
Iron silicate with varying amounts of magnesium	$\text{Fe}^{2+}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
Anthophyllite asbestos	
Magnesium silicate with varying amounts of iron	$\text{Mg}_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
Chrysotile	
Hydrated magnesium silicate	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$
Crocidolite	
Complex sodium iron silicate (riebeckite) commonly called Blue Asbestos	$\text{Na}_2(\text{Fe}^{+2}_3\text{Fe}^{+3}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$
Tremolite asbestos	
Calcium magnesium silicate	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$

Source: Skinner, Ross, and Frondel 1988; Leake et al. 1997.

United States and then in Western Europe and the former Soviet Union, continued until about 1970 with few interruptions. The development of equipment to manufacture asbestos-cement pipe and sheet and the introduction of asbestos automobile brakes and clutches contributed to this rapid growth in the early 1900s.

During the early 1930s, however, there was a brief period of stagnation in world asbestos production that can be attributed mainly to the economic depression in the United States, which was the largest user of asbestos in the world. By 1935, world production increased as the U.S. economy began to recover (Figure 1). With the onset of World War II, production declined in most regions except Canada, South Africa, and the United States. U.S. war demands absorbed much of the increased production from these regions. Postwar reconstruction and expanding economies renewed the need for asbestos after the war and increased production of asbestos worldwide, which continued through the early 1970s. By this time, thousands of asbestos products were being produced in about 85 countries, and record asbestos production levels were achieved in many countries. At its peak around 1975, asbestos was mined in nearly 25 countries (Virta 2003).



Source: USBM 1934–1996; USGS 1924–1932, 1997–2004.

Figure 1. Estimated world asbestos production from 1931 to 2002

In the early 1970s, growing opposition to the use of asbestos began to affect demand on a worldwide basis. Regulations became increasingly strict in most user countries, and liability started to become a major issue. Companies that mined asbestos, manufactured asbestos products, and, much later, installed or used asbestos products began to face an increasing number of class-action lawsuits (Anon. 2002). Compounding the legal problems was the shift from asbestos-based products to the use of asbestos substitutes or alternative products (e.g., ductile-iron or polyvinyl-chloride pipe instead of asbestos-cement pipe) in response to public opposition to the use of asbestos. As a result, the United States saw asbestos production decline from a peak of 136,000 t in 1973 to 2,720 t in 2002. Production of chrysotile in the United States stopped in 2002. World production experienced a similar decline from a peak of about 5.09 Mt (probably including sales of serpentinite waste from processing asbestos ore) in 1975 to 2.13 Mt in 2002 (Virta 2003). Table 2 breaks out production, by major producing countries, in 10-year intervals from 1900 to 2000.

About 174 Mt of asbestos was produced between 1900 and 2000, of which an estimated 167 Mt was chrysotile. About 2.8 Mt of amosite was mined during this time, nearly all from South Africa, which also produced most of the approximately 3.9 Mt of crocidolite mined in this period. Small amounts of crocidolite also were mined in Australia and Bolivia. An estimated 460,000 t of anthophyllite were mined between 1900 and 2000, mostly in Finland and the United States. Since 1900, small but unrecorded amounts of actinolite, anthophyllite, and tremolite asbestos have been produced in Bulgaria, India, Italy, Pakistan, Romania, South Africa, Turkey, and perhaps others. Figure 2 shows the production trends for all types of asbestos combined.

In 2002, almost all of the world's production of asbestos was chrysotile. Small amounts, probably less than a few thousand tons, of actinolite, anthophyllite, and tremolite asbestos are produced for local use in countries such as India, Pakistan, and Turkey (Hodgson 1986; Virta 2003). Russia led all producing countries, with 35.3% of the world's total asbestos production, and was followed, in descending order of tonnage, by China with 16.9%, Kazakhstan with 13.7%, Canada with 12.8%, Brazil with 9.8%, and Zimbabwe with 6.1%. In 2002, these countries accounted for 94.6% of world asbestos production, which was all chrysotile. Ten other countries also mined asbestos in 2002 (Table 3).

Production Localities

Historically, asbestos mining (almost all of which was chrysotile) was concentrated in relatively few areas. The same was true in 2002.

Three mines in Quebec, including the Jeffrey mine (until recently the world's largest chrysotile mine), accounted for all of the Canadian production of chrysotile. These mines are located near the towns of Asbestos and Thetford in a serpentinite belt that extends from eastern Canada to Alabama in the United States. Of historical note is that the Jeffrey mine scaled back its operations in 2002, with mining and processing occurring on a part-time basis to fill special orders. As the customer base has shifted away from the use of asbestos, production in Canada declined after peaking at about 1.7 Mt in 1973; in 2002, it was less than 250,000 t (USGS 1997–2004; Virta 2003).

In Russia, chrysotile continues to be produced near Asbest in the Bazhenovo District, east of Orsk in the Orenburg District, and near Ak-Dovurak in the Tuva District. The bulk of the production is from mines located in the serpentinites in the Ural Mountains. In Kazakhstan, asbestos is mined southwest of Kustanay in the Dzhetysay District. In 2002, combined production from Kazakhstan and Russia was much lower than in the 1980s. The reporting of major increases in production between 1998 and 2000 in Russia and 1998 and 2002 in Kazakhstan may have resulted from the inclusion of mill wastes used as crushed stone rather than from growing markets for asbestos fiber. Combined asbestos production in these two countries peaked at about 2.7 Mt in 1982 and about 1.04 Mt in 2002 (USGS 1997–2004; Virta 2003).

In China, chrysotile is mined in Hebei, Liaoning, Sichuan, Qinghai, and Xinjiang provinces. Mines in northwestern China account for more than 60% of China's asbestos production (Lu 1998). Most of China's asbestos is used in local industrial applications. Going against world trends, production in China has increased over time—from 150,000 t in 1975 to 360,000 t in 2002—because of rising internal demand for asbestos products (USGS 1997–2004; Virta 2003).

In Brazil, chrysotile is mined near Cana Brava. Lower than its peak production of 237,000 t in 1991, Brazilian production has remained relatively steady at a little more than 200,000 tpy for the past 5 years (Virta 2003).

In Africa, chrysotile is produced near Shabani in Zimbabwe. Production peaked at 279,000 t in 1979, declined to 115,000 t in 1999, but rebounded to 130,000 t in 2002. Production in South Africa, once a major producing country, peaked at 380,000 t in 1977 but was only 10,000 t in 2002. Until the early to middle 1990s, South Africa was the world's leading supplier of amosite and crocidolite. In 1992 and 1997, respectively, when it closed its amosite and crocidolite mines, worldwide production of amosite and crocidolite ended (Figure 3).

Industry Changes

Shifts in asbestos production among the major producing countries occurred over time as new deposits were developed, economies changed, armed conflicts occurred, and asbestos-related health risks became a major market influence. Italy was the leading supplier of asbestos until the late 1800s when the Canadian deposits were developed. During the first half of the century, Canada was the dominant producer, accounting for 60% to 90% of the world's production. By the 1950s, Kazakhstan and Russia (combined), South Africa, and Zimbabwe were beginning to produce significant quantities of fiber. These countries continued to increase their production through the early 1980s with the combined production of Kazakhstan and Russia becoming, and remaining today, the world's leading producing region of asbestos. China and Italy in the 1960s and Brazil in the 1970s rose from relative obscurity to become significant producers of asbestos. Since the 1980s, production has declined in all major producing countries, except for China, because of opposition to asbestos use (see Figure 3).

Table 2. World asbestos production of major producer countries, ^t

Year	United States	Canada	South Africa	Zimbabwe	Swaziland	Italy	Brazil	Greece	Kazakhstan and Russia	China	Other	World Production
1900	956	26,400	158	na [†]	0	na	0	0	na	na	3,940	31,500
1910	3,350	92,700	1,350	na	0	na	0	0	11,100	na	611	109,000
1920	1,360	162,000	6,450	17,100	0	165	0	0	1,480	5	4,430	193,000
1930	3,850	220,000	17,500	34,300	0	851	0	2	54,100	315	7,570	338,000
1940	18,200	314,000	24,900	50,800	18,900	8,270	500	na	102,000 [‡]	20,000	17,100	574,000
1950	38,500	794,000	79,300	64,900	29,600	21,400	844	30	217,000	na	46,300	1,290,000
1960	41,000	1,010,000	160,000	121,500	29,100	54,900	3,540	0	599,000	81,600	109,000	2,210,000
1970	114,000	1,510,000	287,000	79,800	33,100	119,000	16,300	0	1,070,000	172,000	99,200	3,490,000
1980	80,100	1,320,000	277,000	251,000	32,800	158,000	169,000	na	2,070,000	132,000	177,000	4,670,000
1990	W [§]	725,000	146,000	161,000	35,900	3,860	205,000	66,000	2,400,000	221,000	50,500	4,010,000
2000	5,260	320,000	18,800	145,000	11,000	0	170,000	0	983,000	370,000	46,800	2,070,000
Total**	3,280,000	60,500,000	9,920,000	8,690,000	1,800,000	3,860,000	4,540,000	917,000	67,100,000	7,700,000	5,940,000	174,000,000

Source: Virta 2003.

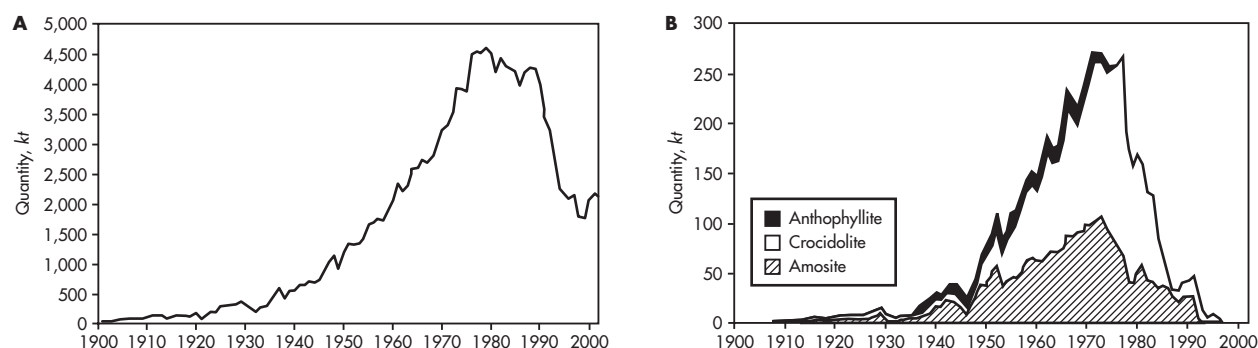
* More than 93%, by weight, of the asbestos produced between 1900 and 2000 was chrysotile.

† na = Not available.

‡ Estimated data.

§ W = Withheld to avoid disclosing company proprietary data.

** Total for 1900 to 2000, all years inclusive.



Source: USBM 1934–1996; USGS 1901–1921, 1924–1932, 1997–2004.

Figure 2. Estimated world production of chrysotile (A) and of amosite, anthophyllite, and crocidolite (B), from 1900 to 2000

Trade

Trade of asbestos also has shifted considerably throughout the 20th century. Until about 1950, the United States was the leading consumer of asbestos worldwide, using 37% to 99% of the world production annually between 1900 and 1950. For much of the 20th century, it was the leading importer of asbestos, mainly from Canada, South Africa, and Zimbabwe.

Canada, the principal producing country through much of the 20th century, supplied most of the asbestos (all chrysotile) used in U.S. markets. As other countries developed asbestos industries, Canada eventually became a major supplier of chrysotile to Asia, Europe, and South America. With the recent downturn in asbestos use in Europe and the United States, Canada's export focus has been to Southeast Asian countries.

By the 1940s, Kazakhstan and Russia (combined) had become a major exporter of chrysotile, supplying it to Eastern and Western Europe for decades, with smaller amounts being shipped to Asian countries. With the decline in asbestos usage in Western Europe since the late 1990s and significant declines occurring even in the former Soviet-bloc countries in Eastern Europe, export markets for Kazakhstan and Russia have declined.

South Africa was a major producer and supplier of asbestos (with more than 50% of production and sales being amosite and crocidolite) to the world. Prior to 1950, the United Kingdom and United States imported about 50% of South Africa's exports. Other important markets included Asia, the Middle East, and Europe. By the 1970s, however, South African export markets had shifted and Japan became the major importing country.

Zimbabwe is also a major world supplier of chrysotile. Its export markets were primarily in the United Kingdom through 1950, at which time the United States became a major consumer. Other export markets included Asia, Europe, and Latin America.

Several other producing countries supplied asbestos to world markets. Brazil exported worldwide but focused on South America and Caribbean countries. Cyprus, Greece, Italy, and Swaziland exported lesser amounts of asbestos to Africa, Europe, and Asia.

In general, the downturn in the asbestos industries of Europe and the United States after 1990 has caused a shift in major import markets to a few European countries (Belarus, Romania, and Spain) and Asia (India, Indonesia, Japan, the Republic of Korea, Thailand, and Turkey). Of these countries, India, Japan,

Table 3. World asbestos production by country, t[†]

Country [†]	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
Argentina	309	260	300	446	264	309	259	254	250	250
Bosnia and Herzegovina [‡]	500	300	0	0	0	0	0	0	0	0
Brazil	185,000	192,000	170,000	170,000	170,000	198,000	188,000	209,000	209,000	209,300
Bulgaria [‡]	500	500	100	400	300	300	350	350	350	300
Canada	523,000	531,000	516,000	506,000	455,000	309,000	337,000	307,000	272,000	272,000
China [‡]	240,000	303,000	263,000	293,000	288,000	314,000	247,000	320,000	360,000	360,000
Colombia, crude ore	na [§]	na	na	na	na	128,000	61,100	59,200	96,100	62,800
Egypt [‡]	436	514	427	1,840	2,000	700	1,000	2,000	2,000	2,000
Greece [‡]	57,000	55,500	76,000	80,200	63,300	50,000	0	0	0	0
India [‡]	44,100	29,800	25,100	23,200	25,100	18,800	20,000	21,000	21,000	19,000
Iran [‡]	4,500	4,500	4,500	4,500	4,300	2,260	2,000	2,000	2,000	1,500
Japan [‡]	24,900	21,000	20,000	18,000	18,000	18,000	18,000	18,000	18,000	18,000
Kazakhstan	130,000	130,000	128,000	128,700	182,000	155,000	139,300	233,200	271,000	291,000
Russia [‡]	1,000,000	700,000	680,000	615,000	710,000	600,000	675,000	750,000	750,000	750,000
Serbia and Montenegro	314	498	497	509	360	633	361	563	194	200
South Africa	131,000	92,100	88,600	57,100	50,000	27,200	18,800	18,800	13,400	10,000
Swaziland	33,900	26,700	28,600	26,000	25,900	27,700	22,900	12,700	0	0
United States (sold or used by producers)	13,700	10,100	9,290	9,550	6,890	5,760	7,190	5,260	5,260	2,720
Zimbabwe	157,000	152,000	169,000	165,000	145,000	123,000	115,000	152,000	136,000	130,000
Total	2,520,000	2,250,000	2,180,000	2,100,000	2,150,000	1,980,000	1,850,000	2,110,000	2,160,000	2,130,000

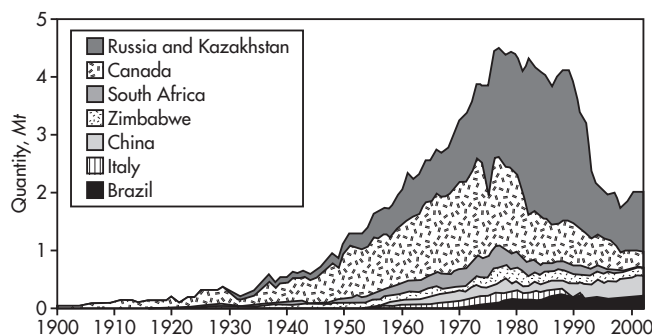
Source: USBM 1934–1996; USGS 1997–2004.

* World totals, U.S. data, and estimated data are rounded to no more than three significant digits; may not add to totals shown. More than 99%, by weight, of the asbestos produced between 1993 and 2002 was chrysotile.

† In addition to the countries listed, Afghanistan, North Korea, Romania, and Slovakia also produce asbestos, but output is not officially reported and available general information is inadequate for the formulation of reliable estimates of output levels.

‡ Estimated.

§ na = Not available.



Source: USBM 1934–1996; USGS 1901–1921, 1924–1932, 1997–2004.

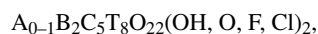
Figure 3. Major producers of asbestos from 1900 to 2000

and Thailand are the leading consumers, dependent on imports for most of their manufacturing needs (Virta 2003).

GEOLOGY

Mineralogy

Chrysotile is a hydrated magnesium silicate with a chemical composition of $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ and may contain small amounts of iron, manganese, and nickel, and trace amounts of aluminum. The compositions of the other common asbestos types, which are amphiboles, are more complex. Amphiboles are represented by the formula



where

A = Na and/or K

B = Na, Ca, Mg, Fe^{2+} , Mn, and/or Li

C = Al, Fe^{2+} , Fe^{3+} , Ti, Mg, Mn, and/or Cr, and

T = Si and/or Al.

The composition of chrysotile and the common amphibole asbestos varieties are given in Table 1, with only the major cations listed (Whittaker 1979; Wicks 1979; Zussman 1979; Hodgson 1986; Skinner, Ross, and Frondel 1988; Leake et al. 1997). Leake et al. (1997) provide a detailed breakout of the amphibole varieties by chemistry, identifying specific compositional ranges of each.

The basic building block of asbestos fibers is the silicate tetrahedron, which typically occur as sheets ($\text{Si}_4\text{O}_{10}^{4-}$ in chrysotile and double chains ($\text{Si}_4\text{O}_{11}^{6-}$ in the amphiboles (Figure 4). The sheets and chains have an overall negative charge so cations as well as hydroxyl units (OH^-) are sandwiched between the sheets in chrysotile and chains in amphiboles to balance out the ionic charge in the structures (Deer, Howie, and Zussman 1966; Skinner, Ross, and Frondel 1988; Frondel 2001).

Owing to a mismatch of the dimensions of the cation layer (composed of $\text{Mg}[\text{OH}]_2$ structures, also called the brucite or octahedral layer) with the silicate layer (Si_2O_5 or tetrahedral layer) in chrysotile, the sheet spirals into an extremely thin fiber having an average diameter of approximately 25 nm (Figure 5, note end structures). Slight variations in the crystal structure result in the formation of three chrysotile polytypes: clinochrysotile, orthochrysotile, and parachrysotile (Wicks 1979; Hodgson 1986).

The structure of the amphiboles consists of two chains based on Si_4O_{11} units separated by a band of seven cations with two

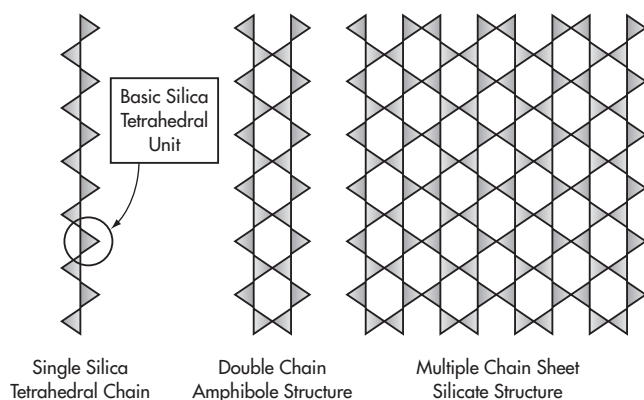
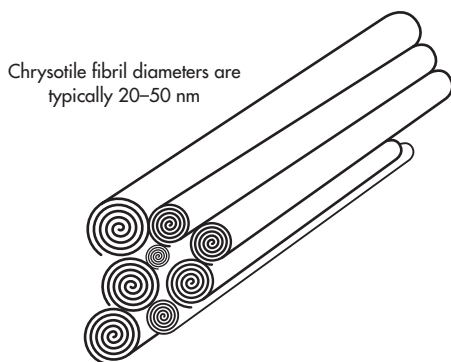


Figure 4. Single silica tetrahedral chain that is the basis for the double-chain-width structure of amphiboles and the multiple-chain-width structure of sheet silicates



Adapted from Hodgson 1986.

Figure 5. Spiraling sheet structure of chrysotile fibrils

hydroxyl groups attached to the central cation of each unit cell. These are often called I-bars because of their shape in cross section. These stack together to form the final structure, with a marked cleavage developed between the ribbons (Figure 6). Under the conditions in which amphibole asbestos forms, crystal growth is preferential in the direction of the chain length, resulting in amphibole fibers that are long and thin (Ross 1981).

Physical Properties

Asbestos fibers are characterized by high tensile strength, flexibility, resistance to chemical attack and thermal degradation, large surface area, and ability of some varieties to be woven. Each type of asbestos has different physical characteristics, as do the same asbestos types from different sources (Sinclair 1959; Zussman 1979).

Chrysotile is a white, fibrous material. The fibers are extremely thin, and most are soft and flexible enough to be woven. Individual chrysotile fibers have diameters ranging from 25 nm to 50 nm (Yada 1967). Commercial grades of chrysotile have lengths ranging from a fraction of a millimeter to several centimeters (Badollet 1951). Chrysotile fiber bundles can have lengths of 5 cm (Selikoff and Lee 1978). Most of the chrysotile fibers used commercially are shorter than 1 cm. Bundle widths can be several millimeters (Virta 2002). There are fundamental differences in fiber lengths of chrysotile from different deposits. In commercial samples defiberized in suspension

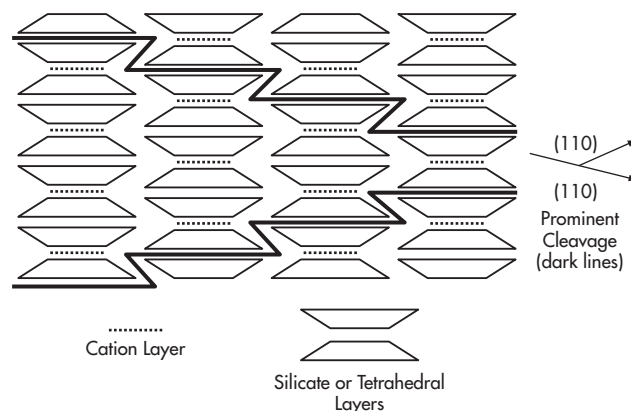


Figure 6. Amphibole structure showing the octahedral cation layer sandwiched between the silicate double chains perpendicular to the C axis

using an anionic surfactant, average chrysotile fiber lengths were 4.0 mm for a Kaapsche Hoop sample (South Africa), 1.8 mm for a Cassiar sample (British Columbia, Canada), 1.4 mm for a Bell mine sample (Quebec, Canada), and 0.6 mm for a Shabani sample (Zimbabwe) (Hodgson 1986).

Tensile strength measurements on asbestos correspond to the strength of fiber bundles rather than individual fibers. Consequently, there is a wide variation in reported values. Data summarized by Hodgson (1986) show the tensile strength of chrysotile to be between 1,107 MN/m² (meganewtons per square meter) and 4,400 MN/m², making it one of the stronger asbestos types. Tensile strength increases slightly when heated until thermal degradation occurs (Bryans and Lincoln 1971; Hodgson 1986).

Because chrysotile is heat resistant, it is used routinely in commercial products that may be exposed to temperatures exceeding 700°C. Around 90°C, chrysotile begins to lose adsorbed water. Dehydroxylation (loss of the OH⁻ in the structure) begins at 640°C and is complete by 810°C. Above 810°C, the chrysotile structure begins to transform into forsterite and silica. These reactions are affected by sample preparation and impurities in the sample (Deer, Howie, and Zussman 1966; Hodgson 1986). The fusion temperature for chrysotile is 1,521°C (Badollet 1951).

Chrysotile has an extremely large surface area, on the order of 13 to 18 m²/g because of its fibrillar structure. Fiberizing the samples has little effect on the measured surface area of chrysotile, which suggests easy penetration of the fiber bundles by gases regardless of the degree of fiberization (Hodgson 1986).

Amphibole asbestos fibers generally are harsher and more brittle than those of chrysotile. They also are more resistant to chemical attack, have very high filtration rates, have a greater hardness (4 to 6 on the Mohs scale), and are comparatively long, ranging up to several inches (Table 4). Their color ranges from white for tremolite through yellowish-brown for amosite to lavender or blue for crocidolite (Badollet 1951). Tensile strengths range from 303 MN/m² for a tremolite asbestos from Pakistan to about 3,089 MN/m² for a crocidolite from South Africa (Aveston 1969; Hodgson 1986). All of the forms of amphibole asbestos withstand temperatures exceeding several hundred degrees Celsius without degradation. The fusion temperature for all of the asbestiform amphiboles exceeds 1,224°C. Their resistance to attack by acids and bases ranges from fair for actinolite asbestos to very good for anthophyllite asbestos (Badollet 1951).

Table 4. Properties of asbestos fibers

Property	Actinolite Asbestos	Anosite	Anthophyllite Asbestos	Chrysotile	Crocidolite	Tremolite Asbestos
Structure	Reticulated long prismatic crystals and fibers	Lamellar; coarse to fine fibrous and asbestiform	Lamellar; fibrous asbestiform	Usually highly fibrous fibers; fine and easily separable	Fibrous in ironstones	Long; prismatic and fibrous aggregates
Mineral association	In limestone and in crystalline schists	In crystalline schists, etc.	In crystalline schists and gneisses	In altered peridotite adjacent to serpentine and limestone; near contact with basic igneous rocks	Iron-rich siliceous argillite in quartzose schists	In Mg limestones as alteration products of highly magnesian rocks; metamorphic and igneous rocks
Origin	Metamorphic	Metamorphic	Metamorphic	Metamorphism of basic igneous rocks	Regional metamorphism	Metamorphic
Veining	Slip or mass fiber	Cross fiber	Slip or mass fiber	Cross and slip fibers	Cross fiber	Slip or mass fiber
Essential composition	Ca, Mg, Fe silicate with some water	Fe, Mg silicate with some water	Mg silicate with some iron	Mg silicate with some water	Na, Fe silicate with some water	Ca, Mg silicate with some water
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Color	Greenish	Ash gray or brown	Grayish white; brown-gray or green	White, gray, green	Lavender blue, metallic blue	Gray-white, greenish, yellowish, bluish
Luster	Silky	Vitreous; somewhat pearly	Vitreous to pearly	Silky	Silky to dull	Silky
Hardness	6±	5.5–6.0	5.5–6.0	2.5–4.0	4	5.5
Specific gravity	3.0–3.2	3.1–3.25	2.85–3.1	2.4–2.6	3.2–3.3	2.9–3.2
Optical properties	Biaxial negative, extinction inclined	Biaxial positive, extinction parallel	Biaxial positive, extinction parallel	Biaxial positive, extinction parallel	Biaxial ±, extinction parallel	Biaxial negative, extinction inclined
Refractive index	1.63 ± weakly pleochroic	1.64 ±	1.61 ±	1.51–1.55	1.7 pleochroic	1.61±
Length	Short to long	51 to 280 mm; varies	Short	Short to long	Short to long	Short to long
Texture	Harsh	Coarse but somewhat pliable	Harsh	Soft to harsh; also silky	Soft to harsh	Generally harsh; sometimes soft
Specific heat, J/kg/°K	505	449	488	619	468	493
Tensile strength, kN/m ²	6,895 and less	110,316–620,528	27,579 and less	551,581–689,476	689,476–2,068,427	6,895–55,158
Temperature at maximum ignition loss, °C	na*	871–982	982	982	648	982
Filtration properties	Medium	Fast	Medium	Slow	Fast	Medium
Electric charge	Negative	Negative	Negative	Positive	Negative	Negative
Fusion point, °C	1,393	1,399	1,468	1,521	1,229	1,316
Spinnability	Poor	Fair	Poor	Very good	Fair	Poor
Resistance to acids and alkalis	Fair	Good	Very good	Poor	Good	Good
Mineral impurities present	Lime, iron	Iron	Iron	Iron, chrome, nickel, lime	Iron	Lime
Flexibility	Poor	Good	Poor	High	Good	Poor
Resistance to heat	na	Good; brittle at high temperatures	Very good	Good; brittle at high temperatures	Poor, fuses	Fair to good

Source: Badollet 1951; ATSDR 2001.

* na = Not available.

Table 5. Chemical analyses of asbestos samples, %

Compound	Chrysotile	Crocidolite	Amosite	Anthophyllite Asbestos	Tremolite Asbestos
SiO ₂	38.75	50.90	49.70	57.20	55.10
MgO	39.78	1.06	6.44	29.21	25.65
FeO	2.03	20.50	39.70	10.12	2.00
Fe ₂ O ₃	1.59	16.85	0.03	0.13	0.32
Al ₂ O ₃	3.09	0	0.40	0	1.14
H ₂ O	12.22	2.37	1.83	2.18	3.52
CaO	0.89	1.45	1.04	1.02	11.45
Na ₂ O	0.10	6.20	0.90	0	0.14

Adapted from Skinner, Ross, and Frondel 1988.

Amphiboles have a surface area of 2 to 9 m²/g, which increases with fiberization. This is not true, however, for chrysotile asbestos (Addison, Neal, and White 1966; Hodgson 1986).

Amphibole fibers generally are more variable in width and less symmetrical than chrysotile fibrils. Franco et al. (1977) examined samples of crocidolite with fiber widths ranging from 50 to 150 nm, although widths up to 350 nm also have been reported for other samples (Wylie 1979). Lengths of fiber bundles up to 8 cm for crocidolite and 30 cm for amosite have been described (Selikoff and Lee 1978).

Chemical Properties

Ideal compositions (Table 1) frequently are different from those observed in deposits. Chrysotile fibers normally contain mineral impurities, including, commonly, magnetite, which accounts for higher than normal iron concentrations. Other minerals that may be present include brucite, calcite, and chrochite (Hodgson 1986). Skinner, Ross, and Frondel (1988) reported analyses for chrysotile from Canada, Swaziland, the former Soviet Union, and Zimbabwe. They found that SiO₂ content ranged from 38.75% to 39.93%, MgO ranged from 38.22% to 40.30%, FeO ranged from 0.45% to 2.03%, and Fe₂O₃ ranged from 0.10% to 1.59%. Hahn-Weinheimer and Hirner (1977) reported the average composition of 28 chrysotile samples from Quebec and Newfoundland as 42.123% SiO₂, 41.868% MgO, 0.48% FeO, and 1.357% Fe₂O₃. They also reported 0.418% Al₂O₃, 0.019% CaO, 0.004% CoO, 0.006% Cr₂O₃, 0.052% MnO, 0.087% NiO, 0.002 TiO₂, and 13.8% H₂O⁺.

The ideal and observed compositions for asbestiform amphiboles often differ because cations are easily substituted for one another in the A, B, and C sites in the amphibole crystal structure. This results in a wide range of compositional variations. Using the nomenclature developed by the International Mineralogical Association, amphiboles are categorized as (1) magnesium-iron-manganese-lithium, (2) calcic, (3) sodic-calcic, and (4) sodic, encompassing about 75 amphibole end members (Leake et al. 1997). The complexity of amphibole nomenclature is pertinent to the asbestos issue in that current asbestos regulations specifically mention actinolite asbestos, amosite (grunerite asbestos), anthophyllite asbestos, crocidolite (riebeckite asbestos), and tremolite asbestos. Wylie and Verkouteren (2000) and Meeker et al. (2003) identified asbestiform varieties of magnesioriebeckite, richterite, tremolite, and winchite in a vermiculite deposit in Libby, Montana. Meeker et al. (2003) further indicated that edenite and magnesioarfvedsonite may also be present in low concentrations. These asbestiform minerals had been identified as soda tremolite, richterite, soda-rich tremolite, and tremolite asbestos in past studies (Larsen 1942; Nolan et al. 1991). So, although only five forms of amphibole asbestos are recognized by regulatory agencies, other amphibole varieties may possess a fibrous

or asbestiform habit. Table 5 lists compositions for the major amphibole asbestos varieties.

Chrysotile has a surface charge that can be positive or negative depending on its source. Most chrysotile has a positive charge, reflecting the net positive charge of the (MgOH)⁺ layer on the outer surface layer of the fiber. Fibers from which weathering has removed the (MgOH)⁺ layer, exposing the silica-rich layer below, have negative charges. The size and sign of the charge also change when the fiber is suspended in solutions of different pH and composition. Ions in the solution may be adsorbed onto the fiber's surface, changing the surface charge (Chowdhury and Kitchener 1975; Hodgson 1986). Zeta potentials for chrysotile range from 13.6 mv to 54 mv for selected samples (Chowdhury and Kitchener 1975; Hahn-Weinheimer and Hirner 1977). Treatment of chrysotile with acid removes (MgOH)⁺ layers, mimicking weathering, and produces a negative surface charge, which ranged to -16.6 mv for a sample from Dzhetysay District in Kazakhstan (Gracheva 1972; Chowdhury and Kitchener 1975).

The surface charge for asbestiform amphiboles is negative with zeta potentials ranging from -10 mv to -40 mv for selected samples (Ralston and Kitchener 1975; Hodgson 1979). The negative charge is attributed to the silica-rich layers exposed on the fiber surface.

The isoelectric point or pH for zero potential for chrysotile ranges from 10.5 to 11.3, depending on the source of the fiber and the method of measurement. Chrysotile flocculates from solution when its isoelectric point is reached. Amphiboles, however, maintain their strongly negative surface charge at higher pH levels and remain dispersed under conditions that cause chrysotile to flocculate. These properties were used to advantage in highly alkaline cement mixes where the amphibole fibers, not being flocculated, helped to disperse the chrysotile, which would normally have flocculated in the cement mix (Hodgson 1986). The isoelectric points for several amosite and crocidolite samples examined were between 2.2 and 4.0 (Prasad and Pooley 1973).

Asbestos often is used in chemical applications where resistance to chemicals is of paramount importance. Table 6 gives data on the effect of various acids and caustic soda on asbestos after long exposure at room temperature and for short exposure at boiling temperatures. Strong acids aggressively attack chrysotile, which is resistant to 25% caustic but is attacked by strong caustic (70%) at its boiling temperature (Badollet 1951).

Most amphibole fiber varieties are more acid resistant than those of chrysotile. They are not entirely acid resistant, however, and can exhibit weight losses of 2% to 23% through dissolution when exposed to concentrated acids at higher temperatures. Because of their higher iron contents, actinolite and amosite exhibit greater weight loss when exposed to acids than do the other amphibole asbestos varieties (Hodgson 1979, 1986).

Table 6. Solubility of asbestos

Type	Percent Loss in Weight, Refluxing 2 hr, 25% Acid or Caustic				
	HCl	CH ₃ COOH	H ₃ PO ₄	H ₂ SO ₄	NaOH
Actinolite	20.31	12.28	20.19	20.38	9.25
Amosite	12.84	2.63	11.67	11.35	6.97
Anthophyllite	2.66	0.60	3.16	2.73	1.22
Chrysotile	55.69	23.42	55.18	55.75	0.99
Crocidolite	4.38	0.91	4.37	3.69	1.35
Tremolite	4.77	1.99	4.99	4.58	1.80

Type	Percent Loss in Weight, Room Temperature 26°C for 528 hr, 25% Acid or Caustic				
	HCl	CH ₃ COOH	H ₃ PO ₄	H ₂ SO ₄	NaOH
Actinolite	22.55	12.14	20.10	20.60	9.43
Amosite	12.00	3.08	11.83	11.71	6.82
Anthophyllite	2.13	1.04	3.29	2.90	1.77
Chrysotile	56.00	24.04	56.45	56.00	1.03
Crocidolite	3.14	1.02	3.81	3.48	1.20
Tremolite	4.22	1.41	4.89	4.74	1.65

Source: Table originally published in a paper by M.S. Badollet in the *CIM Transactions* (1951). Reproduced with permission from the Canadian Institute of Mining, Metallurgy, and Petroleum.

Table 7. Effect of temperature on loss in weight of asbestos fibers

Temp., °C	Time, hr	% Loss in Weight				
		Amosite	Anthophyllite Asbestos	Chrysotile	Crocidolite	Tremolite Asbestos
204	2	0.23	0.05	0.30	0.08	0.04
316	2	0.57	0.24	0.85	0.25	0.08
371	2	0.80	0.30	1.78	0.49	0.13
427	2	0.98	0.38	2.17	0.73	0.22
482	2	1.07	0.41	2.83	0.83	0.26
538	2	1.16	0.44	3.99	0.86	0.29
593	2	1.36	0.52	10.38	1.00	0.37
649	2	1.39	0.54	12.75	1.04	0.37
760	2	1.43	0.54	13.43	1.03	0.47
816	2	na*	0.64	na	na	0.56
871	2	1.52	1.12	13.62	0.93†	0.67
927	2	na	1.73	na	na	1.40
982	2	1.53	2.39	13.77	0.77†	2.18

Source: Badollet 1951; Badollet and Streib 1955.

* na = Not available.

† Iron changing in weight as the result of oxidation.

Higher temperatures also cause other physical changes in asbestos. Besides dissolution of the fiber in boiling acids, weight can also change through water loss. Higher temperatures evaporate adsorbed water first and eventually result in the loss of structure water (OH⁻). The weight loss for the amphiboles is considerably less than that for chrysotile because much less OH⁻ is available to be driven off as water. Weight losses for different types of asbestos when heated for 2 hr at successive temperatures from 204° to 982°C are shown in Table 7 (Badollet 1951; Badollet and Streib 1955).

Table 8 shows the effect of heating on the tensile strength of Canadian chrysotile fiber. The fiber bundles tested were very small so that the heat transfer would be completed in the 3-min heating time. Even after heating at 648°C, chrysotile retained 32% of its strength (Badollet 1951).

Table 8. Effect of heat on tensile strength of Canadian chrysotile fiber

	Tensile Strength, kN/m ²	Percent of Original Tensile Strength
Original crude, no heat	903,000	100.0
Heated 3 min at 316°C	827,000	91.6
Heated 3 min at 427°C	662,000	73.3
Heated 3 min at 538°C	538,000	59.5
Heated 3 min at 649°C	290,000	32.0

Source: Table originally published in a paper by M.S. Badollet in the *CIM Transactions* (1951). Reproduced with permission from the Canadian Institute of Mining, Metallurgy, and Petroleum.

Principal Deposits

Major asbestos deposits occur in mountain chains of all ages where widespread metamorphism has occurred (Figure 7). Deposits in the Urals, the Appalachians, and the Rocky Mountains are classic examples.

Origin and Modes of Geologic Occurrence

The host rock for most of the world's chrysotile production is ultrabasic in composition (Keith and Bain 1932; Berger 1963; Bates 1969; Whittaker 1979)—categorized as Type I or Type II deposits. Type I deposits occur in alpine-type ultramafic rocks, including ophiolites and serpentinites. Type II deposits can be found in stratiform ultramafic intrusions. The remaining chrysotile production is derived from serpentinized dolomitic limestone, or Type III deposits. Amosite and crocidolite are found in metamorphosed ferruginous sedimentary formations, or Type IV deposits, which include banded ironstones, ferruginous quartzites, and iron-rich silicified argillite (Ross and Virta 2001). Tremolite asbestos and anthophyllite asbestos are associated with metamorphosed ultrabasic rocks.

The geologic age of asbestos deposits ranges greatly from earliest Precambrian in Zimbabwe and Swaziland to Upper Jurassic in California. The Ontario, Ungava, and Brazil deposits are Precambrian. Deposits of the Eastern Townships, Vermont, and Newfoundland are Mid-Paleozoic in age and are associated with

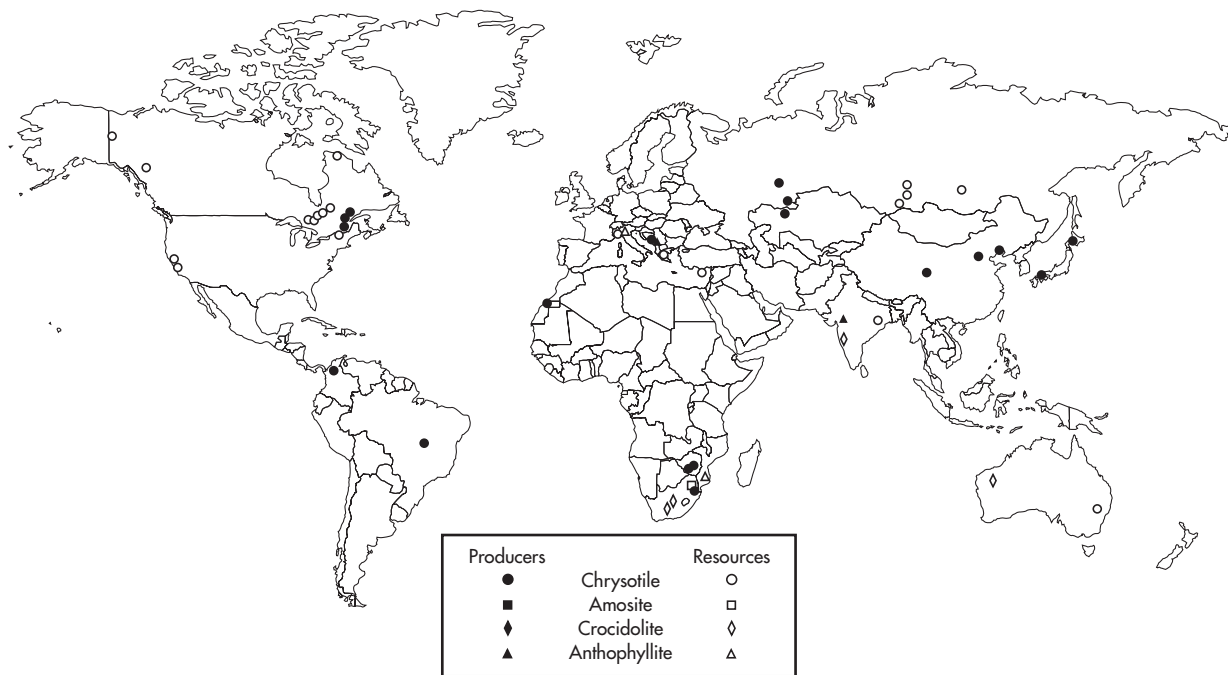


Figure 7. World asbestos deposits

early folding in the Appalachian mountain belt. The deposits of western Canada are associated with mountain building during the Late Paleozoic, while the deposits in Kazakhstan and Russia range from Early Paleozoic to Late Paleozoic or Triassic in age.

Structures

Faulting, folding, or shearing played a major role in the formation of chrysotile deposits in altered ophiolite sequences (Cooke 1937; Lamarche and Wicks 1975). The basic sequence followed was (1) serpentinization of ultramafic rocks; (2) compression associated with volume increase and tectonic collisions resulting in thrust faulting, shearing, more serpentinization, and formation of chrysotile; and (3) release of compression resulting in gravity faulting, jointing, and brecciation; followed by succeeding cycles. The introduction of swarms of small intrusive dikes of acidic to intermediate composition also contributed to the fracturing and opening of the rock. Fracturing, in turn, led to serpentinization and the formation of chrysotile fiber.

Most chrysotile ore deposits are found in serpentinized peridotitic rather than in dunitic host material. It is believed that the serpentinized dunitic bodies tend to flow when subjected to stress, thereby aiding in the development of fracturing in the surrounding, more brittle peridotitic bodies.

Asbestos Veining

Chrysotile asbestos is referred to as *cross fiber* when the fibers lie transverse to the vein, and as *slip fiber* when the fiber lies in the plane of the vein (Cooke 1937; Gold 1967; Whittaker 1979). The orientation of cross-fiber chrysotile ranges from normal to sharply inclined to the vein walls. When sharply inclined, it is referred to as *oblique fiber*. The fiber in cross-fiber and slip-fiber veins may be straight, gently curved, or contorted. Fiber containing sharp flexures is apt to break easily.

Partings are present in many of the veins, either as microscopic discontinuities or as irregularly shaped inclusions composed

of picrolite, serpentine, brucite, and magnetite, or combinations of these. The veins may be relatively persistent or short and lenticular, in the form of stockworks or in parallel systems known as ribbon fiber. They may be fissure fillings, replacements, or stress-relief features, and many are the result of a combination of these processes. Some very short fiber is derived from a variety referred to as mass fiber. Mass fiber consists of either the complete replacement of most of the original mineral constituents by fiber, each grain of which has a different fiber orientation, or by a dense network of fine, reticulating replacement veins. Both varieties result in a very high content of short fiber, and the rock, which appears to be largely fibrous, is sometimes referred to as "fur rock."

Chrysotile Deposits in Ultrabasic Rocks in North America

Ultrabasic deposits encompass the Type I and Type II deposits. Accounting for about 90% of the world production of asbestos, Type I deposits generally contain cross- or slip-fiber veins (Ross and Virda 2001). Examples of these types of deposits occur throughout the world. Typical are the chrysotile deposits in the Eastern Townships, Quebec, Canada, which occur along a major serpentine belt that arcs northeastward into the Gaspé Peninsula and southward into the Appalachian mountain belt of Vermont.

Most of the major deposits are located along a region 90 km long that lies parallel to and 80 km southeast of the St. Lawrence River. The region extends from a point near East Broughton, Quebec, southwestward past Thetford Mines and Black Lake to Asbestos and Danville.

This serpentine belt is a typical ophiolitic complex of gabbroic and dioritic rocks, and of serpentinized pyroxenite, peridotite, and dunite. The complex is associated with granitic, rhyolitic, and talc-carbonate rocks and is a partially serpentinized ultrabasic intrusive emplaced in the crust along faulted zones of weakness. It may have been extruded onto, or just under, unconsolidated aluminous and siliceous sediments in a eugeosyncline ocean basin. Magmatic differentiation within the ultramafic magma is thought to have been

responsible for the formation of the various pyroxenite, peridotite, and dunite phases found in the complex. Chrysotile formed mainly in highly serpentinized peridotite (harzburgite containing 10% to 15% enstatite) and is found in numerous places along the strike of the complex. The complex is believed to have been a submarine extrusive, simplifying the explanation of the source of water for serpentinization, the allowance for large volume change, the presence of fiber as open fracture fillings in stockworks, and the banded fiber in ribbon zones. It also explains the presence of pillows, most of which are gradationally serpentinized from the surface inward (Yamarche and Riordon 1981).

Another example is the Shabani deposit, situated about 160 km east of Bulawayo, Zimbabwe. This deposit is renowned for its low iron content, resulting from the low concentration of magnetite in the fiber, and its long fiber length (Bowles 1959). The deposit lies near the base of a lenticular ultrabasic sill, which is 14 km long and 2 to 5 km wide and intrudes Early Precambrian gneisses. The sill, which strikes northwest and dips about 40° SW, is composed of dunite at the base, overlain by peridotite, pyroxenite, and gabbro. A swarm of younger diabase dikes cuts the ore zone. Strong zones of shearing, both parallel and oblique to the basal contact, truncate the dikes. The intrusion and shearing have caused strong serpentinization of the dunite and heavy talc-carbonate alteration, particularly along the footwall shear zone. The fiber is present as a stockwork of cross-fiber veins described as stress-controlled dilation seams. The quality is good, and the length of the fiber is as much as 38 mm in places (Laubscher 1964, 1968; Oldham 1968; Wilson 1968).

A third example of chrysotile in ultrabasic rock is near Coal-inga, California. Unlike the previous two examples, the Coalinga deposit is a mass fiber deposit of chrysotile. Instead of the fiber being present in veins as cross or slip fibers, it is distributed throughout the entire rock mass. The deposit is an ultrabasic intrusive that trends northwestward, covers an area about 20 km long and 5 to 8 km wide (Munro and Reim 1962), and intrudes into Jurassic sediments in Late Jurassic or Early Cretaceous times. It is a highly sheared serpentinite with abundant slickensides, and the ore is extremely platy. Boulders of massive serpentinized material are scattered throughout the loose platy serpentine. Landslides, for which there is evidence, may have contributed to the extreme deformation of the serpentine. The ore contains abundant short chrysotile fiber.

Chrysotile Deposits in Dolomite

In addition to the large deposits of chrysotile asbestos found in serpentinized peridotite, comparatively small tonnages are mined from Type III, or serpentinized dolomitic limestones (Hall 1930; duToit 1946; Pelletier 1964; Van Biljon 1964; Rowbotham 1970). Much of such fiber is of high quality and free of the magnetite that is commonly associated with most deposits of ultrabasic origin.

Chrysotile of this type was mined in the Carolina District in the Transvaal, South Africa, and in the Salt River and Sierra Ancha regions in Arizona, United States. The Arizona deposits, approximately 60 km northeast of Globe, are tabular in shape and are in a serpentinized dolomitic limestone formation. Serpentinization occurred during the intrusion of diabase sills. Chrysotile is found in thin discontinuous veins. The fiber ranges from harsh to soft and from a few millimeters to several centimeters long. Unlike the ultrabasic deposits, the Globe deposit is relatively free of magnetite (U.S. Bureau of Mines 1945; Li 1975).

Crocidolite and Amosite Deposits

Examples of Type IV deposits occur in South Africa, where crocidolite and amosite are found in deposits known as banded iron-

stones, ferruginous quartzites, or iron-rich silicified argillites (Hall 1930; duToit 1946; Frankel 1953; Cilliers et al. 1961; Keep 1961; Cilliers, Le, and Genis 1964; Pelletier 1964; Dreyer and Robinson 1981). Cross-fiber veins are present as closely spaced ribbons roughly conformable with the bedding, which in some localities is distorted and dips steeply. Most crocidolite veins are less than 50 to 80 mm thick, and most of the fiber is between 6 to 19 mm in length. Amosite veins commonly are 250 to 300 mm thick.

Crocidolite is found over a large area of Cape Province in a belt of the Lower Griquatown series of the Transvaal system. Crocidolite and amosite are found in similar formations in the vicinity of Pietersburg in northern Transvaal. In some places, the two varieties are side by side in the same vein. A vein composed of crocidolite at one end and amosite at the other is called a doublet. In the Pietersburg Area, a silky, dusty blue variety of amosite called montasite, sometimes confused with crocidolite, has been found.

An amosite-bearing banded ironstone formation crops out for a distance of more than 30 km near Penge in the Lydenburg District of the Transvaal. The fiber-bearing banded ironstones and associated sedimentary members dip southwestward at about 20°. Thin, persistent sills of dolerite that are conformable with the bedding have intruded this sequence. Mapping in the Transvaal region revealed that the deposits were located on the loci of intersections of anticlinal or synclinal structures generated by superimposed north- and east-trending folds. Similar patterns of cross-folding were observed in many crocidolite deposits in the Northwest Cape and elsewhere.

Anthophyllite, Tremolite, and Actinolite Deposits

Of the countries in which anthophyllite asbestos deposits are known, Finland was formerly the most important producer with major deposits at Paakkila in the parish of Tuusniemi in eastern Finland and Maljasalmi in Kuusjarvi Parish. The Finnish anthophyllite asbestos deposits were a series of lenses of amphibolitized and serpentinized ultrabasic material, which appeared to have become detached from larger bodies during an early period of severe deformation. The serpentinized amphibolite lenses were in a biotite gneiss that had been intruded by Late Karelian granites and pegmatite (Aurola 1954; Ross and Nolan 2003).

Anthophyllite asbestos is found near Greenmountain in Yancey County, North Carolina. Most of the deposits, which are associated with altered peridotites and pyroxenites, consisted of mass fiber, although cross and slip fibers are more common in other parts of the state. Similar material has been found in the nearby state of Georgia (Conrad, Wilson, and Allen 1963).

Italy has produced some long-fiber tremolite from small deposits at Val Malenco, in the Sondrio District 100 km north of Milan. Tremolite fiber has also been found in the Aosta District north of Turin in the Italian Alps.

Amphibole asbestos also has been found in Bulgaria, India, Romania, Taiwan, Turkey, and the former Yugoslavia. Most of the Indian production is from Rajasthan. Although some deposits of fibrous actinolite have been reported, production is extremely small.

TECHNOLOGY

Exploration Techniques

Geophysical

Where there are few outcrops of asbestos-bearing ultrabasic rocks, aeromagnetic and ground magnetic surveys are employed in the early stages of exploration (Low 1951; Conn 1967). Ground magnetic surveys may be used to check and define in more detail

anomalies obtained by an airborne survey of a large area. If the area for exploration is small, the ground survey may be used by itself.

Magnetic surveys are used to locate ultrabasic bodies and define potential ore deposits because of their association with secondary magnetite formed during extensive serpentinization. Many asbestos deposits in ultrabasic rocks contain more magnetite than does barren serpentine.

Diamond Drilling

Diamond drilling is used to assess and define the limits of an asbestos deposit. Because most asbestos ore bodies are large, it is customary to drill vertical holes on a grid pattern. In the first stages of exploration, a wide interval (often 61 m) is used. When an asbestos-bearing zone is encountered, a narrower interval is used. If a deposit is elongated in one direction, holes are spaced at closer intervals across the strike. Narrow, tabular ore bodies are explored using angled holes to give the attitude and true thickness of the body.

Preliminary drill holes are used to determine whether or not the fiber has a preferential vein angle. If the angles of the vein intersections appear random, no changes are made to the drilling program. If the deposit exhibits prominent vein angles that diverge from the average 45°, the attitude of all later drill holes are corrected for this variation.

When drilling is impractical, trenching or the use of adits or shafts and lateral workings may offer the only means of assessing a deposit.

Evaluation of Deposits

Evaluation

An asbestos deposit is evaluated on size, fiber yield or grade, and quality of fiber (Dean and Mann 1968; Conn and Mann 1971; Stewart 1981). Although the size of a mineral zone is established using geophysical or drilling techniques, yield and quality of fiber are evaluated through laboratory and visual methods. The simplest method for determining yield is visual, using drill core sections. Each vein of cross fiber is recorded and the vein width is measured and recorded in multiples of 1.6 mm. Because many veins are of irregular width, an average vein width is used. Allowances also are made when veins contain partings or the fiber is kinked (which causes the fiber to break into shorter lengths than the vein width), or the fiber is sharply inclined to the vein walls (in which case the vein width is smaller than the fiber length). To estimate fiber yield, the total drill core length is divided into the sum of the average vein widths in the core section. As an example, each 1.6-mm vein of fiber in a 1.5-m section corresponds to about 0.1% fiber in the rock.

Because it is not easy to determine the slip-fiber length by the normal visual methods of logging core, laboratory assistance usually is required.

Fiber Value Determination. After the fiber yield of the ore is determined, the value of the fiber and the value of the ore in dollars per ton are estimated. The fiber is graded using the Quebec Standard (QS) Test developed by the Quebec Asbestos Mining Association (QAMA; see Table 9; Asbestos Textile Institute and QAMA 1975). This test is performed on the QS testing machine, which consists of a stack of three sieve boxes with 12.7-mm (½-in.), 4-mesh-per-inch, and 10-mesh-per-inch screens, stacked top to bottom, and a bottom box serving as a pan. Exactly 454 g of asbestos fiber is placed in the top sieve, and the stack of sieves is shaken using a rotary shaker. The weight of fiber on each screen and the bottom pan is determined.

Table 9. Quebec Asbestos Grading System*

Group No. 1				
No. 1 crude. Cross-fiber veins having ¾-in. staple and longer.				
Group No. 2				
No. 2 crude. Cross-fiber veins having ¾-in. staple up to ¾ in. Run-of-mine crude consists of unsorted crudes. Sundry crudes consist of crudes other than specified here.				
	Guaranteed Minimum Shipping Test			
	½ in., oz	4 mesh, oz	10 mesh, oz	Pan, oz
Group No. 3—Commonly referred to as textile or shipping fibers				
3F	10.5	3.9	1.3	0.3
3K	7	7	1.5	0.5
3R	4	7	4	1
3T	2	8	4	2
3Z	1	9	4	2
Group No. 4—Commonly referred to as asbestos-cement fiber				
4A	0	8	6	2
4D	0	7	6	3
4H	0	5	8	3
4K	0	4	9	3
4M	0	4	8	4
4R	0	3	9	4
4T	0	2	10	4
4Z	0	1.5	9.5	5
Group No. 5—Often referred to as paper stock grades				
5D	0	0.5	10.5	5
5K	0	0	12	4
5M	0	0	11	5
5R	0	0	10	6
5Z	0	0	8.6	7.4
Group No. 6—Paper and shingle fibers				
6D	0	0	7	9
6F	0	0	6	10
Group No. 7—Shorts and floats				
7D	0	0	5	11
7F	0	0	4	12
7H	0	0	3	13
7K	0	0	2	14
7M	0	0	1	15
7R	0	0	0	16
7T	0	0	0	16
7RF and 7TF Floats	0	0	0	16
7W	0	0	0	16
Groups No. 8 and 9—Sands and gravels				
8S	0	0	0	16
		Minimum 50 lb/ft ³		
8T	0	0	0	16
		Minimum 75 lb/ft ³		
9T	0	0	0	16
		More than 75 lb/ft ³		

Adapted from Asbestos Textile Institute and QAMA 1975.

* As of 2003, the grading standards had not been converted to the metric system.

Multiplication factors are applied to the weight in each size fraction, giving a total point score for the sample. Comparing the point score to a graph of point score versus fiber value, which was previously developed for this or similar deposits, determines the average fiber value.

If extraction of the fiber is not done, average fiber value can be approximated on drill cores or face readings. The average vein widths (assumed to equal fiber length) are measured in the drill core or working face. These lengths are sorted into the QS Test screen-size categories. To estimate the fiber fraction in each category, the total length of fiber measured is divided into the total fiber length contained in each QS Test size category. As an example, if the sum of the vein widths measured in a drill core is 57.2 cm and vein widths (assumed to equal fiber lengths) in the +12.7 mm QS Test size category totals 16.5 cm, this size category represents 29% of the total measured fiber length. By multiplying 29% by 454 g, the weight of asbestos fiber used in a QS Test, it is estimated that the +12.7-mm size fraction represents a weight of about 132 g. These calculations are repeated for the other QS Test size categories. Once the weight in each QS Test size fraction is approximated, the procedure previously discussed—using multiplication factors and graphs of point score versus fiber value—is used to estimate average fiber value.

In both of the previous cases, the fiber value must be converted into a dollar-per-ton value, so the yield also must be calculated. As described, the total length of the core section or face measured is divided into the total measured fiber length to determine the percent yield per ton of ore. For example, 57.2 cm of measured fiber in a 25.9-m drill core represents a yield of 2.2%. A correction is made for the average vein angle in the deposit, assumed to be 45° in this example. The corrected yield is equal to 2.2% divided by the $\sin 45^\circ$, or 3.1%. If the average fiber value was determined to be \$400/t, the indicated ore value is calculated to be 3.1% of \$400, or \$12.40/t.

Face Readings

On the surface or in underground workings, channel sampling may be employed. One method is to take a linear reading along either wall of a drift or crosscut. Another method involves taking cross sections at intervals of 1.5 m along the back and both walls to ensure that veins running parallel to the drive are not excluded. Because the rock tends to break along fault planes, it is difficult to obtain representative results.

Bulk Sampling

Because the various methods of logging and sampling seldom give entirely dependable results, bulk sampling is the most accurate means of determining yield, fiber value, and ore value. Even bulk sampling, however, can give an appreciably higher fiber value than that obtained in a commercial mill, because it is not easy in the laboratory to simulate the conditions of an operating mine and mill. From the time of blasting to the final product, the fiber is subjected to a good deal of handling under real operating conditions. Some handling is rather severe, and breakage of fibers can occur.

Bulk sampling often is used as a means to arrive at a suitable factor to be applied to drill-core data, as described with the multiplication factors and point-score-value graphs. The sampling may be done by diamond-drilling a block of ground at close intervals prior to mining and milling. The cores can be read visually and then milled. If precautions are taken to avoid contamination and the sample is sufficiently large, results should be reasonably reliable despite the erratic distribution of fiber in the rock.

Tensile Strength

In the preceding paragraphs, measurements and evaluations are based entirely on the length of the fiber. For many applications, the fiber is valued for the strength it lends to the product. Strength evaluations should include tests on the product made with the subject fiber.

Tonnage and Grade

To estimate the tonnage and grade of a deposit from diamond drill-core data, individual drill holes may be weighted according to their intervals by using the polygonal method. An alternative procedure is to use cross sections, or groups of cross sections and, by weighting the individual holes in each section, determine the average grade for each section.

A third method employs contoured cross sections, which is based on a reasonable interpolation of the intervening area between drill holes. This method permits the estimator to make use of all available geological information in his interpolation. In open-pit operations, contoured horizontal sections corresponding to expected mine level intervals may be prepared and can serve as a useful guide to mining. Separate horizontal sections contoured for rock value and fiber value per ton permit the mine operator to produce a more balanced mill feed with respect to both fiber content and grades.

Mining

Chrysotile mining developed through a succession of mining practices and equipment. Originally, the simplest hand methods were employed in shallow open-pit workings. Later, when pits reached considerable depth, overhead cableway derricks were used. Now, power shovels and heavy-duty trucks have replaced other loading and transporting equipment for open-pit quarry methods.

In its early history, most chrysotile was mined in Canada using underground methods, which included glory holes, shrinkage and sublevel stoping, and block caving. Now open-pit mining prevails. Surface mining offers advantages in recovery, grade control, economy, and safety. The shift to open-pit mining resulted mainly from the introduction of large-capacity power shovels, trucks with higher payload capacities, improved rock-drilling equipment, and new blasting agents and techniques.

In Africa, chrysotile is still mined underground. Most ore bodies are tabular in shape with a pronounced dip so that the economic limit for quarry mining is reached at a comparatively early stage. Ore widths in the larger mines commonly range from 20 to 60 m and as much as 120 m. Some ore bodies, notably in the Shabani District of Zimbabwe, are long. In one case, development extended for 5 km along the strike and was being developed or diamond drilled to more than 300 m in depth.

Several underground methods have been used. Sublevel stoping and caving may be initiated by blasting holes drilled upward from sublevel crosscuts, starting first on the hanging-wall side and retreating over a considerable width toward the footwall. Development and retreat also may be along the strike of the ore. In some cases, high pressures tend to develop from an arching effect. These pressures can be released by cutting a vertical slot that may extend to the surface. In the sublevel stoping method, a slot also may be opened across the center of the ore body. The holes that are fanned out from the sublevel drifts are blasted toward the slot, and mining proceeds as a systematic retreat in two directions away from the opening.

Processing

Mill flow lines are designed to suit the characteristics of a given ore body. Most raw fiber is recovered through a dry process that has

been used almost exclusively since the inception of chrysotile asbestos milling in Canada during the early 1900s.

Mill feed is derived from the underground or pit operation. Primary crushing may be done in underground stations, in the case of an underground mine; or in a surface plant, in the case of an open-pit mine. Although jaw or gyratory crushers are mainly used, some hand sorting may still be done in countries where labor costs are low. Hand sorting removes barren rock and recovers pieces of the larger veins used to produce No. 1 or No. 2 crudes.

Ore concentration is an important step in the milling of chrysotile and is particularly important for lower-grade ore bodies. It is not uncommon to discard as much as 40% of the mine ore through selective impacting and screening in the primary and secondary crushing circuits. Some producers use magnetic pulleys for upgrading the mine ore, although not all asbestos ore bodies are amenable to this type of separation.

The next step is to dry the ore. Most of the moisture is contained in the finer (–38 mm) fraction. At some plants, this fraction is screened and dried separately from the oversize (38 to 178 mm) material. Although the selection of a dryer is based largely on local preference, the two most commonly used are the rotary and vertical dryers. Fluidized-bed dryers also have been used. Generally, there is less mechanical damage to the fiber when vertical-tower and fluidized-bed dryers are used than with rotary kiln-type dryers. Rotary dryers, however, are preferable and are more effective for open-pit ores that might contain snow and ice. Oversize material can be separated before drying and bypassed to reduce the pebble-milling action of rotary dryers.

There should be adequate storage to protect the ore between drying and the main stage of milling. Besides assuring an adequate and more uniform supply of ore to the mill, further drying (up to 1% moisture loss) takes place during storage. The size of storage facilities varies with mill capacity.

Chrysotile fiber is released and separated from gangue by successive stages of crushing or comminuting by impact. Impactors are designed to release the fiber from the host rock and at the same time produce a minimum of fines. Fiber released by crushing is lifted by air suction, leaving most of the rock as a reject to go to the next stage of impacting and eventually to tailings. Finer fractions generally are screened out prior to air separation to avoid aspirating a large portion of host rock fines along with the fiber. Rotary aspirators designed to present a uniform layer of material to the aspirating hood are commonly used to improve the aspirating efficiency. The products of these first stages of separation may be considered as concentrates. They contain a large percentage of rock particles and must be further treated.

The concentrates are further graded and undergo a series of cleaning operations for the purpose of removing sand and dust. Screens, trommels, specific-gravity air separators, and modified forms of these, such as graders and dusters, further clean the fiber and separate it into standard-grade lengths.

In the grading mill, the fiber within each grade is further subdivided according to fiber quality. It is then subjected to several stages of screenings by means of shaking screens, gyratory screens, conventional trommels, trommel-like graders, and rotary dusters.

When well-opened or fluffed-out grades are required, the fiber is specially processed in one or more of a variety of machines. These range from graders or Willows mills (a fixed cylindrical casing with a rotating center shaft to which beater arms are attached) to one of several types of high-speed hammer mills, disk graders, or pulverizers. The type of machine or machines used depends on the length and type of fiber to be processed and the degree of opening or fluffing required. This additional treatment is generally given to

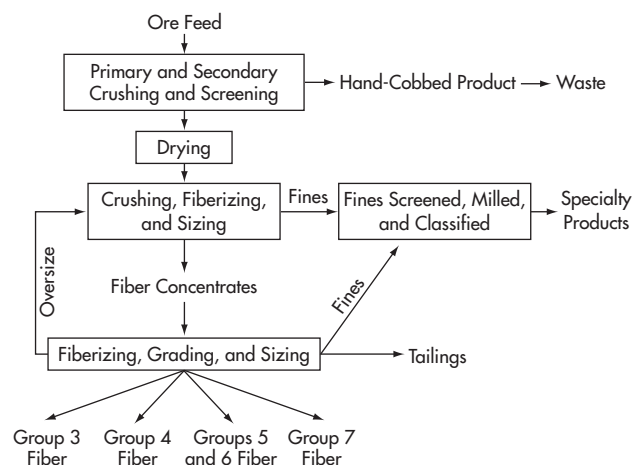


Figure 8. Generalized flow sheet of asbestos processing

the shorter fibers. A generalized flow sheet of the milling process is given in Figure 8.

A large volume of air is used in a chrysotile mill, most of which is for separating fiber from rock and dust by air suction and classification. An additional volume of air is required to reduce dust levels in the mill building to meet regulatory standards. Mills with a capacity of approximately 5,000 tpd of ore use 236 to >378 m³/sec of free air. The average consumption in Canadian mills is approximately 7 to 14 t of air per ton of ore treated (Rozovsky 1957; Kula and Wiser 1970). Modern practice requires that the air be filtered before being discharged from the mill into the open. Extensive bag filter units have been installed in all mills.

In Zimbabwe, South Africa, and Swaziland, beneficiation of chrysotile does not differ greatly from Canadian practice. One feature of African milling is the need to control moisture content carefully; particularly during the dry season it may be too low. Under extremely dry conditions, fibers may break or be damaged more easily.

MARKETING

Product Grades and Specifications

The most widely recognized test for classifying asbestos is the QS Test developed by QAMA, which has specifications for the various fiber grades based on the quantities of fiber that remain on each screen. Used for production control, the test determines the specification of the grade of fiber for sale. This test has been partially adopted by countries other than Canada, but in some cases the results are expressed in percentages instead of the ounces that Canada uses.

Wet classification and screening also have been used to monitor fiber lengths, nonfibrous fractions, and dust content during production. The McNett* or the Clark* wet-testing machine may be used for this purpose (Mining in Canada 1967).

A Ro-Tap* machine is sometimes used to evaluate further the QS sieve fractions. Many asbestos mill operators believe that the Ro-Tap gives a better distribution of the fiber lengths than the QS testing machine does.

Many customers use density measurements as a guide in producing specific products. In this case, the density of the asbestos

* Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the publisher.

fiber is determined by filling a cubic-foot box or a fraction of a cubic-foot box with fiber. The box is then weighed, and the density is expressed as pounds per cubic foot (*Mining in Canada* 1967).

Many customers have developed their own tests for evaluating the performance of fiber in their finished products. The tests cover properties such as absorption, bulk, color, compressibility, flexing, grit, magnetite content, penetration, soluble salts, strength units, surface area, tensile strength, troweling, and viscosity (*Mining in Canada* 1967; Cossette and Delvaux 1979).

Fiber producers in other places, such as the Commonwealth of Independent States (CIS), South Africa, and Zimbabwe, developed their own testing methods for grading. Most fibers are sold according to the QST test because amosite and crocidolite are no longer mined.

Classification standards for grading chrysotile are given in Table 9. Amosite and crocidolite were generally not graded using the QAMA standard.

Uses

Asbestos Use by Group

Several thousand products were manufactured in the past that took advantage of the unique properties of asbestos. Some of the present and past uses for asbestos by grade and product type are discussed in this section (Badollet 1948; *Mining in Canada* 1967; Hodgson 1985; EPA 1988; Roskill Information Services Ltd. 1990; Harrison et al. 1999; Rice and Heineman 2003; also see U.S. Bureau of Mines and U.S. Geological Survey *Minerals Yearbook* chapters on asbestos for U.S. end use breakdown by fiber grade). Demand for crudes and Group 3 fiber has declined as manufacturing has shifted, in response to changing consumption patterns, to a greater use of shorter fiber. Groups 4 through 7 are the most commonly used fibers, with Group 7 fiber dominating. The crudes and groups are as follows:

- Crudes No. 1 and No. 2—Customers employ crudes to produce a long, spinning fiber for use in textiles. A desirable fiber for textiles is flexible, soft, low in soluble salts and magnetite, and easily carded without an excess drop in shorts. Fiber of this quality is desirable for all textile applications. Crude fiber has been used as felts in laminates, along with resins, to form a strong molded sheet for use in airplanes, boats, and so forth. By the late 1980s, demand for crude fibers began to diminish, and comparatively little crude asbestos currently is sold.
- Group 3 Milled Fibers—Chrysotile fibers that meet this classification may be used in textiles. Group 3 fiber also may be employed in asbestos papers, electrolytic diaphragms, gaskets, and insulating blocks. Some of the fibers of this group are used in laminates with resins. Like the No. 1 and No. 2 fibers, demand for Group 3 has declined as manufacturing needs have evolved.
- Group 4 Milled Fibers—Many grades of fibers in this group are used in asbestos-cement products such as boards, jackets, pipe, sheets, and a variety of hand-molded articles. Other applications are for brake linings, clutch facings, gaskets, millboards, papers, and plastics.
- Group 5 Milled Fibers—Products made with these fibers include asbestos-cement pipe and sheets, brake linings, corrugated or flat boards, electrical panels, gaskets, millboards, papers, and plastics.
- Group 6 Milled Fibers—Chrysotile fibers of this group are used in asbestos-cement corrugated and flat sheets, boards, brake linings, gaskets, millboards, papers, and plastics.

- Group 7 Milled Fibers—This grade of chrysotile is used in papers, cements, asphalt road pavement, asphalt roof coatings, brake linings, clutch facings, gaskets, millboard, paints, paper, plastics, and welding rods.
- Floats—Chrysotile floats may be used in coatings.

Asbestos Use by Product Type

The selection of asbestos fiber for a particular application depends on the processing method and the desired properties of the final product. Examples of major uses for asbestos fiber and factors that influence the choice of fiber grade and type are given in this section.

Asbestos-Cement Products

Pressure pipe that must conform to hydrostatic test specifications is produced outside of the United States from Groups 4, 5, and 6 fibers. In the past, chrysotile was blended with crocidolite to ensure a good modulus of rupture, but crocidolite is no longer used to manufacture asbestos-cement pipe. Flexural and impact strength requirements for asbestos-cement sheets usually can be met by using a Group 6 fiber. Formulations for corrugated sheets generally include some Group 5 material to improve adhesion of the wet sheets during the forming process. The asbestos content of pipe ranges from 15% to 25%; for sheet, 20% to 50%; and for shingle, 10% to 30% (EPA 1985, 1988).

In all asbestos-cement products made by the wet-machine process, drainage is an important fiber characteristic because it has direct bearing on the production rate. Preference is given to fast-filtering fibers. Amosite was once included in the formulation as a filter aid but is no longer used.

The strength or drainage requirements for shingles made by a dry process are not so exacting and can be satisfied with Group 6 or a blend of Groups 6 and 7. Other asbestos-cement building products may use fibers from Groups 4, 5, 6, and 7.

Asbestos Paper and Millboard

Asbestos fibers are used with an organic binder to manufacture a variety of millboard and paper products, such as electrical insulation, pipe coverings, and roofing felt. Various blends of Groups 3, 4, 5, and 6 fibers are used for this application, depending on the desired strength and porosity of the paper.

Felt for pipeline wrap applications is composed of 85% asbestos, with the remainder made up of cellulose fiber and binder. Millboard is a heavy cardboard-like material that can contain from 60% to 95% asbestos, although typical formulations use 70% to 80% asbestos. Commercial paper for insulation use, including corrugated paper, contains up to 98% asbestos. Rollboard, which consists of two layers of asbestos paper glued together with sodium silicate, generally is composed of 70% to 80% asbestos (EPA 1988). Average asbestos contents of roofing felts are about 85% but can approach 95% (Meylan et al. 1978; EPA 1988). Paper used in flooring felt as a backing for vinyl sheet floor products contains about 85% asbestos (EPA 1988).

Asphalt Products

Group 7 asbestos fiber, in combination with asphalt and various solvents, forms the basis of a wide variety of products such as caulking compounds and spray or brush-on roof coatings and also for asphalt road pavements. In asphalt products, asbestos contents range from 5% to 12% for bituminous coatings, 10% to 25% for roof putties, and 1% to 5% for liquid sealants (Meylan et al. 1978; EPA 1985, 1988).

Caulking and Sealing Compounds

Combinations of long fiber asbestos with cement and other ingredients, along with waterproofing resins, are used to produce special types of caulking compounds. Some caulks and sealants may use Group 3 fiber; others use short asbestos and floats (Groups 7, 8, and 9). These are combined with various types of resins and other materials to produce a soft plastic caulking compound, which can be controlled either to remain soft or to set up as a hard mass.

In caulking and sealing compounds, asbestos contents range from 1% to 5% for adhesives and cement; 5% to 25% for caulking, glazing, and patching compounds; 2% to 15% for paints; 2% to 10% for plasters; and 3% to 5% for spackles (Meylan et al. 1978; EPA 1985, 1988).

Friction Materials

A wide variety of products are classified under the friction materials category. Products are made with fibers ranging from Group 3 spinning grades to the shorter Group 7, with shorter Groups 5, 6, and 7 dominating.

Brake linings and pads contain 30% to 70% asbestos depending on the application (Rosato 1959; Meylan et al. 1978; Hodgson 1985). Drum brake linings contain as much as 60% asbestos, and disk brake pads from 25% to 30% (Meylan et al. 1978; Pye 1989; Harrison et al. 1999). Brake formulations also are different for cars and trucks. The composition of brake lining compositions in cars averaged 55% asbestos in 1968; that of trucks was 33% asbestos (Meylan et al. 1978).

Some clutch plates are made using asbestos open-weave cloth impregnated with resin and bonded to a steel disk. Most are manufactured by molding a dry resin-fiber blend under conditions of high temperature and pressure onto a packing plate. For the first method, a Group 3 fiber is required, whereas the molding process uses a Group 5, 6, or 7 fiber.

Most automobile brake linings bonded to a steel shoe are made from Group 7 fiber in a semiwet extrusion process, whereas heavy blocks for railcars and large vehicles use Groups 5 or 6 fibers, dry-molded and machined to finished dimensions. Groups 6 and 7 are used in disk brake-pad formulations.

Gaskets

Latex asbestos paper made from Group 7 fiber can be densified and used for gasketing, but most sheet-packing material is formed on a sheet machine by a calendering process. This latter method requires a longer fiber in the Groups 3, 4, or 5 categories that have been cleaned and opened. The fiber is blended with natural or synthetic rubber, plasticizers, and other ingredients in a high-shear mixer to form dough that is later calendered into sheets of various thicknesses. Fibers from Groups 6 and 7 may also be used to manufacture gaskets.

Packings can be made with loose fiber, formed of asbestos and binders, woven into braided asbestos products, and made using asbestos yarns. Asbestos content varies depending on the use, with higher fiber levels associated with higher-temperature applications (EPA 1988). In some packing products, asbestos content is generally more than 75% and often as high as 100% (Meylan et al. 1978).

Plastics

Asbestos, or a combination of asbestos and glass fiber, is used to reinforce some structural plastics. The asbestos may be in the form of a mat, or as paper or cloth, to form laminates with resins such as polyesters, phenolics, thermosetting silicones, melamines, and furanes. Short Group 7 fiber and floats also are used as fibrous filler

for the production of molded phenolic resin and polyester parts. In such applications, freedom from abrasive particles is especially important to hold die wear at a minimum level. Fibers of Groups 3, 4, 5, and 6 also may be used to reinforce plastics.

The average asbestos content of plastic in the mid-1980s was 17% (EPA 1985). Phenolic compounds contained 50% to 60% asbestos, and other resins may have required as little as 5% asbestos (Meylan et al. 1978). Asbestos contents of vinyl flooring ranged from 8% to 30% (Rosato 1959; Meylan et al. 1978; EPA 1980, 1985, 1988).

Textiles

Long spinning grades of chrysotile are used to manufacture textiles for various applications. Fibers of Groups 1, 2, and 3 are used for this process.

Consumption

Current Consumption

The actual worldwide consumption of asbestos, in weight, has been poorly documented in terms of end-use breakdown and even total consumption.

In 2002, brake linings and pads, gaskets, and asphalt roof coatings comprised the bulk of U.S. consumption. Of that, asphalt roofing compounds accounted for about 80% of U.S. consumption, gaskets for 8%, friction products for 4%, electrical and thermal insulation for 4%, and miscellaneous uses for 4%. This is a considerable change from 1978 when asbestos-cement pipe and sheet and flooring were the major U.S. markets. Table 10 presents a timetable of asbestos consumption in the United States from 1965 to 2002.

In 2000, world consumption of asbestos fiber was about 1.83 Mt. The largest consuming region was Asia and the Middle East, with an estimated 861,000 t, followed by Europe with 691,000 t, South America with 207,000 t, Central and North America with 35,000 t, Africa with 30,500 t, and Oceania (consisting of Australia and New Zealand) with 1,250 t. Most of the asbestos was used to manufacture asbestos-cement products. The largest users of asbestos were, in descending order by tonnage, Russia, China, Brazil, India, Thailand, Japan, Ukraine, Indonesia, Uzbekistan, and the Republic of Korea (Table 11). All other countries appear to have consumed less than 20,000 t each since 1998 (Virta 2003).

Historical Consumption

Based on qualitative descriptions, asbestos-cement products are thought to have dominated the asbestos-manufacturing industries since the early 1900s. A description of the 1930s asbestos industries in manufacturing countries implied that asbestos-cement corrugated and flat sheet, pipe, and roofing tile were the major markets for asbestos (Bowles 1955). The low cost of asbestos-cement products, their durability and effectiveness, and the unsophisticated technology required to make these products would have been major factors leading to their widespread use, particularly for developing countries with limited mineral and monetary resources (Bowles 1955). Rosato (1959) indicated that, in the later 1950s, asbestos-cement products for commercial and industrial buildings and private homes consumed the largest quantity of asbestos. No estimate was made, however, on percentage of consumption. In 1980, asbestos-cement products reportedly accounted for about 66% of world consumption of asbestos. In regions where alternative construction materials were available, the demand for asbestos-cement products was proportionally smaller, and a much wider variety of other asbestos products were developed. Asbestos-cement products accounted for only 45% and 43% of the U.S. and Western European markets, respectively (Table 12).

Table 10. U.S. end uses for asbestos, 1965 to 2002, kt

	Asbestos- Cement Pipe	Asbestos- Cement Sheet	Coatings and Compounds	Flooring Products	Friction Products	Electrical Insulation	Thermal Insulation	Packing and Gaskets	Paper Products	Plastics	Roofing Products	Textiles	Other*	Unknown†	Total‡
1965§	137	50	**	181	64	22	††	22	15	**	72	15	144	0	721
1966§	139	51	**	183	65	22	††	22	14	**	73	15	147	0	730
1967§	122	46	**	162	59	20	††	20	13	**	64	13	132	0	650
1968§	141	52	**	185	67	23	††	23	15	**	74	15	148	0	741
1969§	135	50	**	178	64	22	††	22	14	**	72	14	140	0	711
1970§	126	46	**	167	60	20	††	20	14	**	66	14	133	0	666
1971§	131	48	**	173	62	21	††	21	14	**	69	13	137	0	689
1972	140	52	**	183	66	22	††	22	15	**	73	14	147	0	733
1973	151	58	**	198	72	23	††	24	16	**	79	16	158	0	795
1974	202	86	**	139	73	13	††	26	57	**	69	18	85	0	768
1975	139	40	**	123	60	6	††	15	60	**	42	5	62	0	552
1976	127	21	**	104	58	8	††	18	28	**	231	6	59	0	659
1977	115	27	36	150	57	17	4	28	7	8	70	10	143	0	672
1978	106	25	33	138	53	15	4	25	7	7	64	9	133	0	619
1979	96	22	30	125	48	14	3	23	6	7	58	8	121	0	561
1980	42	23	11	70	52	6	3	12	1	2	24	2	111	0	359
1981	42	20	13	67	51	6	1	19	2	1	16	2	109	0	349
1982	38	11	25	49	53	0	1	14	2	0	7	1	46	0	247
1983	26	10	23	45	48	0	1	12	2	1	6	1	42	0	217
1984	37	12	22	46	48	††	2	13	2	1	7	2	33	0	226
1985	28	7	23	7	34	††	††	6	17	††	26	1	5	7	162
1986	20	5	17	5	26	††	††	5	13	††	20	††	4	4	120
1987	11	4	3	0	21	††	0	10	5	1	23	1	2	4	84
1988	12	4	4	††	15	††	††	10	1	††	20	††	††	5	71
1989	8	3	4	0	12	0	0	4	1	1	18	††	1	4	55
1990	5	2	2	0	9	0	0	3	††	††	13	0	1	7	41
1991	4	2	1	0	10	0	0	3	††	††	15	0	1	1	35
1992	2	††	1	0	10	0	0	3	††	††	16	0	1	††	33
1993	1	0	1	0	10	0	0	3	††	††	16	0	1	††	32
1994	0	0	††	0	9	0	0	3	††	††	13	0	1	††	27
1995	0	0	††	0	7	0	0	3	††	††	11	0	1	††	22
1996	0	0	††	0	7	0	0	3	††	††	11	0	1	††	22
1997	0	0	††	0	6	0	0	4	††	††	10	0	1	††	21
1998	0	0	††	0	3	0	0	2	1	††	9	0	1	0	16
1999	0	0	††	0	2	0	0	3	0	††	10	0	1	0	16
2000	0	0	††	0	2	0	††	3	0	††	9	0	1	0	15
2001	0	0	††	0	1	0	0	2	0	††	9	0	1	0	13
2002	0	0	††	0	††	††	††	1	††	0	5	0	††	0	7
Total§§	2,280	776	248	2,680	1,360	279	19	470	339	29	1,490	193	2,250	32	12,400

* "Other" includes known end uses not falling into specified end-use categories.

† Undetermined end uses.

‡ May not add to total because of independent rounding.

§ Estimated.

** Included with "Other."

†† Included with "Electrical Insulation."

‡‡ Less than ½ unit.

§§ Data are rounded to no more than three significant digits; may not add to totals shown.

Table 11. Asbestos production, trade, and consumption in 2000, t

Country	Production	Imports	Exports	Apparent Consumption*	Country	Production	Imports	Exports	Apparent Consumption*
Europe					Central and North America				
Azerbaijan	0	8,250	0	8,250	Canada	320,000	125	315,000	4,800
Belarus	0	0	65	-65	El Salvador	0	1,680	0	1,680
Belgium-Luxembourg	0	98	0	98	Mexico	0	26,900	0	26,900
Bulgaria	350	0	0	350	Panama	0	1,280	0	1,280
Croatia	0	2,590	0	2,590	United States	5,260	14,600	18,800	1,130
Czech Republic	0	1,400	0	1,400	Total (North America)	325,000	44,600	334,000	35,800
Estonia	0	180	0	180	South America				
France	0	16	46	-30	Argentina	254	2,080	0	2,330
Germany	0	189	0	189	Bolivia	0	982	0	982
Greece	0	501	8,950	-8,450	Brazil	209,000	35,500	63,100	182,000
Hungary	0	3,560	0	3,560	Chile	0	1,460	0	1,460
Ireland	0	1,000	0	1,000	Colombia	0	12,200	0	12,200
Italy	0	87	0	87	Ecuador	0	4,390	0	4,390
Kazakhstan	233,000	0	174,000	59,200	Peru	0	na	0	na
Kyrgyzstan	0	17,300	0	17,300	Uruguay	0	809	0	809
Latvia	0	857	0	857	Venezuela	0	2,730	0	2,730
Lithuania	0	1,360	643	713	Total (South America)	210,000	60,100	63,100	207,000
Moldova	0	5	0	5	Asia and Middle East				
Poland	0	19	14	5	China	350,000	72,000	11,800	410,000
Portugal	0	4,710	0	4,710	India	14,500	110,000†	0	125,000†
Romania	0	10,200	0	10,200	Indonesia	0	54,900	0	54,900
Russia	752,000	27,200	332,000	447,000	Iran	2,000	0	0	2,000
Slovenia	0	893	0	893	Japan	0	98,600	0	98,600
Spain	0	15,600	126	15,400	Korea, Republic of	0	29,000	0	29,000
Ukraine	0	80,900	0	80,900	Malaysia	0	na	0	na
United Kingdom	0	246	2	244	Philippines	0	na	0	na
Uzbekistan	0	43,400	0	43,400	Oman	0	2,350	0	2,350
Yugoslavia (former)	563	607	0	1,170	Pakistan	0	4,160	0	4,160
Total (Europe)	986,000	221,000	516,000	691,000	Saudi Arabia	0	0	9,730	-9,730
Africa					Singapore	0	4	0	4
Algeria	0	900†	0	900†	Sri Lanka	0	na	0	na
Egypt	0	na‡	0	na	Taiwan	0	5,420	0	5,420
Morocco	0	na	0	na	Thailand	0	121,000	0	121,000
Nigeria	0	na	0	na	Turkey	0	19,500	0	19,500
Ghana	0	648	0	648	Total (Asia)	367,000	516,000	21,500	861,000†
Senegal	0	1,780	0	1,780	Oceania				
South Africa	18,900	10,200	16,600	12,500	Australia	0	1,250	0	1,250
Swaziland	12,700	0	10,000†	2,690†	Total (Oceania)	0	1,250	0	1,250
Tunisia	0	na	0	na	Grand total (world)	2,070,000	856,000	1,100,000	1,830,000
Zimbabwe	152,000	0	140,000†	12,000†					
Zambia	0	na	0	na					
Total (Africa)	184,000	13,500†	167,000†	30,500†					

* Apparent consumption calculated as production plus imports minus exports, not adjusted to account for changes in government and industry stocks. Negative value indicates shipments from stocks.

† Estimated data.

‡ na = Not available.

With the onset of the asbestos health issue in the 1970s, demand for asbestos products declined in the United States and Western Europe, where noncement applications dominated. Consequently, the percentage of asbestos-cement products in the asbestos world market increased, rising to 80% in Africa; 76% in Asia, Eastern European countries, and South America; and 60% in Oceania in

1980 (Roskill Information Services Ltd. 1983). With the continued decline in the use of asbestos in the 1980s and 1990s, markets have shifted even more toward asbestos-cement products. In 2002, asbestos-cement products are thought to account for more than 98% of the world's consumption of asbestos (Virta 2002). Other markets for asbestos are paper, textiles (comprising yarn, thread, cloth, tape,

Table 12. World consumption of asbestos, 1974 and 1988, kt

Year	Region	Construction	Friction Products	Other	Total
1974	North America	820	105	225	1,150
	Central and South America	150	20	20	190
	Western Europe	830	60	100	990
	Eastern Europe	870	30	150	1,050
	Africa	30	15	5	50
	Asia	680	70	50	800
	Oceania	170	10	10	190
	Total	3,550	310	560	4,420
1988	North America	90	20	10	120
	Central and South America	190	35	25	250
	Western Europe	450	10	20	480
	Eastern Europe	2,100	50	200	2,350
	Africa	40	18	3	61
	Asia	850	18	75	943
	Oceania	110	1	5	116
	Total	3,830	152	338	4,320

Source: Roskill Information Services Ltd. 1990.

or rope), the rmal and electrical insulation, g askets, and friction products, including brake or clutch pads. Some specialty plastic products are still manufactured.

Historical Trends in Consumption, by Region

North America. For much of the 20th century, the United States was the largest user of asbestos. The expanding population, the abundance of available capital for investment in the relatively new asbestos industry, and the large demand for construction of housing, public buildings, and roads were major contributing factors. Within a couple of decades of having begun its asbestos industry, the United States became a world leader in usage and held that position through the 1960s. During that time, the United States accounted for 30% to 83% of world apparent consumption. In the 1960s, the United States was replaced by the former Soviet Union as the leading user of asbestos. After that time, use of asbestos in the United States declined rapidly in response to asbestos-related health issues.

In Central America, Costa Rica, Cuba, the Dominican Republic, El Salvador, Guatemala, Honduras, Jamaica, Nicaragua, and Panama have been small consumers since the 1960s, using only a few thousand tons annually. Canada's exports of asbestos overshadowed its relatively small asbestos-manufacturing industry. From 1940 to 1970, consumption in Canada probably was around 45,000 t annually and currently is estimated to be less than 10,000 t annually. Consumption in Mexico gradually built up to 79,000 t in 1980 and then declined to an estimated 27,000 t in 2000. In that same year, Cuba, the Dominican Republic, El Salvador, and Panama were the only other North American countries believed to be using asbestos.

Europe. After the United States, Europe was the next region to develop a significant asbestos-manufacturing industry. Through the first half of the 20th century, the United Kingdom became the major European consumer, followed by many other European countries. By 1930, Belgium, Germany, Luxembourg, and the United Kingdom were major suppliers of asbestos products throughout Europe and Asia. Demand in the former Soviet Union exceeded

that of the United Kingdom by 1950 and that of the United States by 1970.

Between 1950 and 1960 the asbestos industry in Europe experienced its greatest expansion up to that time, increasing to 1.17 Mt from 507,000 t in 1950. Consumption increased significantly in Austria, Belgium-Luxembourg, Czechoslovakia, Denmark, France, West Germany, Italy, the Netherlands, Poland, the former Soviet Union, Spain, Sweden, Switzerland, the United Kingdom, and the former Yugoslavia. A significant portion of the growth during the 1950s can be attributed to the continuing reconstruction efforts in Europe following World War II.

The asbestos health issue, which affected U.S. markets by the mid-1970s, also began to affect asbestos use in Europe. After 1980, demand in all large consuming European countries, except the former Soviet Union, began to decline. In the 1990s, production in Kazakhstan and Russia declined significantly, and many European countries, and eventually the European Union, voted to ban the use of asbestos. Consumption was estimated to be 691,000 t in Europe in 2000, mostly in the former Soviet Union.

Asia. Growth in the Asian (including Middle Eastern countries) markets lagged behind that of Europe and the United States. Cultural and governmental differences guiding infrastructure and technological development, and fiscal restraints all contributed to the slow growth in the asbestos segment. It was not until the 1950s that significant manufacturing industries developed, increasing consumption to an estimated 667,000 t in 1970 from 25,400 t in 1950. In the early stages of the industry, China and Japan accounted for the largest increases. The 1980s brought about a shift in manufacturing in Asia with increased production in India, Indonesia, Iran, the Republic of Korea, and Thailand. In 2000, China accounted for 48% of the apparent asbestos consumption in Asia, mainly to satisfy its own domestic demands. India was the next largest consumer, with 15% of the market, followed by Thailand with 14%, Japan with 12%, India with 8%, Indonesia with 7%, and the Republic of Korea with 4%.

Africa. Consumption in Africa has been rather low throughout most of the 20th century, peaking in the 1990s. Slow population growth, limitations on land amenable to development, slow dissemination of new technologies, governmental policies toward development, and fiscal restraints influenced the progress of the asbestos industry in Africa. Significant consumption did not occur until the 1970s when 90,300 t were used. Although erratic in its consumption, Nigeria, with the largest African population, was the largest user of asbestos. After the 1970s, consumption in most countries in Africa began to decline. Consumption in Africa was estimated to be about 30,500 t in 2000, distributed among several countries.

South America. The asbestos industry in South America was very small until the 1960s when Brazil began producing asbestos. By 1970, Argentina, Brazil, Colombia, and Venezuela had the most active asbestos-manufacturing industries in South America. By the mid-1970s, Brazilian production expanded, and Brazil soon became the dominant South American producer and consumer of asbestos. With the onset of the asbestos health issue, consumption in most South American countries declined. Consumption in South America was estimated to be 207,000 t in 2000, with Brazil accounting for about 88% of consumption.

Oceania. Both Australia and New Zealand produced and consumed asbestos in the early part of the 20th century. Consumption peaked in 1975 with Australia accounting for most of the volume. With the asbestos health issue of the 1970s, production and consumption declined to 1,250 t in 2000 (Virta 2002).

In looking at the 20th century as a whole, total asbestos production was estimated to be around 174 Mt between 1900 and

Table 13. Changes in apparent consumption, by decade, t

World Consumption	1920	1930	1940	1950	1960	1970	1980	1990	2000
	205,000	389,000	540,000	1,283,000	2,213,000	3,544,000	4,836,000	3,980,000	1,830,000
Changes in Estimated Consumption, by Continent, by Decade, t									
World	na*	184,000	151,000	743,000	930,000	1,330,000	1,290,000	-855,000	-2,150,000
Europe	na	86,800	102,000	277,000	665,000	627,000	1,010,000	-222,000	-1,890,000
Africa	na	11,200	-13,300	8,180	19,000	61,700	-16,500	-10,800	-32,600
Central and North America	na	82,500	18,900	454,000	-4,020	106,000	-255,000	-403,000	-115,000
South America	na	-823	739	10,600	26,400	61,100	168,000	-61,200	-993
Asia and Middle East	na	4,770	26,700	-12,900	197,000	447,000	394,000	-88,300	-104,000
Oceania	na	-758	15,500	6,450	26,600	28,900	-6,130	-69,700	-115,000
Major Changes in Consumption between Decades, by Country, Decreasing Order, t†§									
	1930s	1940s	1950s	1960s	1970s	1980s	1990s	Current Decade	
Europe	FSU +36,700	UK +71,800	FRG +80,000	FSU +317,000	FSU +227,000	FSU +789,000	FSU +681,000	Yugoslavia (former) -33,700	
	BLEU +18,800	FSU +32,800	FSU +65,300	UK +55,400	France +69,000	FRG +191,000	UK -77,800	Italy -62,300	
	Germany +7,060	France +19,100	BLEU +21,500	FRG +52,400	Spain +62,300	Italy +48,200	Italy -118,000	France -63,600	
	Cyprus +6,730	BLEU -19,100	France +19,800	Italy +48,500	Italy +59,000	UK -56,400	Germany -351,000	Poland -65,600	
	Spain +5,480				Poland +49,100			FSU -1,520,000	
Africa	RSA +13,800	RSA -27,100	Algeria +1,550	Egypt +5,950	RSA +48,400	Zambia -15,600	RSA +78,800	RSA +17,400	
			Congo +1,340	Algeria +4,640	Nigeria +34,400	RSA -98,000	Nigeria -12,000	Tunisia -7,180	
				RSA -21,300	Zambia +15,600		Saudi Arabia -50,600	Algeria -16,500	
North America	Canada +61,300	US +44,600	US +423,000	US -16,700	Canada +50,000	US -309,000	Mexico -39,700	Mexico -12,400	
	US +40,700	Canada -26,300			Mexico +27,000	Mexico +39,000	US -326,300	US -31,300	
								Canada -71,200	
South America			Brazil +8,720	Brazil +17,600	Argentina +21,100	Brazil +157,000	Argentina -14,500	Brazil +18,500	
							Brazil -32,000		
Asia and Middle East	Japan +6,230	Japan +15,500	India +5,610	China +81,200	Japan +227,000	Japan +79,400	Indonesia +57,900	China +224,000	
		Korea +5,590	Japan -14,400	Japan +80,200	China +91,400	China +68,300	Iran +48,900	Korea -47,100	
		India +5,520		India +12,500	Korea +36,000	Saudi Arabia +52,200	China -55,300	Iran -70,200	
					India +26,100	India +47,100	Japan -106,000	Japan -194,000	
Oceania		Australia +14,700	Australia +3,360	Australia +25,700	Australia +25,100		Australia -64,800		

Source: Virta 2003.

* na = Not available.

† BLEU = Belgium-Luxembourg; FRG = West Germany; FSU = Former Soviet Union (countries of Kazakhstan, Russia, Ukraine, and Uzbekistan); Korea = Republic of Korea; RSA = South Africa; UK = United Kingdom; US = United States.

‡ Data are rounded to no more than three significant digits; may not add to totals shown.

§ Part of the change in consumption in major asbestos-producing countries such as Canada, FSU, and RSA includes asbestos that has been added to or removed from company stocks in addition to that used in manufacturing.

Table 14. Asbestos prices, US\$/t

Price	Canadian Fiber					South African Fiber		
	Grade 3	Grade 4	Grade 5	Grade 6	Grade 7	Group 5	Group 6	Group 7
	\$2,020-\$2,440	\$1,390-\$1,950	\$924-\$1,280	\$574-\$824	\$284-\$588	\$360-\$440	\$300-\$350	\$200-\$290

Source: Industrial Minerals 2002.

2000. Assuming some loss during processing, the total amount of asbestos consumed for manufacturing during the 20th century would be in the range of 140 Mt to 160 Mt. Decadal changes by region, and countries that account for the bulk of the shift in asbestos consumption between 1920 and 2000, are given in Table 13.

Prices

Table 14 gives the latest published prices for chrysotile from Canada and South Africa.

Asbestos Substitutes

In response to environmental and liability issues, the use of asbestos substitutes and alternative products has increased. Product manufacturers have been replacing asbestos with different materials, redesigning old products to eliminate the need for asbestos, or designing new products that require neither asbestos nor asbestos substitutes. Some of the factors considered in making the switch include the cost of the substitute, cost of the additional manufacturing, and the cost of the product design, plus product performance. Possible health

risks, many of which are unknown over the long term, also have to be considered when using substitutes (Hodgson 1985; EPA 1988).

Examples of materials substituted for asbestos include aramid fiber, cellulose fibers, ceramic fiber, fibrous glass, graphite flake and fiber, mica, polyethylene fiber, polypropylene fiber, polytetrafluoroethylene fiber, steel fibers, and wollastonite. Examples of alternative products include aluminum, vinyl, and wood siding; aluminum pipe and sheet; asphalt coatings; ductile-iron pipe; fiberglass sheet; polyvinyl-chloride pipe; prestressed concrete and reinforced concrete pipe; semimetallic brakes; urethane coatings; and vinyl composition floors (Hodgson 1985; EPA 1988; Harrison et al. 1999; Roskill Information Services Ltd. 1990; also refer to the Asbestos Substitutes chapter in this book). No single substitute has proved to be as versatile as asbestos.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Health and Safety

Asbestos-related disease is one of the most widely studied subjects of modern epidemiology (WHO 1986; Bignon, Peto, and Saracci 1989). It includes asbestosis (a lung fibrosis resulting from long-term, high-level exposures to airborne fibers), lung cancer (usually resulting from long-term high-level exposures and often correlated with asbestosis), and mesothelioma (a rare form of cancer of the lining [mesothelium] of the thoracic and abdominal cavities) (Omenn et al. 1986).

Concerns over its health effects were first raised in the early 1900s in the United Kingdom, but it was not until the early 1960s that researchers established a positive correlation between worker exposure to asbestos fibers and respiratory cancer diseases (Selikoff, Churg, and Hammond 1964; Murray 1990). This triggered a significant research effort to unravel important issues such as the influence of fiber size, shape, durability or persistence in the lungs, trace elements, and exposure levels and duration with health effects (van Oss et al. 1999; Churg and Wright 1994; ATSDR 2001; Rice and Heineman 2003). It is generally agreed that the inhalation of long (generally greater than or equal to 5 μm), thin, and durable fibers in high concentrations over a long period of time pose the greatest health risk. Shorter fibers penetrate deeper into the lung, but longer fibers are more difficult to clear (Timbrell 1982; Finkelstein and Dufresne 1999).

Fiber solubility is suggested to be the second most critical factor. Chrysotile is more soluble than amphibole asbestos and is more rapidly removed, reducing its residence time in the lung. Duration of exposure to asbestos is important because long exposure periods increase lung burden, with long and/or high exposure levels counteracting the effects of fiber solubility. Different asbestos types also appear to activate phagocytic leukocytes differently, with crocidolite and some chrysotile samples being the most active (van Oss et al. 1999). Research suggests that iron content may be important in asbestos-induced toxicity (ATSDR 2001).

Although the subject is still debated, many health scientists believe that there is sufficient evidence to state that the genotoxic and carcinogenic potentials of all asbestos-fiber types are not identical; in particular mesothelial cancer is most strongly associated with amphibole fibers (Gardner and Powell 1986; Dement 2001; Gibbs 2001; Nolan et al. 2001; Wilson and Price 2001; Bernstein, Chevalier, and Smith 2003; Bernstein, Rogers, and Smith 2003).

The issue of asbestos as a contaminant in ore bodies also is a concern (Nolan, Langer, and Wilson 1999; Hull, Abraham, and Case 2002; Peipins et al. 2003). As a means of defining the types that may contain asbestos as a contaminant, two studies were recently conducted on talc and vermiculite deposits. In the study of

U.S. talc deposits, it was determined that talc formed through hydrothermal processes consistently lacks amphiboles as accessory minerals. Talc bodies formed through contact or regional metamorphism, however, consistently contained amphiboles, locally as asbestiform varieties (Van Gosen et al. 2004). In U.S. vermiculite deposits, preliminary studies suggest that fibrous amphiboles are most likely to be associated with zoned, alkalic/calcic, quartz-poor plutons, such as the vermiculite deposit near Libby, Montana (Van Gosen et al. 2002).

Regulation

Environmental and liability issues continue to affect the asbestos industry. As the concern over the health risks posed by low-level exposures to asbestos increased, the United States and other countries have enacted stricter exposure regulations. More emphasis is being placed on environmental exposures than in the past.

Some countries have opted for a broader approach and have adopted regulations that also minimize exposure of the general public to environmental asbestos fibers by banning or restricting asbestos imports and types of applications. Countries that have banned (either a complete ban or a ban with exemptions) or are phasing out the use of asbestos, and in some cases asbestos products, by 2005, include Argentina, Austria, Belgium, Chile, Denmark, Finland, France, Germany, Italy, the Netherlands, Norway, Poland, Saudi Arabia, Sweden, Switzerland, and the United Kingdom (Virta 2002; International Ban Asbestos Secretariat 2004). In 2005, the European Union banned asbestos use by its members in most applications.

OUTLOOK AND FUTURE TRENDS

Legal actions and adverse publicity on asbestos have taken their toll on asbestos markets, despite much stricter asbestos regulations. World consumption declined from an estimated 4.84 Mt in 1980 to about 1.83 Mt in 2000. Although a few countries have increased or maintained their production through 2002, consumption has declined significantly in most countries. This trend is expected to continue because of increased pressure to reduce or ban asbestos usage in major consuming countries.

Despite the current bans and continued opposition to the use of asbestos, markets for asbestos probably will continue to exist into the future. Consumption can be expected to decline as substitutes and alternative products gain favor in remaining world markets and as additional countries enact bans on the use of asbestos. This process will occur over many years, and even then, there probably will remain specialized applications for asbestos, particularly for matrix-based products.

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Barium Minerals

Paul Mills

INTRODUCTION

The word *barium* comes from the Greek word *barus*, which means heavy. The common barium minerals are *barite* and *witherite*. Barite is by far the predominant barium mineral used by industry. Barite is also known as *barytes*, and in the area around Potosi, Missouri, it is called *tiff*. Barite has been found in many areas around the world, and the mineral is mined and processed in numerous countries. Because the mineral has a high density and is chemically inert, it is ideal for use in the petroleum, automotive, and paint industries, and in other applications. The purpose of this chapter is to help one identify barite, locate the mineral, and understand its uses and the way the mineral is currently being mined. The reader is also referred to the Barium Minerals chapter in *Industrial Minerals and Rocks*, 6th edition (Brobst 1994).

PRODUCTION, RESOURCES, AND RESERVES

The four top barite-producing countries in the world are China, India, Morocco, and the United States, according to the information compiled and reported by the U. S. Geological Survey (USGS). Table 1 is based on information supplied by the USGS (Searls 2004), which outlines the reserves and production for 2002 and estimated values for 2003. Values are given in thousand metric tons.

The reserve base is the in-place demonstrated (measured plus indicated) resource from which reserves are estimated. The reserve base includes those resources that are currently economic and marginally economic, along with some that are not currently economic.

Not all the barite reserves have been identified. There are still possible locations for new or additional barite reserves.

GEOLOGY

Mineralogy

Chemically, barite is barium sulfate with the formula of BaSO_4 . It can be identified by its high specific gravity, which is 4.50 g/cm^3 when in pure form. The mineral has a hardness of 3.0 to 3.5 on the Mohs hardness scale and belongs to the orthorhombic crystal system. It can also be identified by its white streaks and vitreous to pearly luster. The cleavage of the mineral is perfect on {001} but imperfect on {010}. It normally has thick to thin tabular crystals, an example of which is the *desert rose*, a cluster of reddish barite crystals. Barite comes in a variety of colors, including yellow, white, brown, gray, and blue; it can also be colorless.

Table 1. World mine production, reserves, and reserve base, kt

	Mine Production		Reserves 2002	Reserve Base 2002
	2002	2003*		
Algeria	45	50	9,000	15,000
Brazil	55	55	2,100	5,000
China	3,100	3,500	62,000	360,000
France	75	75	2,000	2,500
Germany	120	125	1,000	1,500
India	600	900	53,000	80,000
Iran	220	250	na†	na
Korea, North	70	70	na	na
Mexico	150	180	7,000	8,500
Morocco	470	470	10,000	11,000
Russia	60	60	2,000	3,000
Thailand	24	30	9,000	15,000
Turkey	120	100	4,000	20,000
United Kingdom	60	60	100	600
United States	420	480	26,000	60,000
Other Countries	420	290	12,000	160,000
Total (rounded)	6,000	6,700	200,000	740,000

* Estimated.

† na = not available.

The mineralogical name for the carbonate barium mineral is witherite, which has a chemical formula of BaCO_3 . Unlike barite, witherite is not chemically inert. Witherite can dissolve in water and, when dissolved, can cause an environmental hazard.

Origin and Mode of Occurrence

Barite forms in many geologic environments and can be found with both metallic and nonmetallic minerals. The barite can either be the major component of the material or only a minor fraction. In most cases, the barite must be a major component of the material and must be of substantial thickness for the ore to be economic. There are three main types of deposits: vein, residual, and bedded.

Vein, Filling, and Replacement Deposits

The vein deposits are epigenetic deposits of hydrothermal origin with the barite precipitated from solution and filling or replacing

rocks along fractures or other structures. The barite was often deposited in fault fractures or along bedding planes. Because of the nature of the deposit, the barite-mineralized zone can vary greatly in length and width. It is not uncommon for the main mineralized zone to pinch and swell along the fracture structure, and the zones tend to pinch out on each end. The deposit can have fractures filled with barite radiating from and perpendicular to the main barite zone. The barite is normally white, but sometimes is stained by secondary iron oxides. The common impurity is quartz, but at times the ore is associated with metallic minerals such as pyrite and marcasite. Some veins contain only quartz and perhaps calcite as impurities. Many of the vein deposits with low amounts of impurities have been used by the paint industry.

Residual Deposits

The residual deposits are of hydrothermal origin. The host rock, which in most cases had been limestone or dolomite, has been removed by extensive weathering. The barite, which filled fractures in the host rock, is now contained in unconsolidated material such as clay. The depth to which the barite has been liberated depends on the depth of the weathered zone, which can be as deep as 100 m. Generally the barite content in the unconsolidated material is low. Because it is easier to mine unconsolidated material than rock material, and it is less difficult to separate the barite from unconsolidated material, a residual deposit can still be economical even though the barite content is low. The barite in a residual deposit is white in color. The major impurity associated with the barite is quartz, but pyrite, marcasite, galena, and fluorite can also be present.

Bedded Deposits

The bedded barite deposits are stratiform deposits that are part of a sedimentary sequence. This type of deposit typically is found with units of chert, mudstone, and siltstone. The origin of the bedded barite deposits in Nevada and elsewhere has been a controversial subject. Early workers suggested that the deposits in Nevada were formed by hydrothermal replacement of limestone or chert (Gianella 1940; Ketner 1963). Dunham and Hanor (1967) first suggested that the deposits were penconemporaneous with the enclosed sediments and that the barium was derived from hydrothermal fluids. Numerous studies in the late 1960s to early 1980s added much new data and generally supported the sedimentary-hydrothermal characterization of the deposits. Much of these data were summarized by Papke (1984) and Harben and Bates (1990). It has now been fairly well established that the bedded barite deposits are of submarine-exhalative origin. Barium in fluids moved upward along fissures in the ocean floor and discharged from submarine hot springs, where it combined with sea water sulfate to form barite. This process explains the many sedimentary features as well as the local replacement and alteration of adjacent rocks. Biological activity was no doubt important, especially in producing the sulfide ions that reacted with metal or hydrogen ions, but a source of introduced barium in solution was needed to form the typical bedded deposit of nearly pure, thick barite. Many details about the exact environment of deposition are still being debated, and the origin of the deposits has not been resolved to everyone's satisfaction.

Bedded barite varies in thickness and length. The thickness, length, and purity of the deposit will vary with the relationship of the sedimentary process and submarine hot springs at the time of deposition. The length of the deposit can be more than 300 m and the thickness more than 30 m. The deposit can also be short in length and narrow in thickness. Bedded barite is generally light to dark gray. The barite is normally interbedded with chert or argilla-

ceous material. The major impurity is quartz. Bedded barite contains several percent of organic carbon and is commonly rich in hydrogen sulfide. Brachiopods and other fossils are sometimes present as a mold or replaced by barite.

MAJOR DEPOSITS

United States

Arkansas

The large bedded deposit near Magnet Cove, Arkansas, is a bedded deposit that is folded into a plunging syncline. The barite is gray to blue-gray in color with some interbedded black shale. The barite is tightly bound with quartz and black shale. The mining in this area started in the 1940s, first by the open-pit method and later by underground mining. The deposit was last mined in the late 1970s. Flotation was required to process the ore. The material was used by the petroleum industry.

Georgia

The Cartersville Area contains several barite deposits, which are considered to be hydrothermal in origin, filling fault and fracture zones (Kesler 1940). These are residual deposits because the host rock has been eroded away, leaving the barite ore in the resulting clay beds. Some of the ore is tightly bound with quartz, which means that the ore must be crushed to about 70 mesh for the barite to be separated from the waste material. Flotation or a combination of jigs and flotation have been used to recover the ore. The barite is white in color, but because some iron oxide is present with the processed ore, it has a light brown color. Mechanized mining started in the early 1900s, and continues today. The barite from this area is generally used in the industrial grade market.

Missouri

The Potosi Area has several barite deposits, which are residual deposits. The barite is believed to be hydrothermal filling of fault fractures. The host rock weathered away, leaving the ore in reddish clay. The barite ore is white. The associated minerals are drusey quartz, agate, weathered marcasite, some galena, and goethite. The ore is not tightly bound with any of the associated minerals; therefore, a washing plant has been used to recover the barite. The processed ore was light to dark brown because of the presence of the iron oxide. Hand-mining started in this area in the 1800s, and mechanized mining started in the late 1920s. The last mine in this area was closed in the 1990s. The material has been used by the petroleum, paint, and medical industries after further processing.

Nevada

There are several active barite mines in the Battle Mountain area. The barite deposits in this area are bedded barite deposits. The ore is light to dark gray and is associated with argillaceous rocks and chert. Some of the deposits in this area are pure enough to be mined and shipped without any additional processing. The remainder of the ore requires jigs or a combination of jigs and flotation to separate the barite from the waste material. There are also numerous vein and bedded deposits in Nevada. Some of the mining operations in Nevada began in the 1940s. The open-pit mining method is currently used in Nevada. The ore is used in the petroleum industry.

Tennessee

The Sweetwater area has several residual barite deposits. The barite is associated with fluorspar and some iron oxide. A washing plant containing barrel screens, dewatering screws, and jigs was used to recover the ore. The barite deposits in this area were mined until the 1990s. The ore was used mainly by the petroleum industry.

Other Countries

Brazil

There is an active mine in the Camamu Area. The barite is a vein deposit and some goethite and limonite are associated with the ore. The open-pit method is used to mine the ore. The ore is obtained using selective mining and washing/screening to separate the waste product.

Canada

There are several unmined bedded deposits in the Yukon Territory, and there are deposits in Nova Scotia and Newfoundland. The method used to process the ore in Nova Scotia varies with the deposit. One deposit requires flotation, and another requires tables and/or jigs to process the ore. The Newfoundland deposit requires flotation to process the ore.

China

There are several barite deposits in China. A large bedded deposit in the Hunan Province is folded into a plunging syncline. The deposit has a very long strike but is only a few meters in thickness. The ore is mined by the open-pit method, and in some areas, short drifts and shafts are used to retrieve the ore. The ore is mined by hand, the grade is controlled by hand picking and selection.

An ore deposit in Guangxi Province is of vein origin. The ore is white, with some iron oxide associated with the barite. The ore is mined by the open-pit method, and in the area of Yong Fu, the ore is retrieved using the underground mining method. The ore is mined and selected by hand. There are also several residual deposits located in the Guangxi Province.

A deposit of barite in Guizhou Province also is of vein origin. The ore is bright white and can be used by the paint industry. The ore is hand-mined and selected.

India

The major barite mine in India is a bedded deposit. The ore, which is dark gray, has been folded into a plunging syncline. The estimated reserves of the deposit are approximately 70 Mt.

Mexico

There are several bedded deposits in the Hermosillo Area. The deposits are very similar to those in Nevada. Some of these deposits were reported by Poole, Madrid, and Oliva-Becerril (1991). The ore is light to dark gray in color. The ore was separated from the siliceous waste by jigs. There are some deposits that require a combination of jigs and flotation. Other deposits in Mexico are located in the Pueblo, Monterrey, and Durango areas. Open-pit mining has been used to retrieve the ore.

Other Deposits

There are also barite deposits in Morocco, Ireland, France, Germany, Italy, Iran, North Korea, Thailand, Turkey, Algeria, Russia, and several other countries.

TECHNOLOGY

Exploration Techniques

Many barite deposits are located by the discovery of an outcrop or float material found in streams, drainages, and road cuts. After the initial discovery, additional work is done to determine the extent of the deposit. This is normally done through mapping the outcrop or location of the float material. When the outcrop is located, a series of trenches are normally dug perpendicular to its strike to determine the length and size of the deposit. Ore samples are collected from

the trenches to determine the quality, composition of the ore, and rough economics of the deposit. The first tests performed will indicate if the material can be marketed and can also indicate the cost involved to bring the ore to market.

The discovery of the first outcrop or deposit can assist in locating other similar ones. The barite deposit may be displaced into additional segments as a result of faulting. The mapping of the fault structures in the area might lead to locating extensions of the barite deposit. Also, depositional information might assist in locating other deposits. In Arkansas, the barite deposits that have been mined are located at the boundary between the Arkansas Novaculite and the Stanley Shale. The deposit located near Magnet Cove, Arkansas, is about 96 km from the deposits in the Fancy Hill District, but all the deposits are in the same geologic sequence.

After the deposit has been located, and it has been determined that the deposit warrants additional investigation, drilling is used to determine the depth and quality of the ore in vein and bedded deposits. Normally, reverse-circulation, air-hammer drills are generally used for drilling up to several hundred meters in depth. The drill cuttings are collected at intervals, keeping the ore zone samples separate from the overburden samples. The drill cuttings can be used in a series of tests that determine the economics of the deposit. Specific gravity normally is run on every sample collected of the ore zone. On a composite of the ore zone samples, the amount of mercury, cadmium, and water-soluble alkaline earth metals is sometimes tested. The drilling sample can also be used in tests to determine the best method to upgrade the ore. Tests such as liberation size, sink float test, and plant pilot test can be used to determine recovery method and estimated cost for recovery. It should be noted that because of the nature of the reverse-circulation drilling method, some samples can be contaminated with upper formation material.

If higher accuracy or additional information is required, core drilling is then used. Core drilling is also used to reach to greater depths. Core drilling is more expensive than air-hammer drilling, but it can eliminate contamination and allow additional information to be gathered. With the core retrieved, the angle of the ore zone can be measured and any fault zones can be located. In some cases, the direction of movement along fault planes can also be determined. In addition, the relationship between the ore and waste zones can be more clearly defined. Specific gravity and mercury, cadmium, and water-soluble alkaline earth metals contents can be determined from the core samples to estimate the quality and marketability of the ore. Metallurgical testing can be done to determine the recovery method required to market the ore.

When evaluating a residual deposit, auger drilling or trenching using a large backhoe or excavator is used to determine depth, quality, and quantity of the barite. When the ore zone is shallow, the trench method can then be used to collect samples and map the ore zone. When the barite zone is deeper than 6 m or below the reach of the backhoe bucket, drilling is required. The samples collected are tested for the percentage of barite. The mixed clay and barite can be used to determine the recovery method. In most cases, the clay is removed, and liberation and pilot tests are performed on the remaining rock material to determine the method of recovery and economics of the ore.

When evaluating an ore deposit to determine if the ore will be economic, special care needs to be taken to analyze the possible effects of associated minerals. If the mining operation exposes unoxidized minerals such as pyrite, these minerals will possibly react with rainwater and cause an acid water discharge. The state of Nevada now requires that a potential acid generating test be performed on the ore and mining/upgrade process.



Figure 1. The Rossi mine

From the information gathered about a deposit, a mine plan can be developed. Most barite mining operations today use the open-pit method to extract the ore. This type of mining is ideal for near-surface deposits with various angles of dip. Barite has on rare occasions been mined using underground methods. Underground operations are normally used for deeper deposits. Also, this method is sometimes used at the later stages of mining where the open-pit method was used in the beginning phase. The barite operation at Magnet Cove, Arkansas, is a good example of this type of mining. The underground method can also be used when property rights or other factors restrict the extent of the surface disturbance. In all cases, the ore body must be evaluated to determine which method is the best from an economic and safety standpoint. Figure 1 is a photo of the Rossi Mine, an open-pit barite mine located in Nevada.

Much care must be taken to remove the mined barite with as little waste contamination as possible to reduce processing costs. In some cases, it is very difficult to eliminate the waste because of the nature and type of deposit. In a residual deposit, a high percentage of the material is waste, and current mining equipment is not capable of separating the clay waste. Therefore, the ore-bearing waste is mined and hauled to the processing plant for separation. A bedded barite that has thinly bedded shale, chert, or a gillite also is mined and hauled directly to the processing plant with very little waste separation. If the bedded or vein barite zone is pure enough and of sufficient size, the ore zone may then be mined to produce barite that will meet specifications without further processing. In many cases, the waste on the hanging wall of the ore must be removed first. Removal allows the mining equipment to mine the ore cleaner and with less waste contamination. When the dip of the barite is nearly vertical, the barite sometimes can be mined leaving the waste on both sides of the ore. In some of the hand-mining operations in China, the ore is removed and the waste is left in place.

Barite Processing

Several processes have been developed and used to separate the waste material from the barite. Each method has its own unique requirements and limitations. The processes that can be used are hand selection, screens, washing, jigs, tables, spirals, and flotation. One or a combination of several different methods may be required to separate the waste from the barite.

Hand Selection

Hand mining, or selection by hand, can be done in areas where the cost of labor is low and/or where hand selection will achieve the desired quality of barite. In some areas of the world, the cost of labor is low enough that the barite deposit can be mined and the barite separated from the waste by manual labor or hand selection. The laborers must be able to easily identify the ore and determine quality. To aid in the separation, the waste and ore should have different colors or other physical differences that are easily discernible by eye. A deposit of high-purity white barite flanked by brown sandstone would be easy to separate by hand. Separation by hand is used by the Chinese to produce the high brightness barite used in the U.S. paint industry. The barite that is iron stained or contains minerals that will cause the brightness and whiteness to drop is removed by manual labor. There are optical sorters that can remove off-white product, but nothing is better than the human eye and hand.

Screening

Screening or the combination of crushing and screening can remove some clays, fine-grained waste, or other waste with different breaking characteristics than barite. Screens are ideal for removing some clay and subsoil, with the barite produced as oversize and the waste as fines. This removes the lower specific gravity material and raises the specific gravity of the final barite product. In some cases, screening has been used to raise the specific gravity of ore from a deposit that consists of shale and barite. Because the shale breaks in a different manner than the barite, some of the shale can be removed by screening. Some screening is currently being done in Nevada.

Washing

Washing the ore with a dewatering screw, barrel screen, or logs removes special types of clays and subsoils where material is hard to break up. A washing-type system is used mainly with residual type deposits, but can be used on other deposits as well. The object of this method is to remove large amounts of clay from the rock material. The material can be either ore-bearing material that will be sent to an additional process to complete the separation or material that will meet specifications without any additional work. In one area in China, dewatering screws are used to wash away the clay material and the resulting material is drilling-grade barite. The barite processing plants in Georgia, Tennessee, Missouri, and Brazil all use or used washing in the first stages of operation.

Jigs

Jigs are used all over the world to separate barite from other rocks and minerals. Jigs use pulsating water to separate barite from the waste by gravity. The feed must be crushed finer than a predetermined liberation size, namely the size to which the ore must be crushed to liberate the barite from the waste. The feed size also must be the size that the jig can handle.

Several different brands of jigs and several different jig configurations are available. Some jigs are capable of handling crushed material the size of a large sand grain. Most jigs operating today handle crushed material that is 12.5 mm in diameter or less. The way the jig works is that crushed feed is constantly being added on top of a screen. Water is added in the lower part of the jig below the screen, filling the jig several centimeters above the screen. Excess water runs off the end of the screen, carrying with it some of the waste material. The jig has a plunger or other method to pulsate the water. The pulsating water lifts the feed material, allowing the heavy barite

to sink to the bottom. The lighter waste stays at the top and is washed off the end of the jig. The barite is removed from the bottom by what are called "cups." A cup is a pipe about 1 cm above the screen to the top of the jig. The barite fills the pipe from the bottom. The material is then removed by a series of pipe or slides. In some cases, jigs are used in series to upgrade the material. There must be a difference in the specific gravity between the waste product and the barite for this method to work. In Nevada, jigs are used to separate waste from ore. The waste material has a specific gravity of about 2.75, while that of the barite ore is greater than 4.20. Figure 2 is a diagram of a typical jig plant.

Spirals and Tables

Spirals and tables are used infrequently because of the cost to operate the units. Both methods use specific gravity and the material movement to separate the waste from the ore.

Flotation

Flotation can also be used to separate the waste from the barite. This method is used when the liberation size is finer than what a jig or other equipment can handle. Normally, the feed for a flotation cell is 40 mesh or finer. The flotation method uses a chemical to float either the barite or waste into a froth. The separated barite is normally called a filter cake, because a filter is used to remove the excess water from the barite.

MARKETING

Uses and Specifications

According to the USGS (Searls 2004), during 2003, approximately 95% of all the barite mined and processed in the United States was used by the petroleum industry. The remaining 5% was used by the industrial market and the medical field.

In the petroleum industry, the barite is used to make what is known as "drilling mud." Barite and other additives in drilling mud assist in several ways during drilling. The barite serves as a weighting material that increases the hydrostatic pressure of the drilling mud and thus controls high-pressure zones that are encountered during drilling. Proper weighting prevents what industry calls a "blowout." Because the barite is soft, it does not damage or cause abrasion problems to drilling tools such as the bits and drill pipe. Also because of its softness, it will also act much like a lubricant. Finally, because barite is chemically inert, it does not react with or interfere with other components used in the mud.

The American Petroleum Institute (API) has set specifications for the barite used in the oil industry. These specifications primarily deal with specific gravity, particle size, and maximum quantities of some impurities. The barite must have a minimum specific gravity of 4.20 g/cm³. It must also be ground to a powder where at least 97% will go through a 200 mesh sieve. The amount of water-soluble alkaline earth metals must be below a prescribed amount, 250 mg/kg. In addition to the specifications set by API, the barite used in the drilling fluids on the offshore drilling rigs in the Gulf of Mexico must meet specifications set by the U.S. Environmental Protection Agency (EPA) on mercury and cadmium content.

Barite is used in the industrial market in such products as traffic cones; brake linings; paint; sound-deadening materials in automobiles, golf balls, and foam; and as filler in several other products. The barite specifications for industrial products also involve specific gravity, particle size, and quantities of impurities. Some of these products have an additional specification for brightness or whiteness. The barite specifications vary depending on the needs required by the final product. For example, the barite in automobile brake lin-

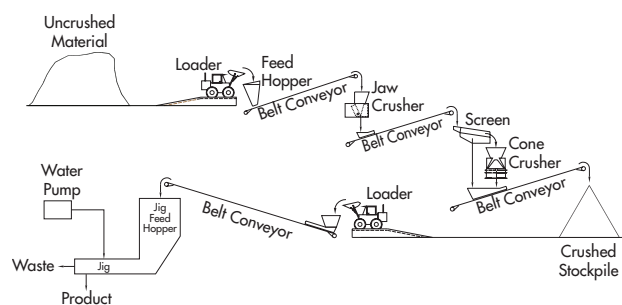


Figure 2. Typical jig plant

ing normally has a specific gravity of 4.35 or higher. A barite with higher specific gravity normally contains fewer impurities such as quartz. The lower quartz or silica content results in a higher-quality brake lining because quartz is very abrasive. In addition, many of the industrial products have a specification on maximum particle size. The maximum particle size is important in some products such as brake pads and sound-deadening sheets that have a particular thickness. If the ground barite is larger than the thickness of the material, it could cause holes in the product. Color can be a factor in the sound-deadening barriers for automobiles if it is visible. Color can also be a factor to a paint manufacturer. In paint applications, a very white barite with a high brightness is preferred because it is easier to tint or control the final color of the product. In the paint industry, grind size of the barite is also important because particle fineness will affect paint gloss. An instrument used in the paint industry, a Hegman gauge, is used to determine the maximum size and fineness of the ground barite.

The medical industry uses barite that has been through a special process that produces a very high-purity barite. This barite is used in lower and upper gastrointestinal tests. Because barite is dense, x-rays do not penetrate the material and it shows up on the x-ray. The mineral witherite, which is a barium carbonate, cannot be used by the medical profession because it dissolves in water and is poisonous to humans.

Therefore, not all barite deposits are suited for every barite use. If one is looking for barite for use in the paint industry, one would need to locate a deposit that has a high whiteness and brightness. The material would need to have a specific gravity exceeding 4.35 and also a low calcium and silica content. The deposit should not have minerals or contaminants that would cause the barite to become discolored. For example, the barite in Georgia is white, but iron oxide is present, which causes the final product to be light brown. Barite that meets the high-purity, high-gravity, and high-brightness/whiteness standards is normally referred to as paint-grade barite. The value of paint-grade barite is much higher than drilling fluid-grade barite because of these requirements.

A barite with a specific gravity that exceeds 4.35 but has an associated mineral that results in a lower brightness or whiteness may be ideal for the brake industry. This material, however, would also need to be low in silica and calcium content to be usable in the brake industry.

Barite deposits useful for oil and gas drilling must have barite that can be separated to give a minimum specific gravity of at least 4.20. The color of the barite is not a factor. The deposit must be low in mercury, cadmium, and water-soluble alkaline earth metals to be usable for offshore drilling rigs. The selling price of crude drilling-grade barite is relatively low. Therefore, processing and

transportation costs are leading factors in determining whether a deposit is economic.

Competitive Substitutes

As reported by the USGS (Searls 2004), alternatives to barite in the drilling market include celestite, ilmenite, iron ore, and synthetic hematite. Normally, iron ore, ilmenite, or hematite is used when a drilling mud with a very high density is required. All three minerals have a higher density than barite. Ilmenite, iron ore, and hematite are also harder than barite. The greater hardness of these minerals can result in higher wear than experienced with barite. Celestite has the same hardness as barite, but is lower in density. None of these minerals have had a major impact on the barite usage in the drilling-fluid industry.

The industrial sound-deadening market can use calcium carbonate instead of barite when the thickness of the sound-deadening sheet is not an issue.

Packaging and Transportation

Crude barite is normally transported by ship, barge, rail, and/or truck. In most cases, the material is transported from the mine to its final destination by a combination of several different modes. The means of travel depends greatly on what types of transportation are available in the area. Crude ore is generally transported in open-top barges, railcars, or trucks. In the case of white barite, which is used in the filler industry, special care must be taken to prevent color contamination. Therefore, the barite is transported in barges and railcars with tops to prevent contamination from river water and other possible contaminants.

The finished barite in the drilling fluid market is normally sold in bulk, bulk sacks, or paper bags. In the United States, the majority is shipped in bulk by truck, rail, ship, or barge. Paper bags are the second most popular means of packaging, followed by bulk super-sacks. Because a large amount is shipped in bulk, temporary silos are used at the oil well sites to hold the bulk material. Grinding plants and warehouse locations have large bulk silos with warehouse space for bagged material. The bag material is normally labeled with lot numbers that relate to production dates and quality records. Bulk shipments can also be traced to production and quality records.

In the industrial/filler barite market, the finished barite is also sold and shipped in bulk, bulk sacks, and paper bags. Bulk is still a major way that the barite is sold, but paper sacks and bulk sacks are playing a much bigger role. Many industrial barite consumers use batch methods to make their products, and paper bags fit their needs better than large bulk silos. Most of this barite is shipped by truck. Generally, every truckload is certified individually with the lot number and quality results recorded.

Economics or Competitive Factors

The United States imports barite from several different sources. Today, much of the imported barite is from China and India. The duty and fees associated with importing barite must be taken into consideration. The current costs of these fees can be obtained by contacting the U.S. Customs and Border Protection (CBP) agency. The fees can change; therefore, it is recommended that one check the current rate with CBP. The product CAS (Chemical Abstracts Service) numbers, such as 2511.1-05000 for crude barite and 2511.10.1000 for ground barite, are required.

Each country has different import requirements, and some countries have barriers to stop or restrict barite import. These requirements and laws can change rapidly, so it is best to check with the country's custom officials to determine current laws pertaining to barite import and export.

When determining the economics of a barite deposit, one must consider not only the cost to mine and process the ore but also the cost to obtain proper permits. Mining laws can vary for every country and every state or province of that country. When evaluating a barite deposit, a copy of current mining law for that country or state should be obtained. Local government officials should be able to explain which permits are required to perform exploration and/or mining in the area. In most cases, the governing agency will require a mining and reclamation plan to obtain a mining or exploration permit, and possibly several environmental and area impact studies will be required. These could include cultural, archaeological, animal habitat, and water usage studies of the effect of the ore on rain runoff and dam safety, and assessments of the effect of the mining on groundwater and any other environmental issues pertaining to that area. When a permit is issued, a bond is required prior to any disturbance of the area. The bonding amount required in many cases will be equal to or slightly greater than the amount estimated to complete the reclamation of the planned disturbed area. Depending on the size of the project and government permitting requirements, it could take anywhere from a few months to several years to obtain the permits required to begin the exploration and/or mining of a deposit.

The initial study of a deposit can determine the type of mining required to retrieve the ore and a rough idea of the method required to process the ore. A rough estimate of mining and processing costs can be estimated from this information.

Other costs that need to be considered when determining the economics of a deposit include the cost to maintain the permits, the cost of any testing or monitoring required by a permit, the cost of utilities, the cost of operating the processing plant, the cost of labor in the area, the cost to acquire the property, and the cost for the mineral right by purchase or royalties. Another item to consider is the revenue that the processed ore will generate. If a competitor locates a deposit where the mining or processing gives them a price advantage, this advantage could affect the amount of revenue that would be received from the finished ore. Also, if the total demand were to drop and affect the total tons produced and sold, this would affect the cost structure of the operation.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Environmental, Health, and Safety

As mentioned before, minerals associated with the ore are a main concern when mining and processing barite. In many barite deposits, quartz is present with the barite. If the level of quartz is high enough, the ore must be handled so as to reduce the respirable silica level. Dust masks may be required when processing and handling some barite because of the silica level. Water trucks are used during mining to reduce the amount of dust in the air.

If unoxidized minerals such as pyrite are present with the barite, acid mine drainage or low-pH runoff could result from groundwater or storm water contact with the pyrite. The acidic runoff may also leach additional minerals from the ore, resulting in runoff with a low pH and high minerals concentration. Both the runoff of this water as well as the accumulation of this water in mining pits are of possible environmental concern. These issues must be addressed within the context of the environmental requirements in place in the jurisdiction within which the mining occurs.

Reclamation

After the exploration and/or mining has been completed, reclamation of the disturbed areas must be performed. Generally, open pits are left open with fences along the high walls for safety reasons. In some areas, where acid mine runoff is not a concern, the mining pit

will fill with water, forming a lake that can be used for recreation purposes or wildlife habitat. In some rare cases, the mining pits are backfilled to prevent the mine from filling with water. The area is sloped to blend with the surroundings. Under ground mining entrances are sealed to prevent entrance by unauthorized personnel. The waste piles are sloped to a 3:1 ratio to minimize erosion. The slopes may also have earthen terraces to minimize the effects of runoff. After the area has been sloped, it is planted with an assortment of local vegetation. Using plants not native to the area is not recommended unless approved by the governing agency. There have been several cases in history when non-native plants have caused major problems.

Haul roads, trenches, plants sites, and other disturbances are sloped to blend with the surrounding topography and seeded. All buildings are dismantled, and water wells are sealed.

Closure and Decommissioning

The appropriate governing agency will monitor progress during reclamation. Often, the amount of bonding can be reduced as some areas are completed. When the total area is completed, a request can be submitted to close the operation and release all bonding. The amount of time required to complete the closure process will vary. The governing agency will want to make sure that the vegetation is well established and that all runoff is controlled. They will also want to determine if the water discharge from that area meets their requirements. Areas deemed by an inspector as not meeting the requirements may have to be reworked. After the agency has determined that the area is stable and up to requirements, the complete bonding is then released.

Variations

In the United States, each state has different methods for handling bonding and release. Also, some states require special permits for water dams, which will affect the tailing ponds used in the jig and flotation methods. Some states restrict the amount of land that can be reclaimed for a particular end use. For example, Missouri will not allow more than 10% of the disturbed area to be used for wildlife habitat. In addition, a 3:1 slope is widely accepted for reclaimed land, but on some occasions, other slopes are used because of local requirements or variances. Some barite deposits may be located in air-sensitive zones where the air emission requirements are much more restrictive. These are just some of the possible variances that can be encountered concerning environmental, health, and safety issues. Local governmental agencies will be able to supply information on the requirements for their area.

Many countries around the world have regulations and requirements very similar to those in the United States. A few countries have mining regulations that are not as strict or as demanding as those in the United States and other countries. Regulations for each country of interest can be obtained from the governmental agency dealing with mining.

OUTLOOK AND FUTURE TRENDS

The use of barite has been historically tied to the oil industry because more than 95% of the produced barite is used in that

market. As the price of crude oil increases, normally there is more activity in the search for new oil fields. Greater activity means that more barite is needed for the drilling mud used in oil exploration. With the price of crude oil reaching all-time highs in 2004 and with predictions that worldwide oil consumption will increase by about 2% annually, the immediate future for the barite industry appears to be good. The long-term future of barite usage in the petroleum market depends on the development and use of alternate energy sources and how such use will affect the oil industry. The development of new energy sources that will lower the demand for crude oil should also decrease the demand for barite. The barite market would also be affected if a replacement for barite could be located. Of course, any replacement material for the oil business would need to be as soft as barite to prevent excessive wear, have sufficient weight to be an effective weighting material, and be chemically inert so that it would not harm the environment.

The other 5% of the barite market is for industrial uses. The largest user in this market is the automotive-related industry. Their uses include sound-deadening materials, brake linings, and automotive paint. The demand or the lack of demand for new automobiles affects this market. The new automobile market is consumer driven. Part of the brake market is for after-market or replacement-type parts. As a result, part of the brake market is driven by new car production, and part is driven by car maintenance. A possible indicator for the automotive market is the information released by the automakers concerning plant closures, layoffs, callbacks, and manufacturing expansions.

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Bauxite

Vincent G. Hill and Errol D. Sehnke

Bauxite is the primary raw material used to produce aluminum metal. In addition to this dominant industrial end use are a number of very significant nonmetallurgical applications for bauxite-based and -sourced materials. These specialty applications include such critical industrial uses as abrasives, cements, chemicals, and refractories. Bauxite used in producing end products for these and other specialty applications must meet more stringent compositional and physical requirements than the crude ore commonly employed for aluminum production. Although there are substantial bauxite resources in the world, premium-grade bauxite ores suitable for use in these special niche markets have, over time, been limited to a few principal sources, such as China and Guyana. Precluding any major disruptions within these leading producer nations, adequate supplies of nonmetallurgical-grade bauxite are expected to be available to satisfy worldwide demand well into the next century. Now, as in the future, it is presumed that basic raw material costs will remain the determining factor controlling the economic competitiveness of bauxite-based products in the diverse and extremely competitive industrial minerals sector of the international marketplace. Furthermore, there appears to be an increasing trend toward supplying alumina (Al_2O_3), the refined form of bauxite, to meet ever more demanding high-end requirements in the world's nonmetallurgical markets. Under these circumstances, metallurgical-grade bauxite is being increasingly refined into specialty-grade alumina in production facilities that have been specifically modified to produce high-purity alumina for these rapidly expanding markets.

Bauxite is a naturally occurring, heterogeneous weathering product composed primarily of one or more aluminum hydroxide minerals, plus various mixtures of silica (SiO_2), iron oxide (Fe_2O_3), titania (TiO_2), aluminosilicate (clay, etc.), and other impurities in minor or trace amounts (Shaffer 1975, 1983; Patterson et al. 1986). The principal aluminum hydroxide minerals found in varying proportions within bauxite are gibbsite, $\text{Al}(\text{OH})_3$, and the polymorphs boehmite and diasporite, both $\text{AlO}(\text{OH})$. Table 1 gives selected properties of these principal bauxite minerals.

Bauxite is typically classified according to its intended commercial application: abrasive, chemical, metallurgical, refractory, and so forth (Andrews 1984; Hill 1994). Of all bauxite mined, approximately 85% is ultimately converted into aluminum metal; an additional 10% goes to nonmetal uses, such as various forms of alumina, the oxide of aluminum; and the remaining 5% goes to nonmetallurgical-grade bauxite applications (Figure 1). As

a result, the bulk of bauxite produced in the world is currently used as feed for manufacturing alumina via the wet-chemical caustic-leach method commonly known as the Bayer process. Subsequently, the majority of the resulting alumina is in turn employed as the feedstock for the production of aluminum metal by the electrolytic reduction of alumina in a molten bath of natural or synthetic cryolite (Na_3AlF_6). This is called the Hall-Héroult process. Depending on the grade and mineralogy of the bauxite used, the industry standard is that it takes approximately 4–6 t of dried bauxite to produce 2 t of alumina, which in turn yields 1 t of aluminum metal. In current market terms, the approximate value for 0.45 kg (1 lb) of each of these aluminum industry products, in U.S. dollars, is as follows: \$0.01 for metallurgical-grade bauxite, \$0.10 for alumina, and \$0.75 for primary aluminum metal. It should be noted here that, within the industry, the term *metallurgical grade* refers to bauxite conventionally used to produce alumina via the Bayer process and thus is primarily for aluminum production.

Beyond this use of bauxite—to produce primary aluminum metal—lies the critical area of nonmetallurgical or specialty applications that quantitatively comprise about 5% of total worldwide crude ore production. Precise figures on worldwide bauxite production and consumption levels within nonmetallurgical markets are not commonly available on a systematic or routine basis for collection and analysis. It is currently accepted, however, that the principal industrial end uses for nonmetallurgical-grade bauxite, ranked in order of total market value, are in the refractories and abrasives fields. In addition, the cement, chemical, and steel industries also consume significant quantities of bauxite for other industrial applications (Clarke 1977; Harben and Dickson 1983; Benbow 1988; Bolger 1997; Crossley 2001; Taylor 2003c). Furthermore, a wide variety of high-quality abrasive, ceramic, chemical, and refractory products are also produced directly from bauxite-derived, specialty-grade Bayer process alumina (Figure 1). This recently growing and expanding group of high-quality, high-end products includes

- Aluminum chemicals (e.g., aluminum fluoride, aluminum sulfate, and sodium aluminate)
- Flame retardants, fillers, and pigments for various paint, paper, plastic, and polymer products
- Activated aluminas for adsorbents, desiccants, catalysts, and catalyst supports
- Calcined aluminas for abrasives, ceramics, and refractories

Table 1. Properties of major bauxite minerals

Chemical Composition	Gibbsite, $\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$	Boehmite, $\text{AlO}(\text{OH})$ or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$	Diaspore, $\text{AlO}(\text{OH})$ or $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$
Al_2O_3 content, wt %	65.35	84.97	84.98
Combined hydroxyl (OH) group content, wt %	34.65	15.03	15.02
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Hardness, Mohs scale	2.2–3.5	3.5–5.0	6.5–7.0
Specific gravity	2.3–2.4	3.01–3.06	3.3–3.5

Source: Shaffer 1983; Patterson et al. 1986.

* Diaspore differs from boehmite by having a more closely packed and tightly bonded atomic structure.

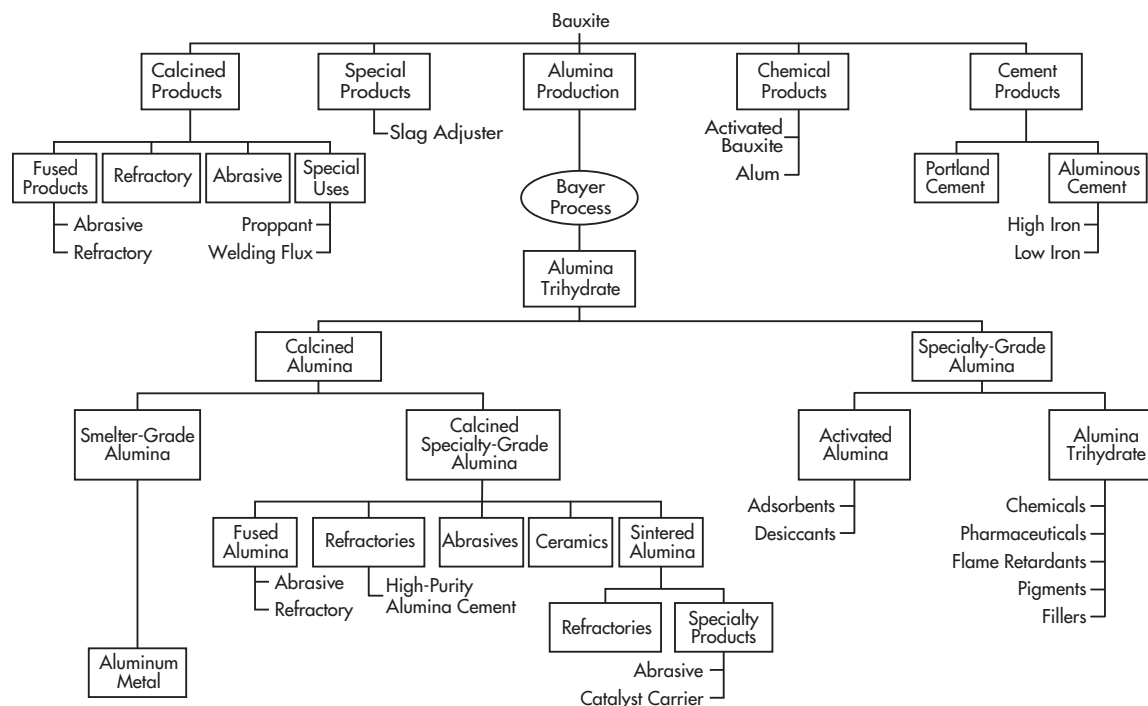


Figure 1. Aluminum industry flow diagram

- Hard-burned (sintered) calcined aluminas to produce tabular alumina, principally for high-performance refractory materials
- Fused aluminas, mainly for abrasives and refractories

This generalized aluminum industry flow diagram, from bauxite ore through alumina production to aluminum metal, gives a broad overview of the numerous products and end uses that are derived from bauxite.

The rock name *bauxite* was first used in 1845 for an earthy, red rock that had been discovered in 1821 by Pierre Berthier, a French chemist, close to the small village of Les Baux de Provence in southern France. Berthier's initial data suggested that this material was an alumina hydrate with two molecules of water. It was subsequently determined by thermal analysis, however, that the substance was a mixture of monohydrate and trihydrate minerals, as well as minor amounts of iron oxides, clays, and fine-crystalline silica. Diaspore had been discovered in 1801 and gibbsite in 1822. The rock name was, however, retained for this impure mixture of aluminous minerals. When the name of the village was changed to Les Baux around 1885, Sainte Claire De ville suggested that the

rock name should reflect this, and it was changed to the term known today—bauxite (Bracewell 1962; Regnier 1988).

In 2002, the most recent year for which complete annual production data are available, 22 countries reported bauxite mine production, and total world production amounted to 144 Mt of bauxite. This was an increase of 5% over 2001 production. The U.S. Geological Survey (USGS) estimates the 2003 total world bauxite production, from a similar number of producing nations, as essentially unchanged from that for 2002. Australia, Guinea, Jamaica, Brazil, and China, in order of volume, accounted for slightly more than 75% of the total bauxite mined during 2002, with a similar volume projected for 2003 (Plunkert 2004). In terms of nonmetallurgical-grade bauxite production, the principal sources of supply presently are very limited and comprise only a handful of possible source nations; that is, abrasive grade: Australia, China, Greece, Guinea, Guyana, and Italy; and refractory grade—Brazil, China, and Guyana. In addition, with the current world bauxite production at the 144-Mt level, the size of the total world nonmetallurgical bauxite sector is estimated at 7.2 Mtpy.

Total known world reserves for all types of bauxite are sufficient to meet cumulative world aluminum metal demand well into the next century. Although bauxite reserves are known to occur in as many as 50 different countries, nearly 90% of the reserves occur in only a dozen countries. The sheer magnitude of these reserves (23 billion t) is sufficient to ensure a readily accessible supply for the future (Table 2).

Past estimates of world bauxite reserves were about 1 billion t in 1945, almost 3 billion t by 1955, nearly 6 billion t in 1965, about 17 billion t in 1975, approximately 21 billion t by 1985, and roughly 23 billion t in 1995. It is expected that in 2005 the estimate of total world bauxite reserves will remain near or be slightly above the 1995 level of 23 billion t. Currently, Guinea, with 7.4 billion t of bauxite reserves, and Australia, with 4.4 billion t, together possess approximately one-half of the world's known reserves. Growth in reserves has more or less paralleled the expansion of world bauxite production capacity. Although major new discoveries are the primary factor in reserve increases, production economies resulting from technological advances and large-scale operations have also permitted the inclusion of lower grade bauxite previously considered subeconomic. In the early 1990s, it was reported that there were at least 211 known bauxite deposits in the world containing a minimum of 1 Mt of reserves (Roullier 1990; Bárdossy and Bourke 1993). Considering the added probability of discovering additional bauxite deposits, plus the likely possibility of employing lower grade bauxitic materials and other alternative sources of alumina, resources for the production of aluminum metal remain adequate to satisfy demand well into the future. The case is not quite as compelling for nonmetallurgical grades of bauxite, which normally must meet very rigorous quality requirements and are supplied from a markedly smaller number of worldwide sources. Even so, precluding any major disruptions within the small number of current producer nations, adequate reserves of nonmetallurgical-grade bauxite are available to satisfy probable future worldwide industrial demand (Table 2).

The annual world "in place" nonmetallurgical-grade bauxite mine production capacity at the end of 2003 was estimated at approximately 8.1 Mt, about 5% of the estimated total worldwide crude bauxite production capacity (Table 3).

Table 4 lists the principal nonmetallurgical-grade bauxite producers of the world for 2003.

GEOLOGY

Aluminum is the earth's most abundant metallic element, making up approximately 8% of the planet's crust; it is present in virtually every common rock type. Consequently, the derivation of bauxite is extremely variable and includes a wide variety of source rocks. It is principally a weathering product formed as residual deposits at or near the earth's surface under tropical or subtropical weathering conditions. As such, bauxite is classified as a specific type of laterite, a highly weathered residual subsoil or material rich in secondary oxides of iron, aluminum, or both, nearly devoid of primary silicates, and commonly containing quartz and kaolin. The formation of laterite is the direct result of intense chemical weathering, or degradation, of preexisting rock units. When this weathered rock is enriched in iron oxides and hydroxides, it is termed *ferruginous laterite*. If, however, it is enriched in aluminum hydroxides, such as gibbsite, boehmite, or diaspore, it is termed *bauxite*. As might be expected, there is commonly a complete compositional continuum of these weathering products extending from ferruginous laterite, through aluminous laterite and bauxitic laterite to bauxite, depending on the amount of aluminum versus iron enrichment.

Table 2. World bauxite resources, January 2004, Mt*

	Reserves [†]	Reserve Base [†]
Australia	4,400	8,700
Brazil	1,900	2,500
China	700	2,300
Guinea	7,400	8,600
Guyana	700	900
India	770	1,400
Jamaica	2,000	2,500
Russia	200	250
Suriname	580	600
Venezuela	320	350
Other countries	4,300	5,000
World total[‡]	23,000	33,000

Source: USGS 2004.

* Total world resources: Bauxite resources are estimated to be 55 to 75 billion t, located in South America (33%), Africa (27%), Asia (17%), Oceania (13%), and elsewhere (10%).

[†] USGS resource/reserve definition.

[‡] Data may not add to totals shown because of independent rounding.

In the weathering process, aluminum is retained in aluminum hydroxide minerals while other constituents are leached from the parent rock. Throughout geologic time, conditions favorable for formation of bauxite existed in areas and geological periods that provided warm, wet climates with alternating wet and dry periods; aluminous parent rocks with high permeability and readily soluble minerals; good subsurface drainage; and long periods of tectonic stability which permitted deep weathering and preservation of residual land surfaces.

Bauxite has formed intermittently throughout most of geologic history, from the Precambrian to the present. This "bauxitization" process, and the preservation of its products, appears to have been more intense during certain periods than others and more than three-fourths of the world's bauxite resources occur in geologically young deposits. Moreover, most of these occurrences started to form in the late Tertiary or earlier, and continued to be enriched in aluminum throughout the Quaternary, with the conditions for their formation even persisting to the present. Throughout the Tertiary, conditions were particularly favorable for widespread laterization and the formation of many large, high-grade bauxite deposits. The deposits from this time tend to be predominately of gibbsitic composition with minor amounts of boehmite. During the Mesozoic, bauxite developed extensively on carbonate rocks in karst terrain predominately with boehmite and locally important diaspore, as well as minor gibbsite. Paleozoic bauxite deposits, mainly in the Devonian and Carboniferous periods, are more restricted and chiefly contain diaspore and boehmite minerals. A broad time relationship has been recognized with boehmite and diaspore tending to be more abundant in older bauxite deposits and gibbsite more dominant in the younger deposits. Commonly, diaspore is found to be far more abundant in Paleozoic bauxite than in more recent deposits, boehmite dominates in Mesozoic bauxite deposits, and gibbsite is the key mineral in Cenozoic deposits.

Mineralogy and Physical Properties

Although bauxite deposits contain a wide variety of minerals, most of the nonmetallurgical bauxite ores consist almost entirely of the aluminum hydroxide minerals, gibbsite, boehmite, and diaspore.

Table 3. Worldwide summary of metallurgical- and nonmetallurgical-grade bauxite mines (2003)

Region and Country	Number of Mining Operations	Total Year-End Metallurgical-Grade Capacity, <i>ktpy</i>	Total Year-End Nonmetallurgical-Grade Capacity, <i>ktpy</i>
North America and Caribbean			
United States	1		500*
Jamaica	5	13,400	
South America			
Brazil	9†	13,500	390
Guyana	3†	1,300	275
Suriname	2	4,700	
Venezuela	1	5,000	
Europe and Central Eurasia			
Albania	2†		0‡
Azerbaijan§	1	170	
Bosnia and Herzegovina	2†	0‡	10
Croatia	2†	0‡	10
France	2		200
Greece	5†	2,000	515
Hungary	2	1,000	
Italy	1		250
Kazakhstan	2	4,400	
Romania	1†	0‡	
Russia§	5	4,000	100
Serbia and Montenegro	1	630	
Turkey	1	300	
Africa			
Ghana	1	500	200
Guinea	3	15,800	100
Mozambique	1		9
Sierra Leone	1†	0‡	
Asia			
China	20–50†**	8,500	3,500
India	12	8,500	1,500
Indonesia	1	1,300	
Iran	1	400	
Malaysia	1		40
Pakistan	1		8
Oceania			
Australia	6	54,500	50
		139,900††	8,107

* Bauxitic clay mining operation.

† Includes idled mining operations.

‡ Temporarily idled capacity.

§ Includes mining operations producing materials that substitute for metallurgical-grade bauxite.

** Includes numerous small-scale nonmetallurgical mining operations.

†† Bauxite and bauxite equivalents.

(Table 1). Mixtures of gibbsite and boehmite are common in all types of bauxite, boehmite and diasporite less common, and gibbsite and diasporite rare. In this regard, some high-grade refractory bauxite consists solely of gibbsite with minor amounts of kaolin [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$]. The common impurities found in both metallurgical and nonmetallurgical bauxite are aluminosilicate (clays, etc.), quartz (SiO_2), hematite (Fe_2O_3), goethite [$\text{FeO}(\text{OH})$], rutile (TiO_2), and anatase (TiO_2). The most common high-alumina clay minerals associated with bauxite are the kaolin group of minerals; however, illite and chlorite occur in small amounts in some deposits. Hematite and goethite are the most abundant iron impurities in many

bauxites and the principal reason for the red and brown colors that are characteristic of countless bauxite deposits. They often occur as nodules, as concretions, and as finely disseminated forms intergrown with aluminous minerals. Aluminum substitution for iron in goethite results in the formation of aluminous goethite that is known to occur in various bauxite deposits, especially in Jamaica and Suriname. In fact, the amount of alumina present in the form of aluminum substitution within goethite can reach substantial amounts, as much as 5%–7% in Jamaican ores and 9%–25% in various Surinamese deposits. Magnetite [$(\text{Fe}, \text{Mg})\text{Fe}_2\text{O}_4$] and ilmenite (FeTiO_3), also occur in some bauxites, particularly those that are

Table 4. Principal nonmetallurgical-grade bauxite producers (2003)

Region and Country	Company	Mine Location	Estimated Total Year-End Nonmetallurgical-Grade Capacity, ktpy	Type of Nonmetallurgical-Grade Bauxite
North America				
United States	C-E Minerals/Imerys Group	Andersonville, Georgia	500	Refractory bauxitic clay/refractory grog
South America				
Brazil	Cia Brasileira de Bauxita	Paragominas, Pará	20	Refractory and abrasive
	Mineração Curimbaba Ltda.	Poços de Caldas, Minas Gerais	225	Abrasive, chemical, proppant, sintered product, and slag adjuster
Guyana	MSL Minerais S.A.	Caracuru, Pará	145*	Refractory, abrasive, and chemical
	Berbice Mining Enterprise Ltd. (Bermine)/Aroaima Mining Co.	Berbice—Kwakwani/Aroaima	175	Chemical and cement, refractory and abrasive capacity idled
	Linden Mining Enterprise Ltd. (Linmine)/Omai Bauxite Co.	Linden—Mackenzie/Kara	100	Refractory, abrasive, chemical, and cement
Europe				
Bosnia and Herzegovina	Energoinvest	Jajce and Bosanska Krupa	10†	Cement
Croatia	Istrian Bauxite Mines	Rovinj, Istrian Peninsula	10†	Cement
France	Mines et Minerais du Languedoc/Garrot-Chaillac S.A.	Bédarieux area, Hérault	80	Cement (reprocessed bauxite mine waste dump material)
	Sodicapei	Villeveyrac, Hérault	120	Cement
Greece	Hellenic Mining Enterprises S.A. (Elmin S.A.)	Ghiona and Oeta mountains—Lamia area	215	Abrasive, cement, and slag adjuster
	Silver & Baryte Ores Mining Co. S.A.	Ghiona and Parnasse mountains	300	Cement, abrasive, and slag adjuster
Italy	Sardabauxiti SpA	Olmedo, Sardinia	250	Cement, abrasive, and slag adjuster
Russia	Severnaya Onega	South of Archangelsk	100	Refractory: 5–20 ktpy Cement: 20–100 ktpy
Africa				
Ghana	Ghana Bauxite Co. Ltd.	Awaso/Sefwi Bekwai	200	Chemical grade—Variable output, depends on demand
Guinea	Compagnie des Bauxites de Guinée	Sangaredi, Bidikoum, and Silidara	60–100‡	Abrasive
Mozambique	E.C. Meikle Plc of Zimbabwe	Alumen and Morondo	9	Chemical
Asia				
China§	Dengfeng Clay Mine	Dengfeng, Henan	40	Calcined product
	Gongyi Refractories	Gongyi, Henan	40	Calcined product
	Guiyang Refractories	Guiyang, Guizhou	80**	Calcined product
	Guiyang Shawen Yindu Cement	Guiyang, Guizhou	40	Calcined product
	Guizhou Star Minerals (C-E Minerals j-v)	Guiyang, Guizhou	100	Calcined product
	Henan Bo'ai Refractories	Bo'ai, Henan	100**	Calcined product
	Henan Mianchi CalBaux	Mianchi, Henan	60**	Calcined product
	Henan Mines & Refractories	Zhengshou, Henan	200**	Calcined product
	Jie Xiu Bauxite Plant	Jie Xiu, Shanxi	35	Calcined product
	Jiaozuo Xizhangzhuang Clay	Jiaozuo, Henan	20	Calcined product
	Nanchaun Minerals Group Co. Ltd.	Nanchaun, Chongqing	150	Calcined product—Abrasive
	Qinyang Mines	Qinyang, Henan	20	Calcined product
	Shandong Boshan Bauxite	Zibo, Shandong	20	Calcined product
	Shandong Hongshan Bauxite	Zibo, Shandong	46	Calcined product
	Shandong Wangcun Bauxite	Zibo, Shandong	100	Calcined product
	Shanxi Yangquan Bauxite	Yangquan, Shanxi	220**	Calcined product
	Shanxi Yangquan Refractories	Yangquan, Shanxi	300**	Calcined product
	Xiaoyi Bauxite Plant	Xiaoyi, Shanxi	30–40	Calcined product
	Yuci	Yuci, Shanxi	<30	Calcined product
	India	Ashapura MineChem Ltd.	500	Cement, chemical, and abrasive
		Raigad (Western Ghats), Maharashtra; Kutch and Jamnagar, Gujarat		
	Gujarat Minerals	Kutch and Saurashtra, Gujarat	500	Abrasive, chemical, refractory, and cement
	Saurashtra Calcine Bauxite (SCABAL)	Western Ghats and Gujarat	500	Calcined and green product
Malaysia	Johore Mining & Stevedoring Co.	Pengerang, Johore	40	Cement, refractory, and chemical
Pakistan	Black Mountain Minerals	Manshera	8	Specialty product
Oceania				
Australia	Comalco	Weipa, Queensland	200	Abrasive and slag adjuster
	Alcan Gove PTY Ltd.	Gove, Northern Territory	300	Abrasive and cement

Note: j-v = Joint-venture company.

* Closure planned by end of 2003.

† Temporarily idled capacity.

‡ Abrasive-grade bauxite production discontinued at the end of 2001.

§ Numerous small-scale bauxite mining operations are not listed.

** Possible partial or total closure.

derived from mafic igneous rocks. The titanium minerals found in bauxite include the primary minerals ilmenite or rutile and titaniferous magnetite, and the secondary minerals anatase and leucosine (TiO_2) formed during weathering. Titaniferous hematite and sphene (CaTiSiO_5) have also been noted in some bauxite deposits (Patterson et al. 1986).

To be technically correct, it must be noted that the aluminum hydroxide minerals present in bauxite are true hydroxides and do not contain water of hydration, as frequently referred to in some older publications. Nevertheless, the commercial terms *trihydrate* and *monohydrate* are commonly used by industry to differentiate various types of bauxite (Table 1). Bauxite that is totally or nearly all gibbsite bearing is called a trihydrate ore; if boehmite or diasporite or mixtures of both are the dominant minerals, the bauxite is typically referred to as a monohydrate ore. If substantial amounts of both gibbsite and boehmite are present, the bauxite is commonly termed a "mixed ore" (Shaffer 1983).

Bauxite occurs in many different forms, and its physical properties, structure, and texture vary markedly between and within deposits. It may occur as botryoidal, brecciated, clayey, earthy, fine-grained to massive, nodular, platy, pisolitic or coarsely oolitic, saccharoidal, vermicular, or even vesicular forms. Additionally, the color of bauxite ranges widely, with the most common ones being shades of red and brown. In terms of other physical properties, the in-situ specific gravity of most bauxite is normally between 1.5–2.4, but some types have been found to be as high as 3.7. This wide range is principally the result of variations in porosity, amounts of iron-bearing minerals present, and types of bauxite minerals in the ore (Shaffer 1983; Patterson et al. 1986). With regard to hardness, diasporite usually has a greater hardness than either gibbsite or boehmite because of its tightly bonded and denser atomic structure.

Classification of Deposits

Bauxite deposits occur in an extremely wide variety of geologic circumstances and physical shape; consequently, many classifications have been proposed by geologists to describe the occurrence of bauxite. Bauxite deposits have been variously classified according to their chemical composition, geologic origin, mineral composition, texture, topographic position, underlying rock type, and mode of occurrence. Each of these classification schemes and several others that have been proposed based on other attributes have all added to the general knowledge of the world's bauxite deposits, and each has its own merits. The geology of bauxite deposits has been treated at great length by three excellent works to which readers are referred: Bárdossy 1982; Bárdossy and Aleva 1990; and Patterson et al. 1986.

A widely applied method of classification is to assign all bauxite to either karst or lateritic types or, as modified, to carbonate and silicate deposit types. Yet another classification system, which has also received wide acceptance, is based on the shapes and occurrences of bauxite deposits. A modification of this latter classification organizes the varied kinds of bauxite deposits into blanket, pocket, interlayered, and transported (detrital) deposit types (Figure 2).

Blanket deposits of bauxite and aluminous laterite occur at or near the earth's surface and consist of flat or nearly flat-lying layers of variable thickness and wide lateral extent (Figure 2A, B, C). Thickness may vary from 1 m or less to 40 m in special instances, although 4–6 m is the average. Laterally the layers may extend over an area covering many kilometers. The majority of these deposits are residual, having formed from underlying aluminosilicate-bearing rocks of varying types, and only a very few contain transported material. Overburden on these deposits may be absent or extend up

to 10 m in thickness. Large blanket deposits are known to occur in Australia, India, South America, and West Africa.

Pocket deposits occur principally as infillings of karst depressions formed on limestone and dolomite, but some are associated with other rock types (Figure 2D, E). They vary greatly in shape and volume. The size of these pocket deposit depressions may range in depth from less than 1.0 m to greater than 30 m. In some cases, the bauxite-filled depressions occur as isolated, independent bodies, while at other locations the depressions coalesce and contain large and extensive amounts of bauxite. They occur on the Caribbean Islands of Jamaica and Hispaniola, as well as across southern Europe.

Interlayered bauxite deposits occur as discontinuous beds and lenses interstratified in sedimentary or volcanic rocks, and in some cases, along the contact between igneous or metamorphic rocks and overlying younger units (Figure 2E, F). They normally formed at a weathering surface as one of the other types of bauxite deposits and subsequently were buried. Thus, they are mainly remnants of old residual blanket deposits that were covered by younger rocks, but they may also include transported bauxite that has been enclosed by sedimentary rocks. Interlayered bauxite deposits have been found in Brazil, China, Guyana, Russia, Suriname, the United States, and southern Europe.

Detrital bauxite deposits result from the accumulation and preservation of transported bauxite that has eroded from other deposits (Figure 2F). Examples of this type of deposit were known to occur in the now depleted bauxite mining areas of central Arkansas. Detrital deposits that overlie eroded aluminosilicate rocks have been termed Tikhvin-type deposits, named after a type locality in Russia, and are found at localities scattered throughout Eurasia and northern China.

Major Bauxite Provinces of the World

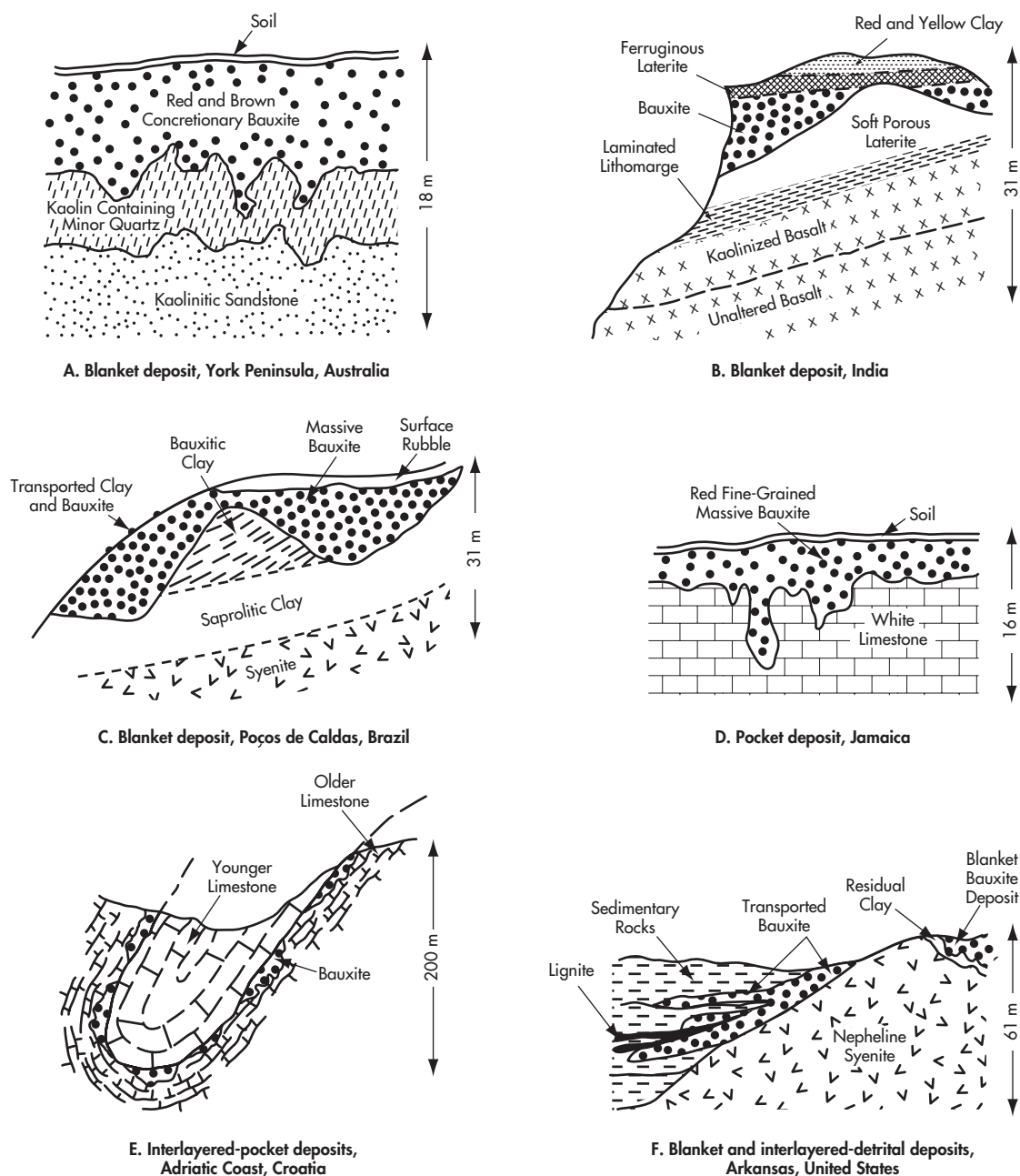
The major bauxite deposits of the world may be grouped into a series of provinces that are identified in the following sections and are shown in Figure 3.

As noted, bauxite is commonly divided or classified on its mode of occurrence and parent rock, as karst bauxite (deposits overlying weathered carbonate rocks) and lateritic bauxite (deposits derived from underlying aluminosilicate rocks). The first four provinces presented in this listing contain predominantly karst-type deposits, with the remaining four containing principally lateritic-type deposits. The areal extent and distribution of these bauxite provinces is as follows.

Caribbean Province

This province extends from Jamaica through Haiti and the Dominican Republic to Puerto Rico. The known deposits occur mainly as infillings in steep-walled depressions formed by the coalescence of typically uniform, vertical, cylindrical pipes that are located along intersecting faults in the limestone bedrock. Postdepositional faulting and erosion have resulted in the subsequent transport and deposition of the bauxite to form larger deposits. Metallurgical-grade bauxite is the principal bauxite produced from this province.

In Jamaica, the deposits fill sinkholes and channels and blanket uneven depressions in the karst surface of middle Tertiary age limestone. Individual ore bodies range from pockets containing a few hundred metric tons of bauxite to basins containing millions of metric tons. The soil overburden is only about 0.3–0.6 m thick. Jamaican bauxite in the plateau area is largely gibbsitic, with less than 3% boehmite. In contrast, the bauxite in the downfaulted blocks contains up to 20% boehmite, and aluminous goethite is the principal iron mineral. Ore grade is 45%–49% Al_2O_3 , 0.8%–8.0% SiO_2 , 17%–22% Fe_2O_3 , and 2.5% TiO_2 . Particle size varies from less than



Adapted from Patterson et al. 1986.

Figure 2. Typical occurrences of bauxite

1 to 40 μm . The bauxite deposits of the Dominican Republic and Haiti are similar in age, genesis, and grade, and are identified as a “Jamaican-type” or *terra rossa* bauxite, occurring as concentrations of soft, earthy material in karst depressions (Figure 2D).

Mediterranean Province

This province extends from Turkey through Greece, Albania, Serbia and Montenegro, Bosnia and Herzegovina, Croatia, Hungary,

Italy, and into France, with smaller associated deposits in Spain and Austria. The principal ore mineral is boehmite, although a few bauxite deposits contain a mixture of both boehmite and gibbsite—in an even smaller number, gibbsite is predominant (Hungary), and in others, significant amounts of diasporite are present (Turkey). This is the bauxite province in which bauxite mining and processing was first developed and put into production, and where bauxite is still mined by underground methods.

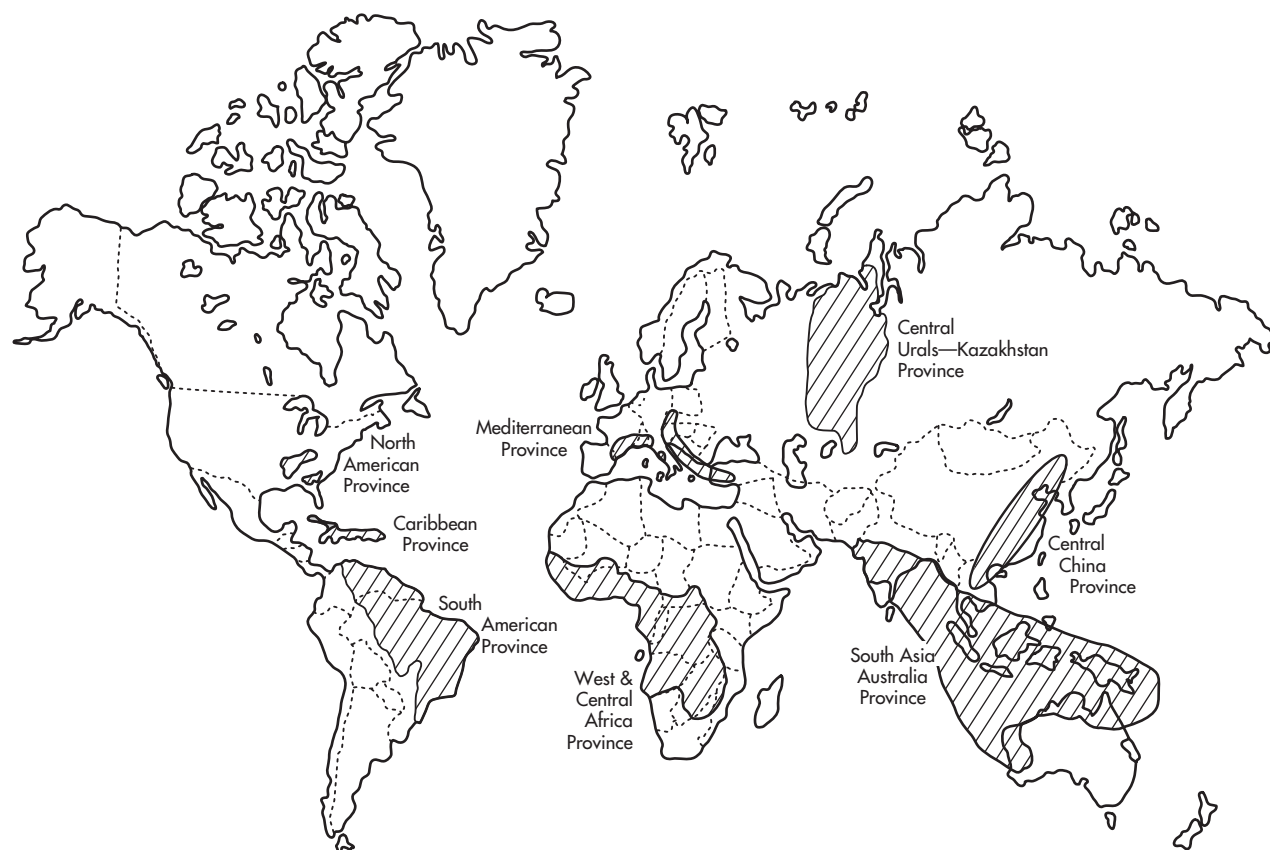


Figure 3. Major bauxite provinces

Many of the European deposits are associated with pockets and depressions in the karst weathering surface of Mesozoic carbonate beds that have been buried, folded, and faulted subsequent to the development of the bauxite (Figure 2E).

Central Urals—Kazakhstan Province

This province includes subsidiary occurrences in the Tikhvin area near Boksitogorsk, east of St. Petersburg on the northwestern margin of the Moscow Basin, and also areas in Ukraine. Deposits vary from bauxite horizons grading into bauxitic clay, and finally clay into a series of bauxite horizons in clay. The deposits in the Ural Mountains are mainly karst-type bauxites. The mineralogy varies from predominantly gibbsite in many areas of Kazakhstan to predominantly boehmite in the Urals. Much of the bauxite from this province is a high silica variety and low grade in comparison with ores from other parts of the world. The deposits in the Tikhvin district, the Urals, and Ukraine are relatively lower in silica content. Most of the mining in the Urals region is by underground methods, but open-pit mining methods are used in Kazakhstan and elsewhere.

China Province

This province extends from the Benxi-Fuxian region in Liaoning Province in northern China southwestward to Guangxi in southern China, and then into Vietnam. Most of the deposits occur in Carboniferous and Permian sedimentary rocks and consist chiefly of monohydrate-type bauxite, mainly diaspore, with significant amounts of boehmite, particularly in Guizhou Province and Vietnam. Virtually all the Chinese deposits either contain or are closely

associated with kaolinitic flint clay, which means that they have high reactive silica (aluminosilicate) levels. In fact, commercial definitions of what is actually termed bauxite differ between China and the rest of the world, with Chinese diasporic high-alumina clay being classified as “equivalent” to bauxite. China is noted for its nonmetallurgical-grade bauxite production, which is centered in Guizhou, Henan, Shandong, and Shanxi provinces.

African Province

This province comprises the Guinea and Cameroon shields. The Guinea Shield area extends from Guinea-Bissau to Ghana and northward into Burkina Faso and Mali. Deposits are part of an extensive area of laterization associated with Precambrian igneous basement terrain, and include a boehmite content of as much as 15%. The Cameroon Shield contains deposits developed on the extensively laterized terrain in this central African shield area. The continuation of this province extends southeastward from the South Atlantic coast across south-central Africa and beyond to Malawi and Mozambique.

In Guinea, the reported bauxite reserves are the largest known for any country in the world (Table 2) and mining is currently conducted in the Fria, Kindia, and Sangaredi districts. At the Fria deposit, the bauxite is composed of red gibbsitic earth with hard concretions, lumps, and crusts. Gibbsite is the principal bauxite mineral. The ore horizon is about 8–12 m thick and covered by a thin soil that is 0.1–0.2 m thick. Typical ore grade is 48% total Al_2O_3 , 21% Fe_2O_3 , and 2.5% SiO_2 , of which about 30% is very fine-grained quartz.

The D  b  l   deposit near Kindia is generally 6–8 m thick with a thin soil cover of between 0.3 and 0.5 m. Gibbsite is the principal ore mineral in the Kindia district. Typically, D  b  l   ore averages 48% Al_2O_3 and 1%–3% SiO_2 .

The large bauxite deposits of the Sangaredi district occur as lateritic caps on inland plateaus at elevations of about 275 m or more above sea level. The deposits have been dissected by stream drainage systems. Most of the bauxite is believed to have formed through weathering of Devonian or post-Devonian schists and sandstones. The thickness of the Sangaredi deposit averages more than 20 m and, before mining, exceeded 40 m in some locations. Overburden, where present, consists of thin topsoil. Typical ore contains 57%–60% Al_2O_3 , less than 1% SiO_2 , and 2%–4% Fe_2O_3 . When mining commenced in 1973, this was the richest single bauxite deposit known to exist anywhere in the world. The upper zone of the Sangaredi deposit contained only a few percent boehmite, but mining has now progressed to lower benches where the monohydrate content has increased to almost 10%. To extend the overall life of the mining project, operations have been expanded to the adjacent Bidikoum and Silidara ore bodies.

There are a number of large bauxite deposits known to be present in central Guinea, which remain undeveloped because of access and infrastructure issues. Extensive deposits occur in the Dabola and Tougu   districts with bauxites that reportedly contain 47%–52% Al_2O_3 and 3%–4% SiO_2 .

South Asia—Australian Province

This province consists of the Australian, Indian, and Southeast Asian subprovinces, described in the following paragraphs.

The Australian Subprovince includes Australia's major bauxite deposits of the Darling Range, Gove Peninsula, Mitchell Plateau, and Cape York Peninsula. These contain both in situ and transported materials that were deeply weathered during Cretaceous and Miocene times. The mineralogy is dominated by gibbsite, but a significant amount of boehmite is present.

The bauxite deposits of the Darling Range in Western Australia occur as a residual capping on Precambrian granite, gneiss, and intrusive crystalline rocks. They occur in a belt approximately 350 km long and 60 km wide located about 30 km inland and parallel to Australia's western coastline. A loose blanket of soil (0.3–0.6 m thick) mixed with loose pisolites covers the deposits. The upper portion of the ore is characterized by a ferruginous hardcap about 1.5 m in maximum thickness. The bauxite zone has an average thickness of about 4 m, but locally may be more than 12 m thick. The ore is characterized by a low alumina and high quartz-sand content; however, the reactive silica is typically less than 2%. General composition is 38%–46% Al_2O_3 , 10%–23% SiO_2 , 11%–16% Fe_2O_3 , and about 4% TiO_2 .

The Gove deposits in the Northern Territory are large lateritic-type bauxite deposits that underlie remnants of an undulating plateau of laterized sediments. Most deposits in the district are 3–4 m thick, but may range up to 10 m. The bauxite consists chiefly of gibbsite, but some boehmite is present, especially at shallow depths. Silica contents are low and occur mainly in kaolinite. A typical section of bauxite exposed by mining operations has 2 m of overburden, below which is 3 m of loose pisolitic bauxite, 1.5 m of cemented pisolitic bauxite, 1 m of tubular bauxite, and 5 m of ferruginous and siliceous barren laterite. The pisolites are usually about 5 mm in diameter. The normal grade for Gove bauxite is reported as 48.7% Al_2O_3 , 3.6% reactive silica, and 17% Fe_2O_3 (Shaffer 1983).

The major Weipa deposits in Queensland, Australia, occur in the upper portion of a flat lying to gently undulating laterite that

extends for more than 160 km along the western coastline of the Cape York Peninsula. The bauxite ranges in thickness from a few meters to nearly 10 m and is covered by a 0.3–1.0 m soil overburden (Figure 2A). Average ore thickness is about 4 m. The upper portion of the bauxite deposits contains spherical pisolites, which occur in a loose, reddish brown, silty sand matrix. The pisolites are normally 1–20 mm in diameter. Below the pisolitic bauxite there is a marked change to a zone of nodules and concretions usually high in iron and silica. The ore is a mixture of gibbsite and boehmite. The deposits are associated with underlying Tertiary kaolinitic sands, from which they were probably derived. The grade of the beneficiated bauxite is 53%–58% Al_2O_3 , 4%–7% SiO_2 , and 12% Fe_2O_3 .

Other significant Australian bauxite deposits are the extensive and undeveloped deposits of the Mitchell Plateau and nearby Cape Bougainville in the Kimberley region of Western Australia.

The Indian Subprovince includes the deposits of India in Andhra Pradesh, Bihar, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, and the western state of Gujarat. Smaller deposits occur in Jammu and Kashmir, with additional occurrences in nearby Pakistan. Deposits are usually of the blanket type (Figure 2B) and are part of a widely developed lateritic terrain. Gibbsite dominates in this subprovince.

The Southeast Asian Subprovince includes the bauxite deposits in Malaysia and Indonesia. Gibbsite dominates, with goethite and some clay minerals being the principal impurities. Both in situ and transported bauxite are present, the latter associated with sediments fringing nepheline syenite intrusions.

North American Province

This province consists of the Arkansas region and the Appalachian Valley and Ridge province, plus the Coastal Plain region of the southeastern United States. These deposits are generally gibbsitic in nature. It should be noted here that the United States is no longer a major producer of bauxite, and, in recent times, domestic mines have supplied less than 1% of the U.S. requirement for bauxite. The only active bauxite mines remaining in the United States are surface operations in the southeastern United States that produce bauxitic materials, a natural mixture of bauxitic clay and bauxite with a very low iron oxide content, used primarily for the production of alumina calcines.

South American Province

This province includes the bauxite deposits associated with the Atlantic Shield, the Central Brazilian Shield, the Guiana Shield, and the recent sediments of the Amazon synclinal basin. This province extends from Colombia through Venezuela, Guyana, Suriname, and French Guiana into Brazil. Throughout this province, laterization developed on the extensive erosion surface that overlies Precambrian basement rocks. The province contains major reserves of nonmetallurgical bauxite.

Bauxite deposits in Guyana and Suriname are scattered throughout a narrow belt extending along the contact between the Precambrian crystalline rocks of the Guiana Shield and the sedimentary beds of Tertiary or later age that form the Atlantic Ocean coastal plain, an area roughly paralleling the coastline and ranging from 24 to 110 km. These deposits usually rest on kaolinitic clay and range from exposed outcrops to ore bodies overlain by as much as 60 m of sand and clay, although the average overburden is about 20 m. Other deposits of bauxite and laterite occur in these countries at higher elevations on hill and plateau tops south of the coastal belt. The principal alumina mineral is gibbsite and the ore is high grade; typically 55%–60% Al_2O_3 , 2%–5% SiO_2 , and less than 3% Fe_2O_3 . Both countries have been exporters of abrasive- and refractory-grade

bauxite, with Guyana known throughout the world as a premier producer of nonmetallurgical-grade bauxite.

In the large blanket deposits scattered throughout the Amazon Basin of northern Brazil, bauxite occurs as a residual capping on dissected plateaus a few hundred meters above the Amazon or other nearby rivers. The ore in these deposits has normally developed as two distinct horizons on unconsolidated Tertiary sediments and is usually covered by 4–10 m of yellow plastic clay. The upper zone consists of a layer up to 1.5 m thick of nodular gibbsitic bauxite that is rich in iron oxide and underlain by a similar thickness of hard, blocky, ferruginous, and siliceous concretions in clay or ferruginous laterite. The lower ore zone consists of a 1- to 7-m layer of hard, massive bauxite with clay seams and an underlying mottled kaolin clay. Ore thickness averages about 5 m. The approximate grade after washing is 55% Al_2O_3 , 3.5% SiO_2 , and 11% Fe_2O_3 . The bauxite in northern Brazil and Venezuela is of the gibbsitic type and contains only minor amounts of boehmite. In addition, several small- to medium-size deposits of nonmetallurgical-grade bauxite are known to occur in the Almeirim district of the lower Amazon Basin, Brazil.

The bauxite occurrences described in these eight broad geographical provinces hold most of the known bauxite reserves of the world, but there are minor areas outside of these regions that contain other, less significant, bauxite deposits.

TECHNOLOGY

The exploration and development of nonmetallurgical-grade bauxite deposits generally involves the same basic techniques as those employed for metallurgical-grade deposits.

Exploration and Evaluation Techniques

In the search for bauxite, the exploration geologist primarily focuses on areas where geological evidence indicates that conditions were favorable at one time for the formation of laterite. Regions where the paleoclimate was tropical in the geological past are deemed prime target areas because, as previously stated, laterite and bauxite are believed to have formed under similar tropical or subtropical weathering conditions. In these tropical areas, landforms that have remained tectonically stable and have been preserved from erosional destruction are considered to be very good bauxite exploration targets. Such weathered landforms or erosion remnants include mesas, plateaus, peneplains, base-leveled areas, gently rolling areas, or gradual slopes—all of which have or did have adequate drainage to promote the formation of bauxite (Schellmann 1975; Shaffer 1975, 1983).

The first stage of planning a bauxite exploration program usually entails a thorough study of the regional geology, physiography, and any previous reports on exploration or mining operations within the area of interest. The initial regional appraisal should include a review of topographic maps (rarely available for remote tropical areas), aerial photographs, satellite imagery, and mosaics prepared from airborne side-looking radar (SLR) surveys. In the Amazon Basin of Brazil, where extensive cloud cover and dense rain forest canopy masks the underlying land surface, SLR methods have proven effective in revealing the hidden topography. In some cases, geobotanical techniques using true- or false-color air photos and satellite images have been used to identify vegetation types associated with aluminous laterites (Henderson, Penfield, and Grubbs 1984).

After specific target areas have been defined, reconnaissance by helicopter or fixed-wing aircraft can provide valuable accessibility and logistical support information. Surface prospecting for float samples in river drainage systems has long been a reliable

guide in the discovery of bauxite deposits. Furthermore, vertical channel sampling of indurated and resistant outcrops exposed in stream valleys can often furnish the first positive identification of the presence of bauxite in an exploration area. Detailed evaluation and development require drilling, pitting, or trenching to provide samples for chemical analysis. Accurately recovering those samples, however, can be a major problem because of the widely variable physical nature of bauxite ores. Drilling equipment appropriate for drilling the soft terra rossa-type bauxites of the Caribbean area is completely unsuited for testing the hard massive diasporic deposits of China or Turkey. To overcome this problem, a wide variety of test pitting and drilling techniques have been employed to evaluate bauxite deposits. The drilling methods have included various percussion and rotary drilling systems, such as churn or cable-tool drills, rotary auger drills, rotary core drills with diamond or tungsten carbide bits using air or water to lift the cuttings, and reverse circulation or vacuum rotary drills. Detailed surface mapping and topographic surveying are essential to document drill-collar and test-pit locations and elevations. In the case of nonmetallurgical bauxite targets, development drilling is usually more closely spaced in order to facilitate selective mining of this high-quality material.

It is difficult, if not impossible, to visually identify the minerals present in bauxite because of their extremely fine particle size. Consequently, sophisticated laboratory techniques are required for their qualitative and quantitative analyses. As a result, exploration and development samples are usually shipped to well-equipped laboratories for detailed analysis. Before the early 1970s, exploration samples were analyzed for iron oxide, silica, titania, and loss on ignition (LOI), and the alumina content was mathematically estimated by difference. This information was supplemented by analyzing composite samples for minor constituents. The most significant determinations for bauxite are its alumina and silica contents. The available or extractable alumina and reactive silica were determined by laboratory bomb (autoclave) digestion tests for metallurgical-grade bauxite. The experience from these tests provided the background for evaluating and predicting the behavior of a particular bauxite in a specific Bayer process refining plant. Both total alumina and available alumina (alumina recoverable by low- and high-temperature Bayer processes) were normally determined. In addition to total silica, it was important to analyze for reactive silica because the latter combines with alumina and soda in the Bayer process to form insoluble sodium aluminum silicates that are lost as red mud in an alumina plant's waste stream.

The current availability of x-ray diffraction and x-ray fluorescence spectroscopy equipment with integrated computer systems now permit the rapid qualitative and quantitative determination of the mineralogy and chemical composition of a sample, which serve as the basis for the determination of a bauxite's Bayer plant processing characteristics.

The determination of the suitability or value of a particular bauxite to produce smelter-grade or specialty alumina basically depends on the amount of bauxite, caustic soda (NaOH), and energy consumed to produce 1 t of alumina. As previously indicated, this is principally controlled by the amount of available alumina and reactive silica present in the bauxite. Reactive silica contents of more than 8% are usually uneconomical for treatment by the normal Bayer process because approximately 1.1 units (weight unit) of alumina and 1.2 units of soda are lost for each unit of reactive silica in the ore (McCawley and Baumgardner 1985). The "average bauxite usage rate" and the "average caustic soda usage rate" are parameters developed by the alumina industry to assess the feasibility of employing a specific ore for use as a metallurgical-grade bauxite/Bayer refinery

Table 5. Ideal characteristics for metallurgical-grade bauxite (Bayer plant feed)

Ideal Grade Characteristic	Impact if Inadequate
Low "reactive silica" (>1.5%–<3.0%) (kaolinite)	Increases caustic usage, a critical operating cost factor.
High extractable alumina (>49%)	Increases capital and operating costs for mining, processing, and especially mud disposal (larger equipment, bigger containment dams, and increased materials handling).
Low organic carbon	Increases operating costs by reducing plant efficiency and lowers product quality. Alternatively increases capital costs by adding organics removal facility.
Low boehmite (<3%)	Precludes low-temperature processing that can increase capital and operating costs.
Low goethite (tolerable in a high-temperature plant or with high hematite)	Slows clarification, lowers product quality, and increases alumina loss via mud circuit. Increases capital (equipment size) and operating costs (plant efficiency).
Low moisture (can create dust nuisance if too low)	Increases capital costs (larger evaporation facility), fuel consumption, and shipping costs.
Iron content (ideally >5%–<15%)	Low iron can lower product quality. High iron dilutes alumina content of bauxite.
Low quartz	Increases maintenance costs (pipe wear). Increases caustic usage in high-temperature plants.
Low impurities and trace elements	Can lower process efficiency (sulfur, chlorine, calcium) and metal quality (gallium, zinc, vanadium, phosphorus)
Soft and friable	Increases mining and grinding costs.
Dissolves readily	Increases capital (larger digestion equipment) and operating costs (reduces plant efficiency, longer residence times).
Low titania	Can increase caustic usage in high-temperature plants.
Low carbonates	Can require special processing.

Source: Bárdossy and Bourke 1993.

feedstock. In 1993, Bárdossy and Bourke presented a listing of 13 parameters they felt would define an "ideal" bauxite ore for use by a Bayer process refinery (Table 5). These are all critical factors that should be given detailed consideration during the determination of the economic viability of developing a bauxite deposit as a source to provide feed for a Bayer plant.

One important measure of the quality of a crude bauxite ore noted in Table 5 is the amount of organic carbon contaminants it contains; this is especially significant for the production of specialty-grade alumina products. During the Bayer processing of bauxite ores, organic carbon contaminants in the ores undergo degradation to sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) that builds up to equilibrium concentrations and remains in the recycled liquor of an alumina plant. In turn, this sodium oxalate in the leach liquors causes processing, disposal, and product quality problems during the production of alumina and, hence, must be removed from the leach solution when its concentration reaches the supersaturation point. Extensive amounts of research have been devoted to the best and most economical means for removal and disposal of sodium oxalate from Bayer refinery circuits.

Mining and Beneficiation

Bauxite mining is analogous to the mining or quarrying of other ores and industrial minerals, and does not employ any unusual or unique methods. Moreover, the mining of nonmetallurgical-grade bauxite consists of the same standard procedures and techniques that are customarily applied to the extraction of metallurgical-grade bauxite ores. In fact, in some cases, special quality grades of bauxite are selectively mined simultaneously with associated metallurgical ore-grade material. In these instances, the high-quality crude bauxite is stockpiled in separate holding areas to await the special handling and processing that is required for nonmetallurgical-grade raw materials (Everts 1984).

An industry survey conducted by the International Aluminium Institute found that mines producing metallurgical-grade

bauxite for export markets in 1998 generated about \$1.4 million in revenue per hectare mined, and a typical mining operation employed about 200 people for each million metric ton of bauxite produced (International Aluminium Institute 2000).

In recent years, 85%–90% of total world bauxite production has been by open-pit mining methods, with the remainder recovered from underground operations, principally in China, eastern and southern Europe, and Russia (Patterson et al. 1986; Martyn 1992). In open-pit operations, bauxite is normally extracted from strata typically 4–6 m thick under overburden that may range up to 10 m thick, covered by a thin layer of topsoil with its associated vegetation. At some nonmetallurgical mining sites, the overburden thickness may reach 70 m or more. In most instances, the topsoil is removed and stockpiled for use in reclamation programs at mine closure. Many ores are soft and sufficiently unconsolidated to be easily loosened and loaded by mechanized heavy equipment, while others consist of hard, dense bauxite requiring blasting to release and prepare the ore for recovery. Open-pit bauxite mining operations ordinarily employ various combinations of backhoes, bucket wheel excavators, bulldozers, draglines, power shovels, and scrapers for the stripping of overburden from the ore. In addition, draglines, front-end loaders, and power shovels are commonly used to excavate and load the crude ore. Loading is usually into haul trucks, or directly into rail cars or onto conveyor systems, for transport to bauxite processing facilities or stockpiles.

Depending on the nature of the bauxite, underground operations typically use a basic array of standard underground mining techniques, which include block caving combined with shrinkage stoping, sublevel stoping, top slicing, longwall, and room-and-pillar methods. Excessive water inflow is a significant problem at most of these mines, particularly in workings developed below the karst water table. In these cases, dewatering shafts are often drilled to lower the active water level at the mine site (Shaffer 1983).

Normally, the beneficiation or treatment of bauxite is typically limited to crushing, washing, and drying of the crude ore. After the

bauxite is mined, it is crushed and screened to remove fines, and in some instances is washed or wet screened to eliminate clay and silica contaminants. At a few special mining operations, heavy media separation techniques are employed to reduce the iron content or remove calcareous contaminants from the ore. Free moisture in crude bauxite, as mined, may range from 5% to 30%. Consequently, metallurgical and nonmetallurgical grades of bauxite that must be transported appreciable distances are normally dried before shipment. Drying facilitates the handling of some types of bauxite, and the degree to which a specific type of bauxite is dried depends in part on its individual handling and dusting characteristics. As indicated, because crude bauxite may contain substantial amounts of free moisture, drying results in savings on freight charges that may more than offset the drying costs. Bauxite from Guinea is usually dried to 3%–6% moisture, whereas Jamaican bauxite, because of its fine earthy nature and the potential to create dust problems, is shipped with about 15% moisture. Bauxite destined for use in abrasives and refractories is fired or calcined at 900°–1,650°C to remove both free moisture and chemically combined hydroxyl groups. Usually, abrasive grade material is calcined at around 1,100°C and refractory grade calcination is carried out at a higher temperature, generally about 1,650°C. For most other applications, the normal drying process entails heating crude bauxite in rotary drying kilns at about 300°–315°C, which removes most of the free moisture and produces dried bauxite ready for shipment. It is from this point that nonmetallurgical-grade bauxite undergoes special processing procedures to ensure it meets the strict market specifications demanded by individual end users.

Alumina Production

Practically all alumina produced commercially from bauxite is obtained via a process patented by Karl Josef Bayer in 1888. Although research on aluminum extraction from other mineral raw materials has continued for many years, this method has remained the standard for the industry. Bayer process refining of bauxite is the common starting point for the production of both smelter-grade and specialty aluminas (Figure 1). It employs a caustic leach of bauxite ore in a solution of sodium hydroxide (NaOH) at elevated temperature and pressure, followed by separation of the resulting sodium aluminate (NaAlO_2) solution and selective precipitation of the aluminum as aluminum hydroxide [$\text{Al}(\text{OH})_3$].

The actual processing conditions, such as the leach temperature, digestion holding time, and caustic concentration, as well as the operating costs, are greatly influenced by the type of bauxite to be processed. As a result, a Bayer alumina plant is designed to handle a specific type of ore and, without major plant modifications, ordinarily cannot efficiently process a bauxite that is markedly different from one that the refinery was originally designed to use. A listing of the preferred attributes sought in a metallurgical-grade bauxite and their impact on the efficiency of a Bayer refinery have been outlined in Table 5.

A Bayer process refinery is, in essence, a device for heating and cooling a large, continuously recirculating stream of caustic soda leach solution. Bauxite is added at the high-temperature point, red mud wastes are separated at an intermediate temperature, and alumina is precipitated at the low-temperature point in the cycle. The process is initiated by mixing crude or raw bauxite, which has been washed, and crushed or ground to 90% minus 10-mesh screen size with preheated, recycled, spent leach solution. Lime is added during this initial step to control the phosphorus content and to increase the solubility of alumina within the plant feed. The resulting slurry, containing 40%–50% solids, is pumped along with additional sodium hydroxide leach solution to pressurized digesters

where high-pressure steam is used to raise the temperature. Alumina and some of the silica are dissolved during this step, soluble sodium aluminate is formed, and a complex sodium aluminum silicate is precipitated from the process stream. Because these complex sodium aluminum silicate compounds represent a loss of both alumina and soda, a low reactive silica content is extremely desirable for metallurgical-grade bauxite ores.

Digestion, in digester vessels 3–4.5 m in diameter and up to about 30 m high, takes from 30 min to 8 hr, depending on the plant design and type of bauxite ore. Leaching temperatures may range from about 105°C to about 290°C, with most modern plants typically operating at between 200°C and 240°C, and corresponding pressures ranging from about 4,000 g/cm² to more than 15,000 g/cm². The lower temperature ranges are used for bauxite in which nearly all of the available alumina is present as gibbsite. The higher temperatures are required to digest bauxite having a large percentage of boehmite. Normally, at 140°C or less, only gibbsite and kaolin-group clay minerals are soluble in the caustic soda liquor, while at temperatures greater than 180°C, alumina present as monohydrate or trihydrate and also some alumina combined with clay minerals in the bauxite are recoverable and placed into solution. In terms of reactive silica, below 140°C only the silica in aluminosilicate minerals (clays, etc.) is soluble in the caustic soda solution, whereas above 180°C all or part of the free quartz present in the bauxite feed is also attacked by the liquor. Caustic concentration of the leach solution, expressed as grams per liter of caustic soda, usually ranges from approximately 170 to 400 gpl, depending on whether it is a low- or high-temperature Bayer refinery. The digestion of boehmitic bauxite requires stronger caustic concentrations, for longer holding times at higher pressures and temperatures, than gibbsitic ores (McCawley and Baumgardner 1985; Patterson et al. 1986).

The resulting slurry of sodium aluminate solution and insoluble red mud from the digesters is cooled to atmospheric boiling temperature, and a coarse sand waste fraction (mainly iron oxides and silica) is removed by gravity separators or wet cyclones. The fine solids in the red mud are then separated by decantation of the overflow in settling tanks measuring about 4.5 m in depth and 15 to 40 m in diameter. A flocculating agent such as starch is added to increase the settling rate of the red mud particles. These red mud wastes are then pumped to tailings ponds or containment areas for drying and final disposal. The pregnant overflow solution from these thickening tanks is further clarified by filtration and placed into precipitating tanks ranging in size from 8 to 9 m in diameter and up to 30 m in depth (McCawley and Baumgardner 1985).

In the precipitators, the clarified sodium aluminate-rich liquor is cooled until it becomes supersaturated at approximately 50°–70°C, then is seeded with fine crystals of aluminum hydroxide that initiate precipitation of alumina from the cycling flow of mechanically stirred liquor. The alumina is precipitated as alumina trihydrate, with the coarser fraction (typically >0.044 mm) separated by sedimentation or filtration, and washed (Taylor 2003a). The finer alumina fraction is recycled as nucleation seed for subsequent alumina crystallization, and the remaining spent leach solution containing some caustic soda is filtered and reconstituted and, together with the alumina remaining in solution, is recycled to the plant digesters. This regeneration of the soda lost in the process is ordinarily made up by adding caustic soda or soda ash (Na_2CO_3) and lime to the spent leach solution to bring it up to the appropriate caustic concentration before it is recycled. The majority of the filtered and washed alumina trihydrate is fired or calcined at between 1,000°C and 1,200°C to produce smelter-grade alumina for making aluminum metal. A smaller amount of the alumina, which is destined for some specialty markets, is calcined

Table 6. Chemical analysis of typical raw bauxite ore, by grade*

Grade	Major Oxides†			
	Al ₂ O ₃ ‡	SiO ₂	Fe ₂ O ₃	TiO ₂
Metallurgical§	50–55	0–15	5–30	0–6
Cement	45–55	Maximum 6	20–30	3
Abrasive	Minimum 55	Maximum 5	Maximum 6	Minimum 2.5
Chemical	Minimum 55–60	Maximum 5–18	Maximum 2	0–6
Refractory	Minimum 59–61	Maximum 1.5–5.5	Maximum 2	Maximum 2.5

Source: Everts 1984; Russell 1999.

* All values are in weight percent.

† Most of the remainder represent hydroxyl (OH) groups.

‡ Total alumina.

§ Bauxite conventionally used to produce alumina via the Bayer process (i.e., primarily for the production of aluminum metal).

at about 1,200°–1,400°C to convert the aluminum trihydrate into alpha alumina (α -Al₂O₃). The remaining portion of the washed alumina product may be left in trihydrate form for direct specialty alumina uses or it may be further purified and processed under controlled conditions to produce a variety of high-quality materials for uses other than metal production (Figure 1).

Over time, various modifications to the standard Bayer process have been attempted to resolve the problem of high silica levels in some bauxite ores. Bauxite containing 8%–15% reactive silica may be processed by either a soda-sinter process that is used directly on the high-silica bauxite feed or by a combination Bayer-sinter process applied to bauxite processing plant red mud waste streams. The largest numbers of modified processing plants in operation have been combination Bayer-sinter refineries where the high-silica bauxite is first subjected to a traditional Bayer caustic leach. The resulting red mud residue, containing sodium aluminum silicates, is sintered with limestone and soda ash. Then the sintered mass is leached with water to recover alumina and soda. In other instances where diasporic or other low-grade ores are encountered, as in China and Russia, a soda-sinter process is used to produce alumina. In this process, the low-grade bauxite is sintered with soda ash in rotary sintering kilns. This is followed by a water leach of the sinter residue and a carbon dioxide treatment of the resulting liquor to precipitate aluminum hydroxide. Additional desludging of the liquor is required, and this is achieved in a final autoclaving stage. Alumina produced by either the soda-sinter or combination process is relatively high-purity material and completely free from organic coloring matter and thus very white, so it commands a premium price in the specialty alumina market. In addition, the insoluble residue (brown mud) resulting from leaching the sintered materials has a composition somewhat similar to that of portland cement. The upper limit of reactive silica in bauxite for use by the combination Bayer-sinter process is about 15%. Both the soda-sinter and the combination Bayer-sinter processes are based on bauxite of marginal quality and require extensive amounts of energy, which make them unattractive candidates for widespread application around the world.

MARKETING

Commercial Applications

Nonmetallurgical-Grade Bauxite

The bauxite used for producing abrasive, chemical, and refractory products must meet much more rigid compositional requirements than the crude ore commonly used for aluminum metal production, as shown in Table 6.

Specifications for the premier grades of bauxite are based on the processing requirements and special properties required of their final commercial products. The natural chemical impurities that exist within these specialty-grade raw materials are not chemically removed from the ore during a refining procedure, as is the case with metallurgical-grade bauxite where impurities are eliminated through the Bayer process. Nonmetallurgical ores are used in an essentially unrefined chemical form, as a direct feedstock for the production of their ultimate end products.

The general chemical requirements for the principal classes of specialty-grade bauxite, as outlined in Table 6 and listed in terms of their increasing total alumina content within the raw or crude ore, are as follows

- Cement grade—moderate to moderately high alumina content, low silica. Iron oxide content may be high for production of some grades but should be low in grades requiring structural strength. Diaspore is preferred but not essential for this application.
- Abrasive grade—high alumina content, low silica, moderately low iron oxide, low titania. Iron is often added during the electric arc furnace fusion process to achieve correct iron oxide to silica ratios for formation of ferrosilicon slag.
- Chemical grade—high alumina content, should be gibbsitic ore, very low iron oxide and other acid-soluble oxides, silica (and clays) preferably low but not critical. The silica typically separates out as an insoluble residue during acid digestion; however, very high silica contents do substantially increase material handling costs. In some instances, this material is essentially equivalent to crude or green gibbsitic refractory-grade bauxite that has not been calcined.
- Refractory grade—high alumina content, low silica, low iron oxide, low titania, and very low alkalis.

As a side note, it must be pointed out that when analyzing statistics for these different raw materials and finished products (crude bauxite, dried bauxite, calcined product for abrasives and refractories, fused product, sintered product, etc.), they have different conversion factors from ore to product, and so are not equivalent on a weight-for-weight basis.

The principal nonmetallurgical-grade bauxite markets, in terms of value, are discussed in the following sections.

Refractory Applications

Refractories are commercial products created from heat-resistant materials that possess the capacity to maintain their form and

Table 7. Alumina-silica refractory products

Refractory Type	Raw Materials
Low-medium alumina (30%–50% Al ₂ O ₃)	Flint and semiflint fireclays, plastic and semiplastic fireclays, kaolin, and pyrophyllite
Medium-high alumina (50%–70% Al ₂ O ₃)	The andalusite-kyanite-sillimanite group of minerals, synthetic mullite, kaolin, and various bauxitic clays
High alumina (70%–90% Al ₂ O ₃)	Natural bauxite-based materials (calcined)
Extra-high alumina (90%–100% Al ₂ O ₃)	Calcined Bayer-process alumina, tabular alumina, and fused alumina

Table 8. Typical chemical compositions and physical properties of calcined refractory-grade bauxite^{††}

	Guyanese Bauxite	Chinese Grades of Bauxite			Brazilian Bauxite	Domestic High-Alumina Grades of Bauxite	
	RASC [‡]	85	80	75	Caracuru [§]	70	60
Alumina	89.10	87.50	84.50	78.60	85.00–86.00	70.50	60.50
Silica	6.50	6.00	6.50	14.50	9.60–10.20	25.30	35.80
Iron oxide	1.25	1.50	1.50	1.20	1.80–2.10	1.40	1.31
Titania	3.00	3.75	4.00	3.50	1.60–2.20	2.68	2.25
LOI	0.15	0.20	0.20	0.20	<0.10	na ^{**}	na
Bulk density	3.15	3.10	2.80	2.70	3.20–3.30	2.85	2.80
Pyrometric cone equivalent (PCE)	40+	38	38	37	na	39	37

* Standard producer product specifications. Grade based on alumina content.

† All analytical values except bulk density (g/cm³) and PCE are in weight percent.

‡ Refractory A-grade Super-Calcined.

§ Production ceased at end of 2003.

** na = not available.

strength when subjected to highly elevated temperatures amid varying extremes of mechanical stress and chemical attack by hot gases, liquids, or molten and semimolten substances. In the modern economies of the world, alumina is the primary ingredient for a significant portion of the products used in high-temperature industrial applications. Alumina-based refractories are crucial components in nearly all high-temperature metallurgical, cement, ceramic, glass, and petrochemical manufacturing processes of modern industry (Crookston and Fitzpatrick 1983; Benbow 1989; Ramsahoye 1991; O'Driscoll 2001). The alumina content of a particular refractory may range from 30% to 100%, depending on the exact nature of raw material from which it is made and its intended application. The total spectrum of alumina-silica (Al₂O₃ + SiO₂) refractory products is delineated in Table 7.

Aside from the lower alumina categories, which are based primarily on clay minerals, and those products composed of natural aluminum silicate minerals [andalusite (Al₂SiO₅), kyanite (Al₂SiO₅), or sillimanite (Al₂SiO₅)], refractories containing more than 45%–50% alumina rely heavily on bauxite as the origin of their contained aluminum oxide. In general, the ability of an alumina-based material to resist high temperature increases with increasing alumina content.

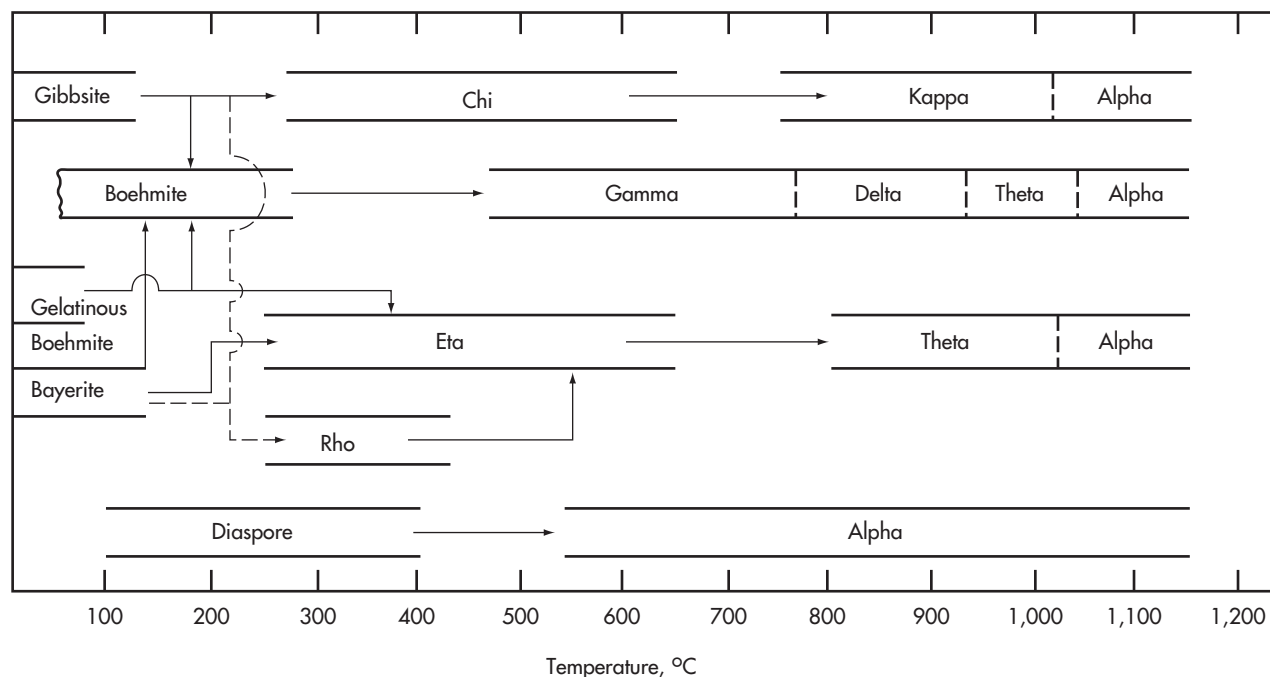
By value, refractory applications remain the premiere non-metal market for bauxite. Some refractories with extra-high alumina content are produced directly from the premium quality alumina derived by processing metallurgical-grade bauxite ores (Figure 1 and Table 7), but the majority of standard refractory products incorporate a calcined or fire-treated form of bauxite for their raw material base. These natural bauxitic materials provide users of refractory products with a reasonably priced, high-alumina feedstock that is readily available and in relatively abundant supply.

Bauxite suitable for use in refractory applications must meet very stringent physicochemical requirements. To satisfy the high-temperature operating demands of quality refractory products, a

high alumina, low iron oxide content bauxite, generally with a 2.5% maximum Fe₂O₃ content after calcination, is required. The alumina content, on a calcined basis, should be at least 86.5%, although it is often closer to 90% for the highest quality products. To keep the formation of low-melting-temperature glasses to a minimum, only trace amounts of alkalis and alkaline earths should be present in the raw ore (0.02%–0.60% on a calcined basis). Excessive titania has an adverse impact on the high-temperature properties of fired shapes, and the titania content commonly must be limited to a 4% maximum in the calcined product. The silica content ought to be low, usually below 7.5%, but levels exceeding 10% may be acceptable; however, it should be present principally within a natural clay mineral and not as free quartz (Wittmer 1982; Andrews 1984). The typical range of chemical compositions and related physical properties that various producers cite for their calcined refractory bauxite are characterized in Table 8.

The final market acceptance of the bauxite for a refractory use is contingent upon the physical and chemical qualities of the commercial end product into which it is to be included or combined. The dimensional stability of fired refractories relies principally on the conversion of the contained alumina and silica within refractory raw materials to the highly stable corundum (α -Al₂O₃) and mullite (3Al₂O₃•2SiO₂ or Al₆Si₂O₁₃) mineral phases of these oxides (Schneider, Seifert-Kraus, and Majdic 1982). Strict control of the feedstock grade and calcination process to achieve these physicochemical conversions, and to maximize the density of the materials on a consistent and unvarying basis, are crucial to the production of quality refractory products (Everts 1984).

A number of physical tests are customarily applied to calcined products to assess their suitability for use as refractory raw materials. Chief among them are the following: determination of PCE, a measure of the material's softening or deformation temperature; measurement of bulk density; and calculation of apparent porosity. These are critical measurements that enable a manufacturer to



Source: Wefers and Misra 1987.

Figure 4. Transformation sequence—aluminum hydroxide minerals to alpha alumina

appraise the potential capability of a raw material to endure the very harsh operating environments continually encountered by refractory products. Because PCE is based on an alumina standard (a PCE of 42 for pure alumina), materials with greater alumina contents may be expected to have higher PCE values. Ordinarily this is the case; however, the presence of alkalis or alkaline earths will significantly decrease the PCE value of a refractory material and the resultant effect will be poor creep resistance in the final refractory product. Bulk density, which imparts a number of critical physical properties to the finished refractory, has also been found to fluctuate with the alumina content of the calcine. A high bulk density normally improves product resistance to shrinkage, hot load strength, cold crushing strength, hot modulus of rupture, and abrasion resistance but, at the same time, decreases the thermal shock resistance (Wittmer 1982). Low porosity, which correlates in a given material with high density, is also a highly valued attribute. It lends a defense against the encroachment of liquids or gases in harsh corrosive operating environments, thereby reducing the rate of erosion sustained by the refractory and increasing its functional life.

The green or raw bauxite that is judged to be of refractory grade is usually fired at temperatures in the range of 1,400°–1,800°C to transform the material into a combined corundum and mullite product. This roasting or firing procedure is termed “calcination,” and it is conventionally carried out in rotary or vertical kilns with the processed material undergoing very pronounced chemical and physical changes. During this intense heating process, all free moisture and chemically combined hydroxyl groups are expelled from the bauxite. The silicate minerals, present principally as clays, sustain solid-state changes and are transformed into mullite. This transformation is accompanied by the release of silica, which in turn combines with the additional amounts of alumina present within the bauxite to form further amounts of mullite. The

alumina minerals present within the bauxite (bayerite, boehmite, diaspore, gelatinous boehmite, gibbsite) experience a series of marked changes following the loss of the ir combined hydroxyl groups and they develop into transitional aluminas or “phases” (chi, eta, gamma, rho, et c.) prior to reaching the high-temperature-derived, alpha-alumina-crystal form (Figure 4).

A portion of this contained alumina is consumed by reaction with the liberated silica, as indicated previously, to form mullite, and the remainder of the aluminum oxide forms corundum (alpha alumina, the stable form of anhydrous alumina). The original alumina content of the crude bauxite is a primary determinant in the resulting total alpha-alumina content of the calcined product, and crude ores with the highest alumina levels produce calcines with the greatest corundum content. Perhaps one of the most significant points to note in Figure 4 is the relatively low temperature at which diaspore converts directly to alpha alumina, starting just above 500°C. This low conversion temperature has major implications on the energy input requirements for the production of a calcined product from bauxite with a high diaspore content. The entire series of phase changes results in an overall densification of the refractory product, and these transformations must be carried to total completion to prevent further shrinkage of the material during subsequent processing and its final utilization within high-temperature operating environments. When the calcination process is completed, the finished product has an aluminum oxide content of 86.5%–89.0%; in some cases it may even reach 90%, and the material has become so solid that its density is 3.10 g/cm³ or greater (Table 8). The optimum bulk density for most commercial applications is 3.25 g/cm³. After calcination, the final product should have maximum density and minimum porosity. Typically, 2 t of crude ore is required to produce approximately 1 t of calcined bauxite. In addition, the LOI of the calcined product is customarily less than 0.5% (Tables 8 and 9).

Table 9. Comparative chemical analyses of calcined refractory-grade bauxite* †

		Guyanese Bauxite	Chinese Bauxite						
			Shaft-Calcined Grades			Rotary-Calcined Grades		Calcined Domestic Bauxite	
			RASC†	85	80	75	85	80	70
Alumina		89.0	87.8	80.9	75.1	89.8	82.0	70.9	66.7
Silica		5.13	5.54	14.5	16.3	4.08	10.1	21.4	27.8
Iron oxide	o	1.76	0.19	1.30	2.27	2.96	2.98	1.70	2.05
Titania		3.47	3.87	3.48	3.45	4.14	3.83	3.49	3.11
CaO		0.02	0.12	0.14	0.34	0.10	0.21	0.03	0.08
K ₂ O		0.006	0.08	0.12	0.18	0.56	0.24	0.01	0.06
Na ₂ O		ND§	0.03	0.04	0.05	0.06	0.07	ND§	0.06
MgO		0.007	0.09	0.09	0.10	0.10	0.08	0.04	0.07
LOI		0.10	0.00	0.08	0.00	0.00	0.00	0.17	0.03

Source: Wittmer 1982.

* Chemical analyses by U.S. Bureau of Mines, Albany Research Center, Albany, Oregon.

† All analytical values are in weight percent.

‡ Refractory A-grade Super-Calcined.

§ Not detected.

Following the calcination step and a subsequent cooling time, calcined refractory-grade bauxite is usually stored in enclosed areas for bulk shipment to its intended industrial markets. The calcined bauxite, which is normally in lump form at this stage, requires crushing, grinding, and sizing before its final use as a refractory product. At this point, maintaining a rigid control on the proportion of fines is of extreme importance because optimum refractory properties require a balanced particle size distribution. In its ultimate use as a refractory, the calcined bauxite product is mixed with binders and pressed, extruded, cast, and shaped into a variety of forms that are then dried and transferred to kilns for firing. The calcined refractory-grade bauxite is also used in unfired monolithic refractories (Shaffer 1983).

It should be noted here that another source of material suitable for use in refractory applications and products is the calcined bauxite used to produce brown fused alumina (Figure 1). Actually, it is estimated that 40%–50% of the brown fused alumina produced from calcined bauxite is used for refractories (O'Driscoll 2001). The chief advantage of fused alumina over other high-alumina refractory raw materials is its higher mechanical and chemical corrosion resistance. Currently, some degree of market growth is anticipated for brown fused alumina in the refractories sector.

Economic Considerations

The principal cost factors associated with the processing and producing calcined refractory-grade bauxite are acquisition of crude ore, labor wage rates, fuel charges, and transportation rates for the movement of the finished product to market. Because of the high energy requirements associated with the processing of these materials, the sensitivity of calcined materials to energy costs is of primary concern in the development and continued viability of refractory operations. This is demonstrated by the fact that the calcination phase of producing a quality high-alumina calcined bauxite (85%–90% Al₂O₃) requires approximately 13×10^6 Btu/t of product produced at a calcining temperature ranging from 1,700°C to 1,800°C (McMichael 1990). In addition, economy of scale plays an extremely crucial role in the cost of production for such bulk mining enterprises, and low costs are usually associated with the highly developed infrastructure and mechanization of large-scale metallurgical bauxite mining operations. This effectively imposes a limiting factor on the number of economically viable nonmetallurgical-grade deposits

capable of potentially providing refractory-grade raw materials for major international markets.

For refractory-grade bauxite, as with most industrial minerals, the basic commodity price is a crucial factor in the economics of development and continued maintenance of product markets. The trade-off between price and product performance is a primary determinant in the choice of refractory-grade bauxite, as opposed to various substitute materials in a variety of refractory applications. Examples of this price versus market tension are provided by synthetic mullite, created from kyanite and sillimanite, and refractory grogs, produced principally from kaolinitic clay, which constitute feasible product substitutes for medium-alumina-content bauxite-based refractories (Dickson 1982; McMichael 1990).

Sources of Supply

A limited number of bauxite ores have been found to meet the stringent physical and chemical specifications expected of refractory-grade bauxite, particularly within the very high-temperature fields encountered in most industrial applications. Consequently, the chief sources of refractory-grade bauxite traditionally have been limited to Guyana, followed by China, and more recently, Brazil. The highest quality materials have historically been supplied from South America, and, in particular, from mines in Guyana. As a result, because of its high quality, the RASC product from Guyana has frequently been used as a reference standard for comparison with calcined refractory bauxite from alternative sources of supply (Tables 8 and 9). In fact, until the late 1970s, refractory-grade bauxite from Guyana amounted to approximately 80% of the world's supply of this product. At that time, a combination of labor, technical, and mining difficulties within Guyana led to a severe market shortage that was only alleviated through the large-scale introduction of refractory raw materials from China into the North American and European markets. The world's refractory materials users accomplished this substitution in source of supply through some fundamental compromises and product adjustments. Chinese bauxite is composed primarily of diasporite [AlO(OH)], which has a greater hardness and, as a result, is more difficult to process than the Guyanese ore, which is composed principally of gibbsite [Al(OH)₃] with subordinate amounts of boehmite [AlO(OH)] (Clarke 1989). Moreover, unfired Chinese refractory bauxites contain greater amounts of alkalis and alkaline

Table 10. Mineralogical composition of calcined refractory-grade bauxite*

Phase	Guyana	China	Brazil
Corundum (alpha alumina)	~65–70	~70–80	55–65
Mullite	>15	<10	30–35
Glass	~12	~20	na†

Source: Schneider, Seifert-Kraus, and Majdic 1982; O'Driscoll 1995.

* All values are in weight percent.

† na = not available.

earths than most other refractory-grade bauxite, resulting in high glass levels within the final calcined product (Table 10).

Currently, China has continued to expand the level of its calcined refractory bauxite exports and strengthen its market position to the degree that it has become the primary supplier of these high-alumina refractory raw materials to the world. In the early 1990s, some diversification of this restricted supply structure began to occur, with the development and expansion of export-oriented refractory bauxite production capacity in Brazil. Initially, the first inroads into world markets by Brazilian refractory bauxite were made at the expense of Guyanese product. That is because both Brazilian and Guyanese refractory-grade bauxite are principally gibbsitic ore, whereas Chinese bauxite is predominately composed of diasporic and diasporic kaolin. By the late 1990s, the Brazilians had captured approximately 13% of the market, compared with a 17% share for the Guyanese, while the Chinese maintained their dominance with an estimated 70% share of the world's refractory bauxite market (Russell 1999). After Brazil, China, and Guyana, other current sources of refractory-grade bauxite are relatively minor. Greece produces some material that has been used largely for domestic and European markets. India has limited production capacities that, until recently, have principally supplied only domestic markets. Production from Suriname, the third largest supplier to the U.S. market in the early 1980s, ceased in 1983. Recently, further restructuring of the world's refractory bauxite producers occurred with the announcement that MSL Minerais S.A., one of Brazil's larger refractory bauxite producers and a major supplier to European markets, closed its operations in November–December of 2003 (Taylor 2003e). This eventually may provide a new marketing opportunity for Guyana and a chance to regain some of its previously lost market share.

Guyana. In Guyana, the source of refractory-grade bauxite over time has been the state-owned Guyana Mining Enterprise Ltd. (Guymine), which was responsible for mining and treating bauxite ore for the Bauxite Industry Development Company Ltd. (Bidco), the government's sales and marketing organization. In 1992, Guyana began restructuring the administration of its bauxite mining industry in an attempt to cut losses and lift productivity in order to eventually privatize its bauxite interests. The reorganization resulted in the formation of two new mining companies responsible for managing the operations that had previously been under the authority of Guymine: Linden Mining Enterprise Ltd. (Linmine) and Berbice Mining Enterprise Ltd. (Bermine). Both Linmine and Bermine are currently under government financial control (Anon. 2002; Taylor 2003e).

As noted, from the late 1970s, a major portion of all bauxite mined in Guyana was used as feed to produce calcined refractory-grade bauxite (Lachmansingh and Nooten 1977). During the 1990s, this percentage dropped and metallurgical-grade bauxite production once again gained a greater share of the country's total bauxite output. This was because a metallurgical-grade bauxite mine opened at

Aroaima on the Berbice River in 1991 and its dried ore was exported for the production of smelter-grade alumina. Refractory-grade bauxite production has been predominantly derived from what are now Linmine's mining operations near Linden on the Demerara River and in limited amounts from the mining operations in the Berbice River area of the Kwakwani district, operated by Bermine. The operations at the Linden location, approximately 100 km south of the nation's capital, Georgetown, have historically provided the majority of Guyana's RASC production (Hinds 1983, 1984). In 2001, Linmine reportedly had the capacity to produce 600,000 tpy of crude ore for nonmetallurgical purposes, and its processing plant's capacity was rated at approximately 300,000 tpy (Crossley 2001). Nevertheless, in recent years, actual production has fallen well below these former output levels (Anon. 2001).

China. Coincident with the supply difficulties that developed within Guyana in the late 1970s, China was gradually able to gain a major point of entry into the world's refractory-grade bauxite markets (Coope 1981; Lebauer 1982; Holroyd and McCracken 1993). In the early 1990s, total Chinese production of refractory-grade bauxite was estimated at approximately 2 Mtpy, with more than 700,000–800,000 tpy exported to international markets (Wang and Liu 1993). Accurate estimates of production levels are complicated, as stated earlier, by the fact that commercial definitions of what is actually classified as bauxite differ between China and the rest of the world. Currently, China is estimated to produce approximately 4.5 Mtpy of refractory clays and bauxite, with exports totaling 1.0–1.2 Mtpy of refractory-grade bauxite (Crossley 2001). The significant level of production and the associated market share that these Chinese refractories have attained since the market squeeze of the late 1970s was accomplished by overcoming a variety of product supply and quality problems.

Unlike Guyana, where a single uniform refractory bauxite product is produced from a few principal sources of ore, Chinese refractory-grade material is produced from many sources throughout the country and this has resulted in a wide variety of calcined refractory-grade bauxite products (Table 9). Guizhou, Henan, Shandong, and Shanxi provinces are the main producing regions of the country and each has a diverse number of independent centers for the calcination of refractory materials (Wang and Liu 1993; Zhong 1993; Crossley 2001). In turn, each calcining operation may have a variety of raw material sources or mining areas from which to draw crude ore. Nonetheless, the two leading refractory-grade producers are Guizhou and Shanxi provinces, with Guizhou providing bauxite of both higher alkalinity and higher density (O'Driscoll 2001). Generally, refractory-grade bauxite from southern China has a higher alkali content than ore from the northern part of the country. Beyond the issue of feedstock quality and variability is the additional complication created by the nature and quality of the calcining processes employed to produce Chinese refractory products. Traditional rudimentary natural draft shaft kilns are apparently used to produce a major portion of the Chinese calcined refractory-grade bauxite. These systems by their very design do not readily provide consistent and reliable quality control for the production of high-quality products that meet strict market specifications. In other calcining operations, antiquated batch "beehive" or round-type kilns, which are even more unreliable, provide a portion of the production. The introduction of modern rotary-type calcining equipment greatly improved the production situation. These systems normally produce a uniform, well-burned bauxite that commands a price superior to that of shaft- and round-kiln products. Despite this improvement in equipment, not all the quality problems were solved, because inadequately designed and operated combustion systems on some of the rotary kilns reportedly caused marked fluctuations in burning

rates, with an associated variability produced in the bulk density of the final calcined product.

In essence, all of these factors led to a very complicated quality control and product reliability problem for the consumers of Chinese abrasive- and refractory-grade products. To overcome these issues, in the mid-to-late 1990s, various Western merchants and consumers created several China-based subsidiaries or joint venture companies and set up processing facilities to supply new and more reliable nonmetallurgical bauxite products to the international markets. Consequently, in recent years, great strides have been made at improving the quality and reliability of Chinese nonmetallurgical-grade bauxite products. It was estimated in early 2003 that rotary kilns produced approximately 15% of China's refractory-grade bauxite (Crossley 2003b). Currently, many of the former state-owned enterprises have been privatized, and the Chinese government's efforts to end calcining operations with poor environmental or safety records, especially shaft and round kilns, has significantly reduced the previous overcapacity of the Chinese refractory bauxite industry. The closing of the polluting kilns, along with the government terminating operations at several illegal and unsafe mines, has increased the price of raw bauxite and reduced overall supply.

Brazil. The expanded development of refractory-grade bauxite deposits in Brazil during the mid-to-late 1980s offered the opportunity for further diversification in the worldwide sources of raw materials available to refractory consumers, especially in the North American and European markets. MSL Minerais S.A., a subsidiary of the private Brazilian industrial group CAEMI Mineração e Metalurgia S.A., entered the international market in the early 1990s with material from its Caracuru bauxite mine in the Jari region of the Amazon River basin, northern Brazil (Dickson and Harben 1986; Clarke 1989). MSL managed this mining operation in the Almeirim district of Pará state from 1985 until the end of 2003. In 1989, a new and modern 200,000 tpy beneficiation plant came on line to upgrade the run-of-mine ore. This development was in turn followed by the start-up in July 1990 of MSL's first 60,000 tpy rotary kiln to produce calcined refractory-grade bauxite. This refractory-grade bauxite production facility was expanded in August 1994 with the addition of a second 60,000 tpy rotary-calcining unit (O'Driscoll 1995). With facility streamlining and both kilns in operation, MSL Minerais upped its production capacity to nearly 150,000 tpy of calcined bauxite. Until the operation's closure at the end of 2003, Europe remained MSL's principal export market, with the United States and Japan taking minor amounts of its product (Taylor 2003e).

United States. Although U.S. sources of bauxite for alumina refineries exist and are being worked, with mining occurring in Andersonville, Georgia (Crossley 2001), the volume of bauxite required by U.S. industry demands that the importation of foreign-derived material be employed to meet market need. This is a fact that was made very evident during shortfall in production from Guyana in the late 1970s and early 1980s. The domestically produced bauxite is, in actuality, a natural mixture of bauxite and bauxitic clay, with a low to intermediate total alumina content, for which U.S. refractory and chemical manufacturers have developed a wide variety of applications (Dickson 1982). It occurs as bauxite and bauxitic clay lenses and pockets developed within the kaolin deposits of the Alabama and Georgia coastal plain. These deposits are usually small and only contain a few tens of thousands of metric tons of ore in each pocket or lens. This ore contains abundant silica, but is generally low in iron and exceptionally low in alkalis (Table 9).

Demand

The refractory industry is neither buoyant nor growing, and worldwide consumption of refractory-grade bauxite is currently esti-

mated to be between 950,000 tpy and 1.1 Mtpy (Russell 1999; Crossley 2001).

Throughout the 1980s, 1990s, and into the early part of the twenty-first century, the total annual consumption of calcined refractory-grade bauxite in the United States by the refractories industry ranged from a high of 524,000 t in 1988 to a low of 115,000 t in 2002, reported on a dry equivalent weight basis by the USGS (Figure 5). This general gradual downward trend parallels the decline in U.S. primary metal production, most notably, U.S. steel production.

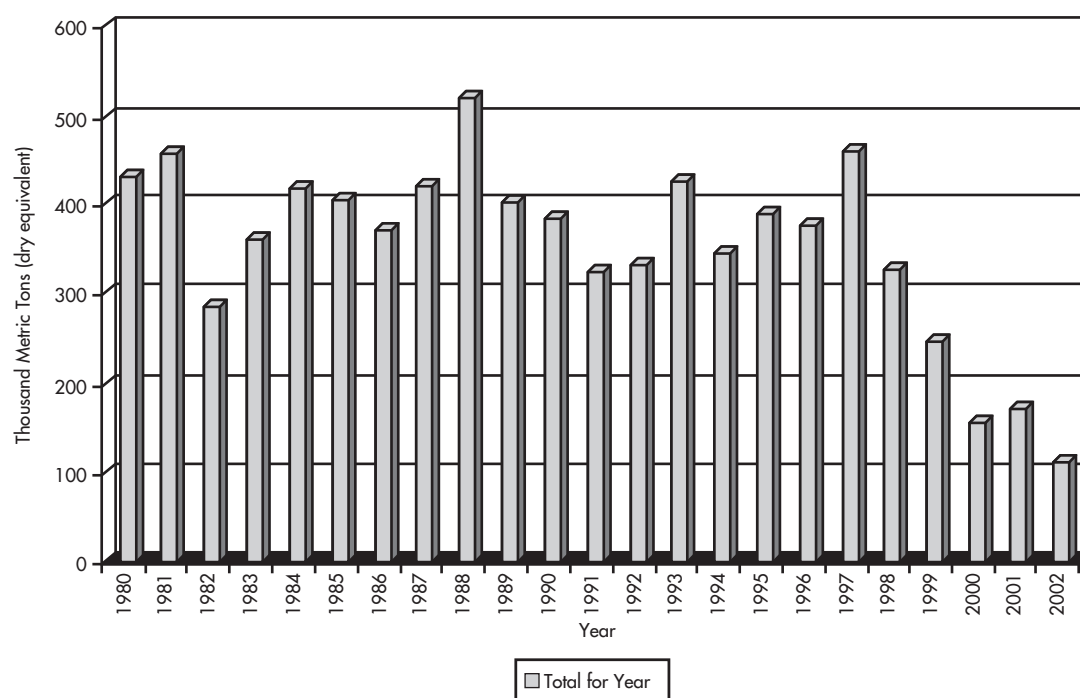
Calcined bauxite consumption in refractories fell from 460,000 t for 1981 to 286,000 t in the economic recession of 1982, but recovered strongly to total 524,000 t in 1988. Affected by an economic slowdown in the early 1990s, the U.S. consumption of calcined bauxite in refractories fell to 328,000 t in 1991, about 28% below the 1981 level of consumption. In 2002, the last year for which reported figures are presently available, the U.S. refractory industry consumption of calcined bauxite had fallen to 115,000 t, as noted, a recent all-time low.

Calcined refractory-grade bauxite has found wide application as a principal feedstock for the 60%–90% alumina content category of refractory shapes and specialty products (castables, plastics, and ramming mixes). This is largely because it is the lowest cost, high-alumina raw material that is readily available and in abundant supply in the world's industrial minerals markets. This usage by the refractories industry is closely tied to the production and consumption of primary metals—in particular, iron and steel. On a worldwide basis, it is estimated that the iron and steel industry consumes approximately 70% of all high-alumina refractories (Everts 1984; Ramsahoye 1991; Cole 2001).

Although the iron and steel industry remains the major market for refractory bauxite products, technological shifts over the last decade or more have resulted in the expanded use of higher performance specialty refractories, bringing about a marked decline in the consumption of refractories per ton of steel produced in the world. It has gone from 23–30 kg of refractories per ton of steel in 1970 to the current level of about 10 kg/t (Crossley 2001; Moore 2004). It is now noted, however, that this downward trend has apparently started to level off. These changes have occurred primarily because of the transition a way from traditional ingot casting methods of producing metal to a continuous casting means of steelmaking, with an accompanying increase in the employment of the basic oxygen furnace and the electric arc furnace within the ferrous metals industry. Although overall demand for refractories in general has been projected to decline, as unit consumption continues to fall within the iron and steel industry, the outlook for high-quality Bayer alumina-based refractories remains somewhat more optimistic (see Specialty-Grade Alumina section, this chapter). A preference has developed for higher performance refractories, such as high-alumina materials, and this has meant that these products have increased their market share over the more traditional lower alumina categories of refractories (fireclay, pyrophyllite [$\text{AlSi}_2\text{O}_5(\text{OH})$], etc.) (Benbow 1989; McMichael 1990).

The entire U.S. demand reportedly accounts for approximately 50% of the western world's refractory-grade bauxite consumption. In 1981, imported refractory-grade bauxite accounted for 65% of the refractory bauxite consumed in the United States. In 1987, imports had increased their market share to 84%. By 2002, imported refractory bauxite amounted to roughly 95% of U.S. refractory bauxite consumption.

Table 11 identifies foreign sources of calcined refractory-grade bauxite for U.S. industrial use.



Source: USBM 1981–1994; USGS 1995–2003.

Figure 5. U.S. refractory industry consumption of calcined bauxite

Table 11. U.S. imports of calcined refractory-grade bauxite, kt

Year	Source					Total*
	Brazil	China	Guyana	Suriname	Other	
1981	0	122	101	28	<0.5	251
1982	0	55	52	22	2	131
1983	0	51	66	0	0	117
1984	0	78	110	1	<0.5	190
1985	0	94†	102	<0.5	<0.5	196
1986	0	112	109	0	0	221
1987	0	163	107	0	0	270
1988	0	103	98	5	<0.5	206
1989	0	176	74	0	5	254
1990	0	126	84	0	<0.5	210
1991	0	104	69	0	7	180
1992	0	174	54	0	9	238
1993	16	66	53	0	0	135
1994	2	153	25	0	0	181
1995	3	131	71	0	17	223
1996	6	119	59	0	17	201
1997	17	84	62	0	17	180
1998	72	92	32	0	22	218
1999	33	75	42	0	17	167
2000	9	117	36	0	20	181
2001	10	59	18	0	4	90
2002	5	97	8	0	<0.5	110

Source: USBM 1981–1994; USGS 1995–2003.

* Data may not add to totals shown because of independent rounding.

† Excludes 75,496 calcined † purchased for the NDS.

Throughout the 1980s imports into the United States principally came from Guyana and China. As previously noted, shipments from Guyana have declined in recent years, while those from China have tended to increase and, currently, the Chinese shipments to the United States remain at higher levels than either Guyanese or Brazilian imports. In 1981, China accounted for 49% of U.S. calcined refractory-grade bauxite imports, Guyana 40%, and Suriname 11%. At the end of the decade, in 1990, China supplied 60% of these imports, Guyana provided 40%, and there were no imports from Suriname, where production of refractory bauxite ceased in 1983 (Dickson and Harben 1986). By 1994, China's share of U.S. calcined refractory-grade bauxite imports had risen to 85%, while Guyana's shipments fell to 14% and Brazil accounted for about 1% of the total. In 2002, China accounted for 88% of these imports, Guyana provided 7%, and Brazil supplied 5%.

Because refractory-grade bauxite plays a critical and strategic role in the economy of the United States, the U.S. government has maintained stocks of this raw material in the National Defense Stockpile (NDS) for use during times of international turmoil and possible supply or market disruption. At the close of the 2003 fiscal year, the Defense Logistics Agency (DLA), manager of the NDS, listed the calcined refractory-grade bauxite inventory as 42,400 metric calcined t (41,800 long calcined t). Under the new Department of Defense Annual Materials Plan (AMP), submitted to the U.S. Congress by the Defense National Stockpile Center, the DLA proposed the sale of up to 43,700 metric calcined t (43,000 long calcined t) of refractory-grade bauxite during the 2004 fiscal year (i.e., all of the current inventory). This or the remaining inventory, whichever is lower, is the maximum amount recommended for disposal during the fiscal year under the new AMP, and the actual level of sales will depend upon the prevailing market conditions. The sales are part of the continuing U.S. government effort, following the end of the Cold War, to eliminate the NDS program.

Prices

Calcined refractory-grade bauxite prices remained relatively stable during 2003, with only a slight increase in the prices of Chinese material imported into the United States in the latter half of the year. This developing trend of increasing Chinese prices continued throughout the first half of 2004. Approximate baseline international market prices for refractory-grade bauxite imported to U.S. markets from Brazil, China, and Guyana are published monthly by the trade journal *Industrial Minerals*. In mid-2004, the price range for bulk Brazilian refractory-grade bauxite was \$115–\$130/t, free on board (f.o.b.) Brazil. The price quotes for Chinese refractory-grade bauxite, minimum 87% Al_2O_3 , f.o.b. trimmed Chinese ports, were as follows: Shanxi, shaft lump, \$125–\$140/t; Shanxi, rotary lump, \$125–\$140/t; and Guizhou, rotary lump, \$110–\$120/t. The price range for Guyanese refractory-grade bauxite was \$160–\$170/t, f.o.b. barge U.S. Gulf Coast. Marketplace adjustments are regularly applied to these base prices, depending on grain size specifications, size of order, and fuel cost factors. Because Chinese bauxite accounts for such a large portion of the refractory-grade market, fluctuations in the pricing of Chinese material have a n immense effect in the entire industry. In 2003, bauxite exported from China was subject to a pay-as-you-go license fee of 230 Chinese yuan (\$27)/t (Crossley 2003b).

Abrasive Applications

Abrasives are materials used to smooth, roughen, polish, or clean surfaces, or simply to remove materials for the purpose of altering surface shape or dimensions. Abrasives generally achieve their objective through a rubbing action but also may work by impact.

Producing calcined abrasive-grade bauxite is equivalent to processing refractory-grade material, except it is calcined at lower temperatures. Some of this calcined bauxite is used directly as an inexpensive abrasive product, but by far the largest amount is used as the feedstock for the manufacture of brown fused alumina.

Fused aluminum oxide abrasive grain (artificial corundum) is produced by the electrofusion of either calcined bauxite or Bayer-process alumina (Figure 1). In both instances, fusion is accomplished in electric arc furnaces at temperatures in excess of 2,000°C, the only difference being the resulting end product. Calcined abrasive-grade bauxite provides the feedstock for the production of brown fused alumina (Figure 1). Brown fused alumina normally contains between 94% and 97% Al_2O_3 . Between 1.2 and 1.5 t of bauxite are required to produce 1 t of brown fused alumina (Crossley 2002a). Fusion of calcined, high-purity, Bayer-process alumina, on the other hand, produces white fused abrasive grain (Figure 1 and Specialty-Grade Alumina section). White fused alumina contains 99.5%–99.9% Al_2O_3 .

Abrasive-grade bauxite, the feedstock for brown fused alumina, is prepared from low-silica, low-alkali material that is calcined at temperatures of approximately 1,100°C. This is lower than the firing temperature normally used for refractory-grade bauxite but high enough to ensure that the calcined product does not readily reabsorb moisture to reform hydrated compounds. The calcined bauxite is then electrofused in the presence of ground coke and iron borings that aid the electromelting process and facilitate the removal of impurities by electromagnetic separation. The mix is usually calcined bauxite (80%), coke (5%), and iron borings (15%). Fusion takes place at temperatures above 2,000°C and usually requires 2,750–4,400 kW-hr of energy per metric ton of brown fused alumina. As indicated, the process requires the addition of special additives to the electric arc furnace to form a ferrosilicon slag that scavenges impurities. A source of carbon is needed to act as the reductant for the oxides of iron and silicon to form the slag, and coke is the preferred source. The iron content is adjusted by the addition of iron borings and the ferrosilicon usually contains about 16%–18% silicon. The magnetic susceptibility of ferrosilicon provides an efficient means of separating it and its associated impurities from the fused alumina product. This separation is achieved by passing the crushed artificial corundum through magnetic separators.

Both chemical and physical criteria are used to determine if a calcined bauxite meets the specifications required for the production of brown fused alumina. As in the case of refractory-grade bauxite, the most critical chemical components for abrasive-grade bauxite are alumina, silica, iron oxide, titania, alkalis, and moisture—as both free and chemically combined hydroxyl groups. To maximize the efficiency of the electrofusion process, the alumina content of bauxite used for abrasive applications should be as high as possible, and a minimum alumina content of 80% on a calcined basis is normally required for this application. Even though the mineralogy of the bauxite itself is not of major significance, gibbsitic bauxite generally comprises the major portion of the feedstock to this industry. Silica is the most significant impurity and very costly to remove. In general, the upper limit on the silica content in calcined abrasive-grade material is 5%. Unlike refractory-grade bauxite, the iron oxide content is not as critical, and it can even reduce the need for iron additives to promote ferrosilicon formation, provided that the iron oxide:silica ratio does not exceed 3:1, although it is reported that the optimum ratio for this grade is closer to a value of 2:1. Titania, which is invariably present in bauxite, ideally needs to be in the range from 2% to 4%. If the titania content is too low, the corundum crystal structure is affected and the toughness of the fused alumina grain is impaired. Alternatively, if

Table 12. Comparison of typical calcined abrasive-grade bauxite*

	Australia (Weipa)	China (Nanchuan)	China (Henan)	Italy	Guinea†	Guiana
Alumina	82–85	90–93	86–89	82–87	89–91	86–89
Silica	4.6–5.6	2.5–3.7	5.0–7.0	4.6–5.6	1.0–2.0	4.0–4.8
Iron oxide	5.5–7.0	0.4–0.9	1.2–2.0	5.5–7.0	4.0–5.0	3.5–5.0
Titania	3.1–3.7	3.0–3.5	3.4–4.0	3.1–3.7	3.8–4.5	3.0–4.0
CaO	0.01–0.02	0.14	0.1–0.2	0.1 maximum	0.01–0.02	0.02–0.03
K ₂ O + Na ₂ O + MgO	na‡	0.4–0.6	0.7–1.0	na	na	na
LOI	0.2–0.8	0.2–0.4	0.2	0.8 maximum	0.7–1.0	0.5–1.0
Bulk density (g/cm ³)	na	2.50–2.60	2.50–2.58	na	na	na

Source: Russell 1999; Crossley 2002a.

* All analytical values except bulk density are in weight percent.

† Production ceased in 2001.

‡ na = not available.

the titania content is above the 4% threshold level, it must be reduced to below 4% in the ferrosilicon phase, which is exceptionally costly. As with refractory-grade bauxite, low concentrations of alkalis are a requisite of abrasive-grade material in order to minimize the formation of a glass phase. This fact is of particular significance if the calcium oxide (CaO) content rises to more than 0.1%. The presence of moisture or chemically combined hydroxyl groups can be a potential hazard leading to the possible explosive generation of superheated steam. Therefore, the LOI of the calcined bauxite should not exceed 1%, and covered storage is commonly used for abrasive-grade products. Table 12 gives a comparison of the chemical composition of a variety of calcined abrasive-grade bauxites.

Besides these strict chemical specifications, a abrasive-grade bauxite also must meet certain physical standards. As previously mentioned, the calcined abrasive-grade feedstock should have been fired at temperatures high enough to ensure that the calcined material does not readily reabsorb moisture to reform hydrated compounds before it is fused in an electric arc furnace. Particle size is especially critical for abrasive production. The upper limit on particle size is 50 mm with the lower threshold set at a 100-mesh (0.150 mm) screen size. If the material is too coarse, complete calcination may not be achieved, and any material finer than 100 mesh is likely to create dusting problems, resulting in material losses during handling, transportation, and fusion.

Depending on the chemical composition of the bauxite feed, two main types of brown fused alumina are produced, regular and semifrable. The primary distinguishing factor is the amount of TiO₂ present, with the semifrable variety having the lower titania content (<2% TiO₂). In the production of the semifrable material, Bayer alumina is added to the process in order to reduce the levels of silicon and titanium impurities in the final brown fused alumina product (O'Driscoll 2003).

As indicated earlier, a significant portion of the world's current brown fused alumina production is used beyond the abrasive sector and a substantial amount finds use in refractory applications, as monolithics and shaped products (Figure 1). In the abrasives market, abrasive grain fused aluminas are used primarily in three basic ways: (1) loose form; (2) dispersed form glued to a flexible backing (coated abrasive product); and (3) bonded form comprising closely packed grains held together in a three-dimensional form by inorganic or organic bonds (bonded abrasive product). Coated and bonded products are the main abrasive markets for brown fused alumina.

Sources of Supply

The principal sources of abrasive-grade bauxite are Australia, China, Greece, Guyana, and Italy. Collectively, these countries supply the majority of the world's abrasive-grade bauxite. The world's production capacity for brown fused alumina is currently estimated at about 1 Mtpy (O'Driscoll 2001). Until 1987, Suriname was also an important supplier of abrasive-grade bauxite, especially to the United States, but has withdrawn from the market. Additionally, Guinea, an intermittent supplier of abrasive-grade bauxite, once again ceased production and dropped out of the market at the end of 2001 (Crossley 2002a). Over the last decade or so, as a result of aggressive product pricing, China has grown into the position of being a key supplier to the world's abrasive bauxite markets (Gasser 2002). China's existing production capacity for brown fused alumina is estimated at some 450,000–500,000 tpy. Reportedly, there are more than 60 producers, with most located in Guizhou and Henan provinces, but some are also located in Guangxi, Shanxi, and Sichuan. Current exports are on the order of 300,000 tpy, which have steadily risen since the mid-1990s (O'Driscoll 2001).

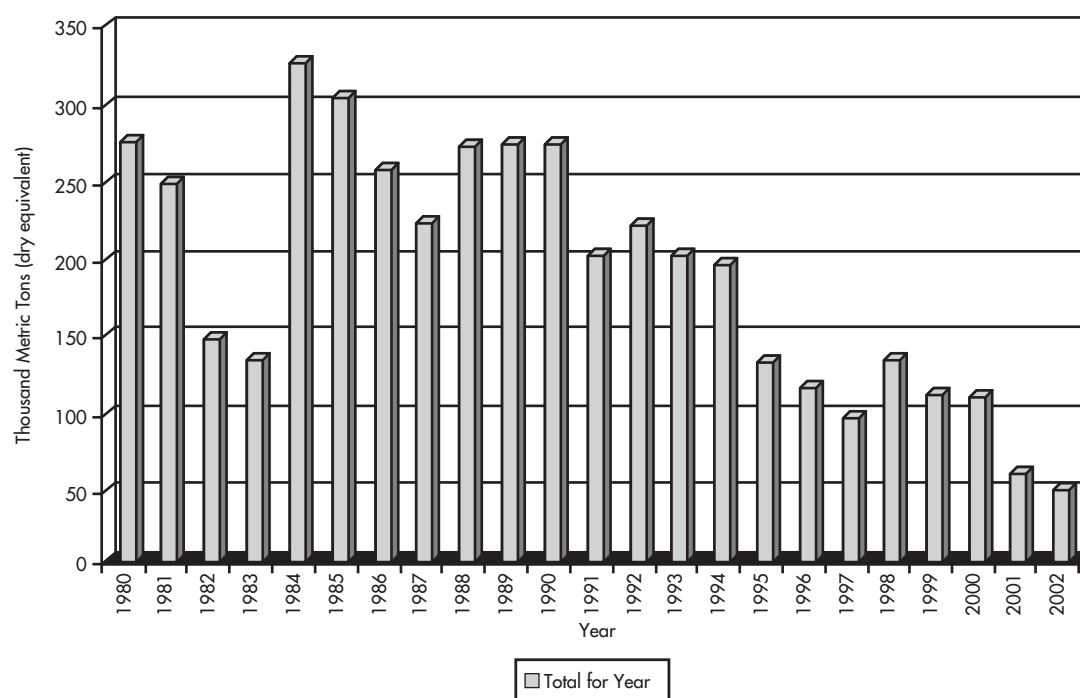
A possible new supplier to international markets may be India (Taylor 2003b). Although India currently imports 40%–60% of its calcined bauxite requirements from China, efforts have recently been made to market abrasive-grade material from the state of Gujarat to world markets. Nonetheless, a fundamental question still exists as to the quality and quantity of nonmetallurgical-grade bauxite that Indian sources will be eventually capable of supplying to export markets. It is noted that calcined nonmetallurgical-grade bauxite from India typically contains more iron, titania, and CaO than similar material from China and Guyana; however, the Indian bauxite is reported to be comparatively easier to grind (Crossley 2001).

Demand

Currently, worldwide demand for calcined abrasive-grade bauxite is estimated at approximately 800,000 tpy to 1 Mtpy (Russell 1999; Crossley 2001). Through the 1980s, 1990s, and into the twenty-first century, the total annual consumption of calcined abrasive-grade bauxite in the United States by the abrasives industry has ranged from a high of 328,000 t in 1984 to a low of 52,000 t in 2002, reported on a dry equivalent weight basis by the USGS (Figure 6).

Table 13 identifies foreign sources of calcined abrasive-grade bauxite destined for U.S. industrial users.

At this time, the overall consensus is that the future for bauxite-based abrasives is not particularly bright. It is a mature market that is



Source: USBM 1981–1994; USGS 1995–2003.

Figure 6. U.S. abrasive industry consumption of calcined bauxite

Table 13. U.S. imports of calcined nonrefractory-grade bauxite, kt

Year	Source						Total [*]
	Australia	Brazil	China	Guyana	Suriname	Other	
1981	15	0	12	35	6	<0.5	68
1982	10	0	18	17	14	<0.5	59
1983	8	0	14	22	47	1	92
1984	24	0	18	0	<0.5	<0.5	42
1985	23	0	41	4	<0.5	<0.5	69
1986	14	0	48	9	11	<0.5	83
1987	6	0	10	22	4	<0.5	43
1988	20	0	152	15	0	<0.5	188
1989	8	0	147	96	0	26	277
1990	14	0	173	52	0	108	348
1991	16	0	96	0	0	5	117
1992	8	0	88	0	0	13	108
1993	12	0	86	0	0	4	102
1994	7	24	137	0	0	0	168
1995	15	38	154	0	0	54	259
1996	<0.5	6	118	26	0	1	151
1997	23	17	125	0	0	25	190
1998	15	2	99	59	0	0	175
1999	22	1	94	12	0	2	132
2000	28	11	82	8	0	>0.5	129
2001	61	2	75	3	0	11	152
2002	47	5	67	8	0	<0.5	127

Source: USBM 1981–1994; USGS 1995–2003.

* Data may not add to totals shown because of independent rounding.

in broad decline, and demand for brown fused alumina in the abrasives sector has slowly declined but is now expected to remain static or drop at only a reduced rate in the future. In recent years, demand for abrasive-grade bauxite in North America and, to some extent, Europe, has decreased because of cheaper Chinese exports of brown fused alumina entering the international marketplace.

Prices

As with many industrial minerals, prices for abrasive-grade bauxite are difficult to trace because a huge amount depends on the precise chemical and physical specifications of the material. As a general tenet, abrasive-grade bauxite ores sell for around two-thirds the price of refractory-grade bauxite. The newsletter *Mineral Price-Watch* quoted the mid-2004 price range for abrasive-grade bauxite, f.o.b. China, as \$65–\$70/t (Anon. 2004b). Chinese abrasive-grade bauxite is typically the cheapest product available because it normally has a relatively high calcium oxide content.

Cement Applications

In terms of volume—metric tons of material used—cement applications have become the largest market for nonmetallurgical-grade bauxite. Two types of aluminous cement are produced directly from bauxite (low- and high-iron varieties; see Figure 1). Additionally, some bauxite is used to upgrade the alumina content of the raw materials used to produce ordinary portland cement.

In cement products, the higher the alumina content, the more rapid the hardening rate and the better the refractory properties. These factors have led to the added use of calcined alumina for the production of a special class of high-purity calcium aluminate cement (CAC). CAC is typically produced from high-purity limestone and calcined alumina in place of bauxite and contain 70%–80% Al_2O_3 , 18%–25% CaO , and less than 2% total silica, soda, magnesia (MgO), and iron oxide impurities. Normally, it is designated as high-grade CAC (>70% Al_2O_3).

High-Alumina Cement

Aluminous cement differs from standard portland cement, both in its chemical composition and its end uses. The raw materials employed to produce high-alumina cements are normally bauxite and limestone, whereas portland cement uses aluminous clay or shale rather than bauxite. As a consequence, high-alumina cement consists of calcium aluminates as opposed to aluminosilicates and it is often termed calcium aluminate cement. It is used principally in the castables sector of the monolithic refractories market. The calcium aluminate cements are commonly classified commercially by their alumina contents as low (CAC40), medium (CAC50), or high (CAC>70) grades, with color grading from dark gray to white. The low- and medium-grade varieties are derived from bauxite raw materials and are differentiated on their iron content, while the high-purity variety is only sourced from alumina feedstock. The most frequently used aluminous cements are in the 40%–50% Al_2O_3 range, which are described as the low-medium grade CAC, with the >70% CAC or higher purity grade CAC being used in lower volumes and more high-end applications. The typical range and associated differences in chemical compositions encountered within the low- and medium-grade calcium aluminate and portland cements are shown in Table 14. Please note that the high-purity calcium aluminate cements are not included in this table, only the low- and medium-alumina grades (CAC40 = high iron, CAC50 = low iron).

Concrete made with high-alumina cements is characterized by their rapid setting times, as short as 2–4 hours, with structural strength developed within 24 hours, as compared with conventional

Table 14. Comparative chemical analyses of high-alumina and portland cements*

	High-Alumina Cement		Portland Cement
	Low Iron (CAC50) [†]	High Iron (CAC40) [‡]	
Calcium oxide	34–40	30–40	58–67
Silica	4–6	3–6	19–26
Alumina	50–57	38–56	4–11
Iron oxide	1–3	10–18	2–5
Titania	0.5–2.5	0.5–2.0	0.5–1.0
Magnesia	0–1	0–1	0–5
Sulfur trioxide	0–1	0–1	0–2.5

Source: Andrews 1984.

* All values are in weight percent.

[†] Medium-grade calcium aluminate cement.

[‡] Low-grade calcium aluminate cement.

Table 15. Typical specifications of high-alumina cements

Parameter	High-Alumina Cement	
	Low Iron (CAC50) [*]	High Iron (CAC40) [†]
$\text{Al}_2\text{O}_3:\text{SiO}_2$	10:1 (minimum)	10:1 (minimum)
$\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$	20:1 (minimum)	2.0–2.5:1 (preferred)
$\text{Al}_2\text{O}_3:\text{TiO}_2$	16:1 (minimum)	na [‡]
Mineralogy	Not critical	Boehmite or diaspore
Free moisture	Preferred dry	5 wt % (preferred maximum)
Particle size	Not critical	50–100 mm

Source: Andrews 1984.

* Medium-grade calcium aluminate cement.

[†] Low-grade calcium aluminate cement.

[‡] na = not available.

portland cement-based concrete that may require several days to harden. In fact, the initial strength of CAC-based concrete after 1 day is proportionally the same as that for portland cement-based concrete after 28 days (MacZura 1992; O'Driscoll 2000).

Fundamentally, there are two principal types of high-alumina cement produced from bauxite feed: high and low iron, which are also termed low- (CAC40) and medium- (CAC50) grade calcium aluminate cements (Table 15). Both varieties can be used in castable refractories with operating temperatures up to 1,200°C. The high-iron type, often termed *Ciment Fondu*, when used in conjunction with a suitable aggregate such as a refractory grog, can be employed as a refractory cement and mortar that retains its integrity up to 1,300°C. These high-alumina cements are also resistant to chemical attack by corrosive agents (i.e., salt water, etc.).

Bauxites used in high-alumina or calcium aluminate cements range considerably in chemical composition. The primary chemical determinant affecting the selection of bauxite for use in high-alumina cement is the silica content, or, more precisely, the alumina-to-silica ratio. A high silica content hampers the rapid hardening property of the cement. This means the silica content must be controlled and a typical industry requirement is that the $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratio should be at least 10:1, which normally excludes bauxite containing more than 6% SiO_2 from use in high-alumina cements. For the low-iron compositions, it is common to specify an iron oxide content of less than 2.5%, whereas for the high-iron grade (*Ciment Fondu*), contents of 25% may be acceptable in certain applications,

although the norm lies in the 10%–18% range (Table 14). Iron contributes to the hardening properties and acts as a flux, but if present in excessive amounts, it may have adverse effects on the cement's refractoriness and overall strength.

The two main methods employed to produce high-alumina cement are the fusion and sintering techniques. In the fusion process, an oil-fired, L-shaped vertical shaft/reverberatory hearth kiln is normally used to produce the high-alumina cement product, whereas a rotary kiln is used to fire the bauxite and limestone raw materials in the sintering process. The production method used often dictates the physical requirements of the bauxite feedstock chosen by a cement producer. In processes using rotary kilns, where the bauxite is ground and mixed with limestone before sintering, particle size of the crude bauxite is of minor importance. On the other hand, the fusion method for manufacturing high-iron Ciment Fondu involves charging a mixture of coarse, lumpy, monohydrate-type bauxite (boehmite or diaspore) with limestone into a combination vertical shaft/reverberatory furnace where rising volatiles from the fusion hearth preheat the descending feed. The molten furnace discharge is cast into pigs that are subsequently ground and size classified to cement fineness. This operation is dependent on coarse feed (50–100 mm) to prevent channeling of the hot gases in the shaft furnace. As indicated, boehmite or diaspore is normally selected because of their low LOI, which results in lower levels of disintegration and thereby presents less interference with gas flow through the furnace feed. Economic concerns provide yet another impetus for selecting monohydrates, because they customarily have free and chemically combined hydroxyl contents of 15%–17%, compared with the normal 35%–40% for gibbsitic bauxite (Table 1). This has an obvious impact on the fuel requirements plus materials handling and transportation costs incurred by cement manufacturers.

The alumina content of low-iron type, high-alumina cements normally ranges from 50%–57% Al_2O_3 , which is slightly above the levels found in the high-iron, Ciment Fondu types but well below the levels found in high-purity CAC (CAC70–80) produced directly from alumina feed stock. Silica also can be tolerated in quantities similar to that permitted in the high iron-grade material, and typically is in the 4%–6% range (Table 14). The most striking difference in chemical composition between the low- and high-iron grades is in their iron oxide content. The maximum acceptable amount of Fe_2O_3 allowed in the low-iron type may reach 3%, although it is actually more commonly maximized at 2.5%. This translates in to a minimum $\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$ ratio of 20:1. The titania content is also of significance for this material, with a minimum $\text{Al}_2\text{O}_3:\text{TiO}_2$ requirement of 16:1. Although the high-iron grade is usually produced in oil-fired vertical shaft/reverberatory hearth furnaces, the low-iron type is ordinarily produced in rotary kilns or in a few instances by fusion in electric arc furnaces (Andrews 1984; O'Driscoll 2000). In this latter case, a product similar to Ciment Fondu is produced though usually lower in iron content ($\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$ usually greater than 20:1) and a finer-sized bauxite feed can be used to manufacture this product, with optimum results obtained using calcined bauxite.

Portland Cement

This is the most frequently used binder in the commercial production of concrete. The essential raw materials for portland cement are limestone and high-alumina clay or shale. In some cases, the alumina content of the clay or shale feedstock is too low for the formation of the required mineral phases during sintering of the cement and, therefore, bauxite is used to upgrade the feed. One of the parameters typically used to determine the suitability of the raw materials for this application is the SiO_2 -to- $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ ratio,

commonly known as the “silica modulus,” which in this case should ideally be in the range of 2.6–2.8 with the alumina content exceeding the iron oxide. The principal criterion for suitability is a high level of alumina content (Andrews 1984).

Beyond the use of bauxite to increase the alumina content within the raw materials employed to produce portland cement, there are several other compelling explanations why the cement industry has turned to bauxite as an additive in the manufacture of this product. By using low-silica bauxite, the industry is able to utilize low-grade, high-silica limestone that has previously been classified as subgrade material and in turn this has greatly increased the limestone reserves available for use as feed to the portland cement industry. Additionally, reduction in alkali content can be achieved by using a bauxite-based feed that in return permits a broader range of reactive aggregates to be incorporated into the final concrete mix. Besides these factors, other advantages include improved kiln control and increased product uniformity, improved materials handling, and a reduction in freight costs. Nevertheless, although chemically ideal for use in cement production, bauxite is usually prohibitively expensive and used only as an additive in portland cement, typically forming only 2%–3% of the raw mix, and not as a basic feedstock.

In addition to the previously mentioned cements, there are also two variants of portland cement, one known as blast furnace cement, which is derived from the aluminous slag produced as a coproduct of the iron industry, and the other based on fly ash wastes from coal power plants. The y are both significant competitors to bauxite's use as an additive to portland cement.

Demand

Worldwide use of bauxite in the cement industry is estimated at about 1.0–1.2 Mtpy (Russell 1999; Crossley 2001). This places the use of bauxite in cement at the top of the list of all nonmetallurgical markets, in terms of tonnage. The total global market for high-purity CAC is currently estimated to be 500,000–550,000 tpy, and is forecast to remain at these levels in the near future (Russell 1999; O'Driscoll 2004).

In 2001, the USGS started reporting the U.S. cement industry's annual consumption of bauxite, as reported on a dry equivalent unit basis. It was found that the cement industry consumed 268,000 t of bauxite in 2000, 302,000 t in 2001, and that the consumption level had risen to 324,000 t by the end of 2002. Although the markets for cement in Europe and North America are growing at moderate rates, demand is expected to substantially increase in Asia, especially in China, where consumption is expanding very rapidly in both the refractory and building materials markets.

Prices

There is a significant price differential between bauxite used for aluminous cement production and that for portland cement, with bauxite used in aluminous cement (55%–56% Al_2O_3) being at least double the price of bauxite for portland cement (Russell 1999). The difference is even greater between the high-end products, with CAC reportedly four or five times more expensive than portland cement (O'Driscoll 2000).

Chemical Applications

The bauxite used directly for chemical applications is very high quality material and, in some cases, is basically equivalent to crude or green gibbsitic refractory-grade bauxite that has not been calcined.

The most direct use of bauxite within the chemicals industry is in the production of aluminum sulfate [$\text{Al}_2(\text{SO}_4)_3$ or $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$], also commonly known or referred to as *alum*,

which is used principally as a flocculating agent in water and effluent treatment. This chemical application is derived from the fact that polyvalent ions such as Al^{+++} , and to a lesser degree Fe^{+++} , have the capacity to function as flocculating and coagulating agents. The tri valent aluminum ion is normally favored over the ferric species because of its greater flocculating capability and absence of color. Dissolving high-quality, specialty-grade bauxite in sulfuric acid (H_2SO_4) commonly produces this compound, and only certain types of bauxite are amenable to this acid treatment. The solubility of gibbsite in H_2SO_4 is significantly higher than that of boehmite and, therefore, gibbsitic bauxite is commonly used for this application. Diaspore is relatively insoluble in sulfuric acid, except at temperatures around 300°C . The kaolin that is often present in bauxite also dissolves at a rate comparable with gibbsite; in fact, kaolin also can be used as a feedstock to produce aluminum sulfate. A much purer chemical form of aluminum sulfate, free from iron contamination, is often produced by direct acid treatment of Bayer-process aluminum hydroxide (Figure 1 and Specialty-Grade Alumina section). This high-quality, colorless, iron-free product is specifically used as a sizing agent in the paper industry.

Some of the other principal chemicals that theoretically can be manufactured from bauxite are aluminum chloride (AlCl_3 or $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$), aluminum fluoride (AlF_3), and sodium aluminate, although the preferred feedstock for the higher purity forms of these chemicals is, once again, aluminum hydroxide derived from the Bayer process (Figure 1 and Specialty-Grade Alumina section). Treating heated bauxite with chlorine gas is a common method used to commercially produce aluminum chloride.

The most significant requirement for chemical-grade bauxite is that its acid-soluble iron oxide content should be low. Chemical manufacturers customarily specify a maximum Fe_2O_3 content of 2.0%–2.5%, or an $\text{Al}_2\text{O}_3:\text{Fe}_2\text{O}_3$ ratio of about 23:1 or higher. Nonetheless, this is not an extremely stringent specification and it is totally dependent on the ultimate end use of the material, because much greater iron oxide levels may be tolerated in some water and effluent treatment applications. Even less crucial is the silica content because silica separates out as an insoluble residue during the acid digestion process. Usually, silica levels of 10% and higher in the raw bauxite ore can be tolerated; however, toxic ions must be avoided and high levels of organic compounds adversely affect water quality (Andrews 1984; Benbow 1988). In practice, the U.S. chemical industry often utilizes bauxite with high silica contents for water treatment applications, even though these high silica levels substantially increase material handling costs.

Another special type of chemical-grade material is prepared by low-temperature roasting ($400^\circ\text{--}800^\circ\text{C}$) of low-iron gibbsitic bauxite. The resultant product is a residue of coarse, abrasion-resistant particles that retain only 4%–10% chemically combined hydroxyl groups. As this is a reversible process, the “activated” bauxite readily recombines or adsorbs moisture. This makes activated bauxite an excellent drying agent for gases and organic liquids. In fact, this partially dehydrated material is also known for its porosity and high surface area, which greatly contribute to its reactivity and enhance its use as an adsorbent for sulfur- and fluorine-based compounds. Activated bauxite is commonly used as a decolorizing and moisture removal agent for the food and chemical processing industries. However, activated bauxite’s use as a Claus catalyst for the removal of sulfur from sour gas in the petroleum industry has been mostly superseded by purer activated aluminas produced directly from Bayer-process aluminas (Figure 1 and Specialty-Grade Alumina section). Actually, in the late 1990s, it was reported that only one signif-

icant producer remained as a supplier of activated bauxite to world markets, the Porocel Corporation that produces both activated bauxite and alumina at its Little Rock, Arkansas, plant (Russell 1999).

Sources of Supply

The principal sources of chemical-grade bauxite are Brazil, Ghana, and Guyana. Currently, it is estimated that around 80% of the world’s chemical-grade bauxite produced each year is supplied by Guyana.

Demand

Currently, worldwide demand for chemical-grade bauxite is roughly estimated at about 300,000–350,000 tpy (Russell 1999; Crossley 2001). Through the 1980s and into the 1990s, the total annual consumption of chemical-grade bauxite in the United States for direct use within the chemical’s industry has ranged from a low of 169,000 t in 1982 to a high of 281,000 t in 1983 (Figure 7). In recent years, this information has been withheld by the U.S. government to avoid disclosing company proprietary data; nonetheless the general level of U.S. consumption through various economic cycles is readily evident in the available data.

The current global outlook for chemical-grade bauxite markets is generally downbeat or negative. Aluminum chemical production is a mature to declining market for bauxite. Increasingly, as noted, Bayer alumina has taken over from bauxite in the production of higher quality aluminum sulfate products. Furthermore, the entire market for alum itself is under great pressure because of technological advances occurring within its water treatment and papermaking applications.

Prices

Because of the high-alumina content of chemical-grade bauxite, it can command a premium price, but below that of refractory grade because no calcination cost is included in its production. Prices for chemical-grade bauxite are reportedly stable and estimated in the range from \$40/t to \$50/t f.o.b. for bulk shipments (Russell 1999).

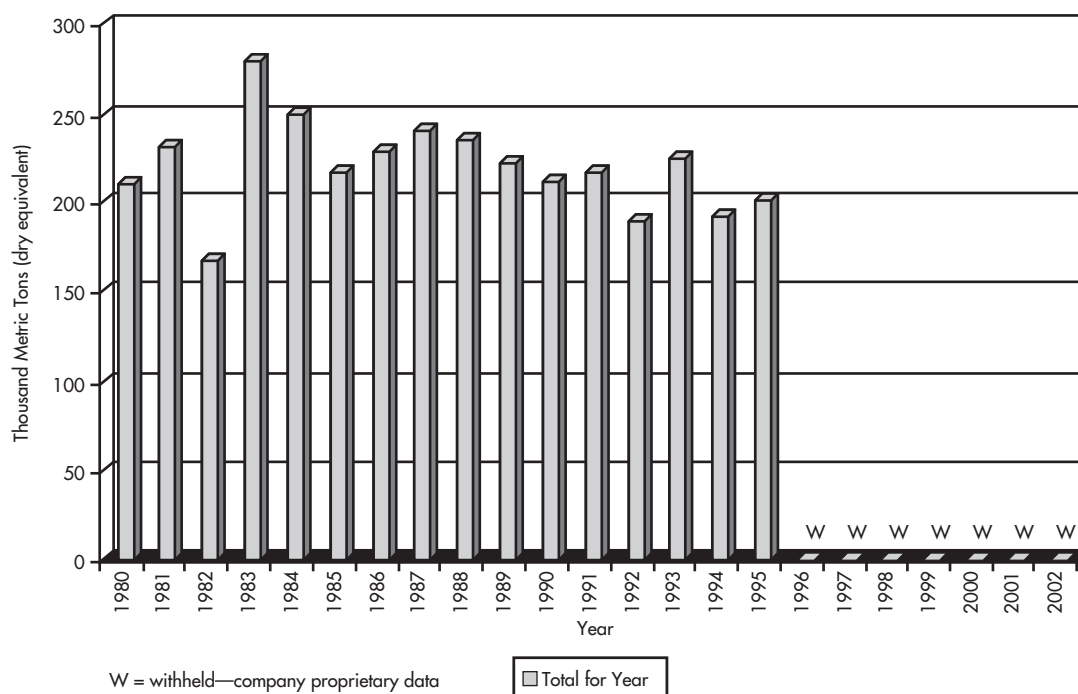
Special Applications

Slag Adjuster

The iron and steel industries commonly use additives to control the viscosity of slags developed in metal production. There are two principal areas in ferrous metallurgy where bauxite may be used as a slag adjuster. The primary use is in iron making, where bauxite is added to control the desulfurization capacity and fluidity of the slag and which, at the same time, provides feed for the manufacture of blast furnace cement. In addition, raw bauxite is also used to control the viscosity of slags during the production of steel. In general, monohydrates (boehmite or diaspore) are favored for these applications. Worldwide consumption of bauxite in steelmaking is estimated to be in the range of 350,000–400,000 tpy (Benbow 1989; Russell 1999; Crossley 2001).

Most bauxite used as a flux in iron and steelmaking must be high in alumina content, usually greater than 55%, and low in silica content. The maximum tolerable SiO_2 content commonly is 7%. Only trace amounts of sulfur and phosphorus may be present in bauxite used in the iron and steel industry. Low moisture content, both free and chemically combined hydroxyl groups, is also desirable.

Bauxite supplied to pig iron producers as a slag adjuster is predicted to be a growth area for the specialty use sector; even so, demand is closely tied to the overall fortunes of the steel industry (Russell 1999).



Source: USBM 1981–1994; USGS 1995–2003.

Figure 7. U.S. chemical industry consumption of bauxite

Proppants

The specialty market products known as *proppants*, or *propping agents*, are associated with hydraulic fracturing, employed in the oil and gas industry to enable hydrocarbon recovery from deep petroleum reservoirs. In the hydraulic fracturing procedure, oil or gas held at great depths in tight rock formations is released by using high-pressure fluids to crack open the host strata. Grains of sand or other materials, known as proppants, are usually introduced into the fractures to keep them open and provide permeable structures through which the gas or oil may migrate and be collected by a recovery well. For shallow reservoirs, selected quartz sands with high natural sphericity and roundness are sufficient to resist the loading pressure of the overlying rock. At greater depths, in excess of 3,000 m, quartz proppants are unable to prevent fracture closure and sintered bauxite is chosen for this application (Crossley 2002a; Taylor 2003c). The general chemical specifications for bauxite used in the manufacture of proppants are high alumina content and low silica and clay content, with the associated iron oxide content not being critical. The bauxite is ground to a particle size of less than 12 μm and then agglomerated into very small spheres prior to being sintered at around 2,000°C. The sintering process forms randomly oriented alpha-alumina crystals that provide the material with its toughness and high-bearing strength. To provide a product with maximum permeability, the proppant is screened into a restricted range of particle sizes, extending from 6- to 80-mesh (3.35- to 0.18-mm) screen size. The most frequently used size is the 20- to 40-mesh (0.85- to 0.425-mm) range (Andrews 1984).

Demand for calcined bauxite in proppant applications is likely to increase in the future because of the hydrocarbon industry's increasing use of high-pressure fluid injection techniques to enhance deep and tight reservoir recoveries, plus the global trend toward greater production depths for both oil and gas.

Miscellaneous Minor Applications

In addition to the uses already described, there are some minor applications that require calcined bauxite as a primary feed stock. Although the principal applications of calcined bauxite remain in the refractory and abrasive industries, a few other very specialized commercial uses have been developed for this fired product, among which are welding flux materials and road surface aggregate. In total, these specialty end uses comprise a very small share of the entire nonmetallurgical-grade market.

Techniques for submerged arc welding require the use of a granular flux to shield the molten weld pool from the atmosphere during the weld's application or placement. Various proprietary compositions exist and in some cases calcined bauxite is incorporated into these formulations. Calcined bauxite may, in some instances, make up to 25% of the welding flux. In this special application, the most crucial specification involves the residual moisture content after calcination. It is mandatory that the moisture content should not exceed that allowed for calcined refractory-grade material (i.e., 0.5%). The reason for this rigorous requirement is the potential for any moisture present within the flux to reduce to hydrogen, if it is exposed to a welding arc. Should this occur, and if the molten weld pool absorbs the hydrogen, it will induce brittleness into the weld. Likewise, tight specifications also govern the presence of sulfur and phosphorus, which are detrimental to the weld. When present at high concentrations, they induce porosity and cracking, and at lower concentrations, they adversely affect the impact strength of the weld. Very few bauxite producers specifically sell welding-grade material, as the market for this product is rather small. Chinese producers are mostly located in Zunyi, Guizhou Province, southern China, and reportedly have a total annual output of 35,000 t. In the past, a Brazilian producer was also known to supply a few thousand metric tons to world markets. During the late

1990s, prices for welding-grade bauxite generally fluctuated in the \$85–\$100/t, f.o.b. China (Zhanjiang), range (Russell 1999).

Another very unique but, nevertheless, potentially significant market for calcined bauxite is as a special anti-skid road aggregate. This use was originally developed in the United Kingdom and has been tested for more than 20 years in that country. As this anti-skid material is the most expensive form of road aggregate, the calcined bauxite-epoxy resin mix is only used at the most crucial road locations to prevent accidents (i.e., road junctions, sharp corners, traffic lights, and pedestrian crossings in residential and urban areas). Even though this is currently only a small-volume usage, it is projected that its consumption will increase as markets are developed, particularly in Europe. This specific specialty application has seen only limited use in U.S. markets.

Specialty-Grade Alumina

A wide variety of high-quality abrasive, ceramic, chemical, and refractory products are produced directly from specialty-grade Bayer-process alumina and calcined alumina (Figure 1). As has been noted, these products and their associated markets require quality raw materials with greater alumina contents than can be provided by naturally occurring nonmetallurgical-grade bauxite. The difference between specialty-grade alumina and nonmetallurgical-grade bauxite as sources of supply to these very demanding markets is primarily one of product purity and cost. Methods of production, product specifications, and commercial markets have been addressed in broad and general terms in the preceding discussion of nonmetallurgical-grade bauxite products. Typically, Bayer-produced alumina is the starting point for most of the calcined alumina and alumina trihydrate used as feedstocks in these specialty alumina applications. Today, specialty-grade alumina plays an increasingly important role in the industrial minerals marketplace as the demand for superior products continues to grow. To take advantage of the higher prices offered for these materials, nearly all major alumina producers have converted a portion of their production capacity to the supply of specialty-grade alumina. Producing specialty-grade aluminum hydroxides, which differ in color, particle size, purity, and various other attributes from normal smelter-grade product, have required substantial capital investment in separate processing and handling facilities. Table 16 lists the key facilities that produce specialty- or nonmetallurgical-grade alumina products.

In 1975, alumina produced for nonmetal applications totaled 1.7 Mt, whereas in the late 1990s the worldwide total was estimated at closer to 5.1 Mt (Russell 1999). The International Aluminium Institute (2000) reported that world alumina production in 2002 totaled 56 Mt and approximately 8% of this (roughly 4.4 Mt) was alumina for nonmetallurgical uses. This may be a slight underestimate for the nonsmelter-grade alumina because some Bayer refineries do not typically differentiate between smelter- and nonsmelter-grade product in their total production figures. It is estimated that about 65% of the nonmetallurgical-grade alumina output is used directly to produce specialty Bayer alumina products; the remainder is processed into calcined specialty-grade alumina (Table 17).

Specialty-grade alumina is normally classified according to its soda (Na_2O) content, crystal size, specific surface area, and particle-size distribution. They are characteristics that influence the commercial applications for which these special products are finally used and the markets in which they compete.

The major specialty-grade products and their markets, listed in the general order of increased energy input requirements for product production, are described in the following sections.

Alumina Trihydrate

A prime workhorse or key feedstock for the specialty alumina market (Figure 1) is alumina trihydrate $[\text{Al}(\text{OH})_3]$, also referred to as aluminum hydroxide $[\text{Al}(\text{OH})_3]$, or less commonly known as hydrated alumina ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$), and often termed ATH by industry. It is used in hundreds of chemical, filler, flame retardant, pharmaceutical, pigment, water treatment, and zeolite applications. Furthermore, it is extremely important to note the great complexity of the alumina trihydrate sector and how, like bauxite, it may be produced in one country, refined or processed in another, and marketed in yet a third.

Alumina trihydrate is the principal high-quality feed for the manufacture of a very wide array of aluminum chemicals. Even though specialty-grade alumina and nonmetallurgical-grade bauxite are considered as the primary sources for a great number of aluminum-based chemicals, only a few are produced in significant commercial quantities (e.g., aluminum chloride, aluminum fluoride, aluminum sulfate, and sodium aluminate). Nevertheless, this results in a considerable tonnage of high-purity aluminum hydroxides with low soda, silica, and iron oxide contents used on an annual basis for the production of aluminum chemicals.

The key end use for anhydrous aluminum chloride is as a catalyst in organic reactions. It is one of the principal catalysts used in the alkylation of aromatic compounds, such as benzene, by alkyl halides (Friedel–Crafts reactions). Aluminum chloride is also used in the production of various cosmetics and pharmaceuticals and in the manufacture of titanium dioxide (TiO_2), which is used as a pigment for paints.

Treating specialty-grade alumina with gaseous hydrogen fluoride, liquid hydrofluoric acid, or fluosilicic acid (H_2SiF_6) produces aluminum fluoride. This product is mainly used as synthetic cryolite in the makeup of the molten bath ($\text{Na}_3\text{AlF}_6 \cdot \text{Al}_2\text{O}_3$) employed in the electrolytic reduction of smelter-grade alumina to a aluminum metal by the Hall–Héroult process. It is currently estimated that aluminum fluoride consumption in the production of primary aluminum metal varies from 10 to 30 kg/t depending on the smelter technology employed, with the worldwide average placed at about 20 kg/t (Roskill Information Services 1993; Russell 1999).

As previously noted, aluminum sulfate (alum) is employed primarily as a flocculating or coagulating agent in water and effluent treatment. In addition, commercial-grade aluminum sulfate is widely used in the manufacture of paper. In the current marketplace, there are basically three grades of aluminum sulfate: industrial, low-iron, and iron-free alum.

Sodium aluminate is used principally for the production of synthetic zeolites used in the manufacture of detergents. The most important commercial form is termed zeolite A $\{\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 27\text{H}_2\text{O}$ or $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4.5\text{H}_2\text{O}\}$, used as a nonphosphate detergent builder that enhances or maintains the cleaning efficiency of the surfactant by controlling water hardness. Since the late 1960s, because of environmental concerns about the ill effects of waste phosphates in natural water systems, governmental legislation restricting or banning the use of phosphates in detergents has boosted the worldwide demand for zeolite A to nearly 1 Mtpy (Russell 1999).

Beyond these wide-ranging applications in the chemical industry, aluminum trihydrate also plays an all-important role as an additive and filler for paint, paper, plastic, and polymer products—most significantly in the field of flame retardants.

Specialty-grade alumina from the Bayer process is an inorganic mineral product that has a large number of the attributes needed to make it an effective and competitive contender in the commercial

Table 16. Principal plants producing specialty-grade alumina products (2003)*

Region and Country	Company	Location	Estimated Total Year-End Specialty-Grade Alumina Capacity, ktpy [†]	Product
North America				
Canada	Alcan	Brockville, Ontario	18	Activated alumina
	Alcan	Vaudreuil, Quebec (Jonquière, Quebec)	142	Specialty hydrate, dry hydrate, specialty calcined aluminas
United States	Alcoa	Point Comfort, Texas	220	Dry hydrate, calcined alumina
	Almatis	Bauxite, Arkansas		Specialty hydrate, reactive alumina, tabular alumina, cement
	Almatis	Dalton, Georgia		Filler, ground alumina hydrate
	Almatis	Leetsdale, Pennsylvania		Calcined and tabular alumina
	Almatis	Port Allen, Louisiana		Activated alumina
	Almatis	Vidalia, Louisiana		Activated alumina, catalysts, absorbents
	Aluchem	Cincinnati, Ohio	25	Secondary production of hard-burned calcined alumina
	Aluchem	Jackson, Ohio	25	Secondary production of intermediate calcined alumina and reactive alumina
	Sherwin Alumina—BPU Reynolds Inc.	Corpus Christi, Texas	300	Wet and dry hydrate, calcined alumina, chemical-grade alumina
	Kaiser Aluminum & Chemical Corp.	Gramercy, Louisiana	200–300	Chemical-grade alumina, flame retardants
	Ormet Corp.	Burnside, Louisiana	6 [‡]	Wet and dry hydrate, chemical-grade alumina
	Porocel Corp.	Little Rock, Arkansas	23	Activated alumina
	UOP L.L.C.	Baton Rouge, Louisiana	22.5	Activated alumina
South America				
Brazil	Alcan	Saramenha, Minas Gerais	10	Specialty alumina
	Alcoa	Poços De Caldas, Minas Gerais	125	Hydrated alumina, calcined alumina
Europe				
Bosnia and Herzegovina	Energoinvest	Birac, Vlasenica	40 (Closed because of civil conflict)	Some chemical-grade alumina
France	Alutech Aluminas (Pechiney)	Gardanne	135	Wet, dry, and ground hydrate, calcined, and very low soda aluminas
Germany	Almatis	Ludwigshafen		Tabular alumina, calcined specialty alumina, spinel
	Aluminium-Oxid Stade GmbH (Hydro Aluminium/Dadco)	Stade	410	Chemical-grade alumina
	Martinswerk GmbH (Albemarle Corp.)	Bergheim	350	Calcined specialty alumina, activated alumina, specialty hydrate
	Nabaltec GmbH	Schwandorf	80 (Bayer plant closed in 1994)	Secondary production of filler and calcined alumina for ceramic and refractory products
Greece	Aluminium de Grece, S.A. (Alutech-Pechiney)	Beotia, Distomon		Small amount of hydrated alumina
Hungary	Ajkai Alumina (Magyar Aluminium—MAL)	Ajka	230	Calcined specialty alumina, specialty hydrate
	Motim Co. Ltd.	Mosonmagyaróvár	80	Calcined specialty alumina, fused alumina
Netherlands	Almatis	Rotterdam		Tabular alumina and calcium aluminate cement (50 ktpy of calcium aluminate cement capacity)
Romania	Oradea Alumina Enterprise	Oradea, Bihor	20 (Plant closed in 2001)	Tabular, hydrate, and specialty aluminas
Russia	Boxitogorsky Glinozem	Boksitogorsk	200	Calcined specialty alumina, specialty hydrate, white fused alumina (110 ktpy of white fused alumina capacity)
Serbia and Montenegro	Aluminijuma Podgorica	Podgorica, Montenegro	140	Chemical-grade alumina
Slovakia	ZSNP	Ziar-nad-Hronom	100 (Plant closed for reconstruction)	Some chemical-grade alumina
Slovenia	Silkem d.o.o. (MAL/Talum)	Kidricevo	66	Specialty alumina—Tabular and ground aluminas, plus zeolites

(Table continued next page)

Table 16. Principal plants producing specialty-grade alumina products (2003)* (continued)

Region and Country	Company	Location	Estimated Total Year-End Specialty-Grade Alumina Capacity, ktpy [†]	Product
Spain	Alumina Española, S.A.	San Ciprian	14	Some chemical-grade alumina
Asia and Eurasia				
China	Namchaun Xianfeng			Alumina hydrate, calcined alumina
	Almatis	Qingdao		Tabular alumina
	Shandong Aluminium Corp. (Chinalco)	Zibo Shi, Shandong		Some specialty-grade alumina (180 ktpy of alumina chemicals)
India	Almatis	Falta		Specialty alumina, ground hydrate
	Indian Aluminium (Indal) (Hindalco Industries)	Belgaum, Karnataka	100	Some chemical-grade alumina
	Indian Aluminium (Indal) (Hindalco Industries)	Muri, Bihar	40	Chemical-grade alumina
	Madras Aluminium (Malco) (Sterlite Industries)	Mettur, Tamil Nadu	12	Some chemical-grade alumina
	National Aluminium (Nalco)	Damanjodi, Orissa	40	Some chemical-grade alumina
Japan	Almatis	Moralco Works, Iwakuni		Tabular alumina
	Almatis	Naoetsue		Ground hydrate
	Nippon Light Metal Co. Ltd.	Shimizu, Shizuoka	215	Calcined specialty alumina, specialty hydrate
	Showa Denko KK	Yokohama, Kanagawa	220	Calcined specialty alumina, specialty hydrate, chemical-grade alumina
	Sumitomo Chemical Co. Ltd.	Kikumoto, Ehime	219	Calcined specialty alumina, specialty hydrate, chemical-grade alumina
Korea	Korea General Chemical Corp.	Mokp'o	70	Chemical-grade alumina
Turkey	Eti Alüminyum, A.S.	Seydisehir, near Konya	120	Specialty alumina (35 ktpy of aluminum sulfate capacity)
Oceania				
Australia	Alcan Gove PTY Ltd.	Gove, Northern Territory	60	Chemical-grade alumina
	Alcoa	Kwinana, Western Australia	270	Dry hydrate
	Australian Fused Materials	Rockingham, Western Australia		Secondary production of calcined alumina

* Bayer process alumina, and excludes most fused alumina production.

† Where available.

‡ Temporarily idled in February 2001; restarted at the end of 2003.

Table 17. Estimated worldwide specialty-grade alumina consumption, ktpy

Calcined Alumina	
Market sector	
Refractories	400
Tabular alumina	300
Whitewares and electrical insulators	250
Fused alumina	225
Activated aluminas	150
Polishing aluminas	60
Total	1,385
Alumina Trihydrate	
Chemical usage (water treatment, TiO ₂ pigment manufacture, etc.)	1,500
Aluminum fluoride production	430
Flame retardants	400
Other fillers	200
Total	2,530

Source: Russell 1999.

filler market. These include a white or near-white color, large volume production base ensuring dependable supply, consistency of chemical and physical properties, availability in a broad range of particle-size distributions, chemical inertness, nontoxicity, and, ultimately, cost-effectiveness. Furthermore, alumina trihydrate's widespread use as a filler is directly related to its fire-retardant and smoke-suppressant properties (Sleppy et al. 1991). The use of alumina trihydrate as a flame-retardant filler in plastics and rubber has developed into a major market for this specialty product. The majority of this alumina trihydrate filler feedstock is used in plastic applications, but a substantial quantity is also used in rubber, particularly for carpet backing applications. In the early 1970s, the demand in this market increased significantly as a result of U.S. legislation designed to restrict the flammability of carpeting materials.

Basically, there are two principal types of fire retardant alumina trihydrate: those produced directly from Bayer-process hydrate by milling and products made by dissolving and re-precipitating Bayer alumina. They are typically referred to as milled and precipitated products. The precipitated grades usually achieve higher prices, profitability, and growth rates than the standard milled products (Rothon 2004).

All flame or fire retardants succeed by disrupting one or more stages of the normal combustion process. In the case of alumina trihydrate, it operates principally in the initial stages of the combustion process: heating and decomposition. Aluminum hydroxide decomposes at above 200°C to give alumina and water vapor. This reaction is strongly endothermic, resulting in the absorption of about 280 calories per gram of aluminum hydroxide. The maximum decomposition rate for aluminum hydroxide occurs between 300°C and 350°C, which roughly corresponds to the range of decomposition temperatures for the most commonly used commercial polymers. Therefore, when a polymer containing alumina trihydrate is heated, the aluminum hydroxide decomposes endothermally, acts as a heat sink, and slows the rate of temperature rise, and the rate of decomposition of the polymer. Additionally, the water vapor given off also serves to dilute any combustible gases generated and acts as a vapor barrier preventing oxygen from reaching the flame, thereby impeding the progression of a fire (Sleppy et al. 1991).

The added smoke-inhibiting capacity of alumina trihydrate fillers is largely attributed to the development of solid-phase charring during the combustion process, instead of soot formation. Moreover, smoke suppression is also probably partly related to the resulting endothermic dehydration of the burning material.

In the early 1990s, it was reported that alumina trihydrate held 45%–50% by volume of the entire flame-retardant market (Schmitt 1993). Annual worldwide consumption for this application is currently estimated to be approximately 400,000 tpy.

Alumina trihydrate suitable for use as a functional filler, extender, or pigment in paper and paint products must meet very strict color and brightness specifications. This is also especially true for specialty filler applications such as alumina trihydrate's use in the manufacture of synthetic marble (onyx), where whiteness is a critical element. The aluminum hydroxide produced by the Bayer process is normally an off-white color because of organic impurities originating from the bauxite ore and present in the caustic liquor, which impart a yellowish color to the hydroxide product. Therefore, special purification techniques are necessary to satisfy the coating and filler market demand for white hydroxide products. These methods include reprocessing the Bayer refining plant hydroxide by further dissolution in caustic and high-temperature treatment (liquor burning) of the Bayer-process liquor to destroy organic impurities and, thereby, whiten the final product (Sleppy et al. 1991).

Other specialty applications for alumina trihydrate include use in the pharmaceutical industry for dental hygiene products such as toothpaste, the manufacture of antiperspirants, and use in stomach antacid products.

Specialty alumina trihydrate, particularly fine, high-whiteness grades, command a noteworthy premium on price over smelter-grade alumina, and are also less susceptible to market volatility. The prices quoted in 2002 for some of these specialty materials were as follows: \$400/t for ground alumina trihydrate, \$700/t for superfine alumina trihydrate, and up to \$1,400/t for coated grades. This compared with \$400/t for calcined alumina and \$500–\$600/t for ground calcined alumina (Crossley 2002b).

Activated Alumina

This category of specialty alumina is produced from dry alumina trihydrate by partial calcination or low-temperature roasting to remove the majority, but not all, of its chemically combined hydroxyl groups. This partial dehydration process is typically carried out at temperatures in the range of 250°–900°C, under strictly controlled circumstances, so that only 4%–10% of the chemically bonded hydroxyl groups in the feed are retained in the final commercial

product. As with activated bauxite, this is a reversible process and it provides an activated alumina that readily adsorbs moisture.

Activated aluminas are employed as desiccants, catalysts, and catalyst supports (Figure 1). The higher purity of activated specialty-alumina products has enabled them to largely replace activated bauxite in many applications and launch a variety of new markets of their own. An actual example of this changing market structure is the case where activated alumina has essentially taken over from bauxite in the Claus catalyst market. The Claus process is principally used to recover sulfur in industrial processing operations where significant amounts of hydrogen sulfide are released (petroleum refineries, natural gas plants, and steel mills). In the early 1970s, activated bauxite was the exclusive Claus catalyst used for sulfur recovery, but by the mid-1970s, activated alumina had become a much more important player. This was driven by a broad industry effort to raise the level of catalyst effectiveness to meet increasingly more stringent air pollution standards.

In the catalyst support sector, activated and calcined aluminas are employed to support a number of catalysts in various applications, mainly in the petroleum refining industry. Moreover, one of the most important uses of alumina as a catalyst support is in the field of catalytic converters for pollution control on automobiles.

Activated alumina products are usually sold as granules or ball shapes, although some are also produced as powder.

The total annual worldwide market for activated alumina has grown rapidly during the last 10 years and is currently estimated to be on the order of 90,000–150,000 tpy (Pearson 1999; Russell 1999).

Calcined Alumina

The other major workhorse or chief feedstock in the area of specialty applications is calcined alumina, which is the primary raw material for numerous high-quality end uses in the abrasives, ceramics, and refractories industries (Figure 1). Beyond the significant role it plays on its own in these various specialty applications, it is also the primary feedstock for the preparation of sintered and fused aluminas that include such high-end products as tabular alumina and white fused alumina. Tabular or sintered alumina is mostly used in high-performance refractory materials, whereas white fused alumina is mainly used for grinding abrasives and in some refractory applications (MacZura 1992).

Basically there are three categories of calcined alumina, which are based on the soda (Na_2O) content and total amount of impurities in the final product. The two most common types are normal- and low-soda calcined alumina, produced by firing Bayer-process alumina, while the third is high-purity calcined alumina, with an alumina content higher than 99.9%. A portion of this latter category consists of ultra-high-purity alumina, with a 99.99% Al_2O_3 content, produced by the decomposition of aluminum-based salts, and thereby not directly derived from Bayer-process products (Russell 1999).

Normal-grade calcined aluminas have a soda content higher than 0.1% and generally less than 0.3%, with a total alumina content of 99.0%–99.5%. Low-soda calcined aluminas, on the other hand, occasionally referred to as thermally reactive aluminas, have an Al_2O_3 content of 99.7% and contain less than 0.1% Na_2O .

The critical economic considerations associated with the processing and producing calcined specialty aluminas are generally the same as those that were discussed for calcined non-metallurgical-grade bauxite products (i.e., fuel costs, economy-of-scale issues, etc.). As previously stated, the calcination process is a very energy-intensive industrial procedure. In the case of calcined alumina, the conversion to alpha alumina occurs at about 1,100°–1,450°C. As with bauxite, the traditional means of calcining specialty-grade alumina is in standard rotary kilns, with typical production rates of

50–350 tpd. Newer fluid-flash or stationary calciners have been developed, however, to replace rotary kilns in the production of all but the higher purity-grade alumina calcines. Flash calciners have a much greater production capacity, up to 1,550 tpd, lower energy use (30%–40% fuel savings), lower capital and maintenance costs, plus lower workforce requirements. They are an excellent fit for Bayer refinery plants producing large volumes of smelter-grade alumina for metal production. Nonetheless, few specialty-calcined products have the volume of commercial applications in their niche markets required to justify the high production capacity of fluid-flash calciners (Sleppy et al. 1991).

The refractory industry is by far the most significant market for calcined specialty alumina; it comprises an estimated 60% of the total production. Calcined alumina is used extensively in the production of high-purity calcium aluminate cement (CA C70–80), which finds wide use as cements, concretes, and mortars in refractory applications and as binders in monolithic formulations, particularly gunning mixes and castables (Russell 1999; O'Driscoll 2000). Additionally, this sector also consumes a major tonnage of tabular alumina that is made directly from calcined alumina feed. Low-soda calcined alumina is used extensively within the ceramics industry for applications in whiteware, porcelain and electrical insulators, tiles, and newly developed high-technology uses such as integrated circuit substrates and bioceramics. The ceramics account for approximately 25% of the calcined alumina market. The key properties that alumina imparts to a ceramic product are high wear resistance, corrosion resistance, excellent electrical insulation, high mechanical strength, and good thermal conductivity (Roskill Information Services 1993). In the abrasives industry, calcined specialty alumina is used in two principal sectors. The previously mentioned and largest volume use is as the primary feedstock for the production of white fused alumina. The other major application is for polishing and lapping compounds.

In the late 1990s, worldwide production capacity for all grades of calcined alumina was estimated at 1.15 Mt of product. This figure could even be placed as high as 2 Mt, if the calcined specialty alumina used to produce white fused and tabular alumina, plus spinel-based refractories, were included in the estimate (Russell 1999; O'Driscoll 2003).

Sintered Alumina

As noted earlier, calcined specialty-alumina feed is used to manufacture tabular alumina, a thermally stable form of alpha alumina (α - Al_2O_3). Tabular alumina is a high-density, high-strength form of α - Al_2O_3 produced by sintering agglomerated shapes of ground calcined alumina at 1,800°–1,900°C in shaft or rotary kilns. At these elevated temperatures, the alpha alumina recrystallizes to form large, elongated, tablet-like corundum crystals from which tabular alumina receives its name. Occasionally in the sintering process temperatures approaching 2,050°C, the fusion point of alumina, are used for some special products. In the firing process, however, other factors such as residence time of the feedstock may significantly influence the development and ultimate size of the tablet-shaped alpha-alumina crystals and, in some special instances, sintering aids such as MgO or SiO_2 may be added to the kiln feed (Russell 1999; Taylor 2003d).

These hard-burned (sintered) calcined alumina have good resistance to thermal shock and physical erosion, so they are principally used as raw materials for high-performance refractory materials (Figure 1). In fact, the largest consumer of tabular alumina is the refractories industry, which reportedly accounts for about 95% of the product demand (Russell 1999; Taylor 2003d). One of its most important applications is its use in blast furnaces and steel mills for

the handling of molten metal in the production of steel. Smaller end markets include abrasives, electrical insulators, and catalyst carriers.

The total worldwide market for tabular alumina is currently estimated at 270,000–300,000 tpy. Nevertheless, at present, the global supply of tabular alumina exceeds demand, and this oversupply situation is likely to continue in the near future. Significant short-term growth is not expected, owing to an increase in competition from low-cost alternative raw materials across the entire refractories market, as tabular alumina finds itself in direct competition with white fused alumina, brown fused alumina, and other specialty fused or sintered materials for this ever-tightening market.

In mid-2003, average selling prices for tabular alumina were reported around \$800/t, with considerable variation depending on the specifications and volumes sold (Taylor 2003d).

Fused Alumina

This category of specialty alumina is used primarily as a feedstock to the abrasives and refractories industries because of fused alumina's extreme hardness and high melting point. There are a variety of fused aluminas, however; the two most common types are brown and white fused, with brown being the most widely manufactured type. As already observed, brown fused alumina is produced from calcined nonmetallurgical bauxite, while the higher purity white fused alumina is manufactured directly from calcined specialty-grade alumina with a minimum 99.5% Al_2O_3 content (Figure 1). The feed for this application should also have a coarse particle size and a low soda (Na_2O) content. Pink and ruby fused aluminas are also derived from this same calcined specialty-alumina raw material. The overall toughness of the white fused product is increased by adding up to 2% chromium oxide (Cr_2O_3), which produces a pink, red, or ruby fused alumina product. These latter grades are used entirely for grinding wheel applications (O'Driscoll 2003).

Like brown fused alumina, white fused alumina is produced in electric arc furnaces at temperatures above 2,000°C. White fused alumina contains 99.5%–99.9% Al_2O_3 , and, after fusion, is crushed and ground, magnetically separated, and often acid washed.

There are three basic categories of white fused alumina, which are defined by their soda content: regular (0.4% Na_2O), medium (0.05% Na_2O), and low (0.018% Na_2O). In addition, another critical parameter is the crystal size of the product (Russell 1999; O'Driscoll 2003).

The high-energy inputs required for the production of fused aluminas have determined that these production facilities should be sited in areas producing abundant supplies of low-cost electricity, such as regions with plentiful sources of hydroelectric power.

White fused alumina is used mainly for grinding abrasives but also in the refractory industry, where it is often employed when dense refractories requiring high purity at high temperatures are needed, with the regular and medium soda grades most widely used in these applications.

In mid-September 2003, white fused alumina prices were quoted at \$530/t, f.o.b. China, and were on the rise because of increasing calcined alumina costs (O'Driscoll 2003). In comparison, at the same time, prices for Chinese brown fused alumina (lump <40 mm, f.o.b. China) were \$200–\$220/t (O'Driscoll 2003). White fused alumina abrasive grain is traditionally more expensive than its fellow fused product, brown fused alumina.

Transportation

The aluminum industry derives its supply of bauxite and alumina raw materials from mines and Bayer refineries that are spread throughout the world. Thus the industry developed the adage, "What is bauxite? It is red and comes in ships." On a more serious note, ocean freight

charges and other transportation costs can be very high in relation to the actual overall value of the basic metallurgical-grade raw material used by the industry. Consequently, the economics of transporting and handling these bulk materials are extremely important factors in determining expansions of production and siting new alumina refineries and smelters for the production of aluminum. The potential for obtaining substantial savings on raw materials shipping costs is a major part of the logic behind locating Bayer alumina refineries at or near bauxite mines. As noted earlier, on average it takes roughly 2 to 3 t of bauxite to produce 1 t of alumina, which has significant implications for the volume of materials shipped through the aluminum production cycle. The same general type of transportation and handling cost issues are also at play when the choice is made by a particular nonmetallurgical bauxite producer to supply a specific sector of the industrial minerals market. In the case of the nonmetallurgical-grade trade, higher value products are usually involved that are shipped in smaller tonnages or lots. In fact, these smaller tonnages may even be "piggybacked" with other industrial mineral bulk cargoes for shipment to market. Because of the great international distances between the source of supply and markets, shipping and handling charges are a sizeable component of the entire industry's total raw materials budget, and transportation efficiency is essential to achieving and maintaining industry profitability.

Because of its low cost, water transport via ship and barge is the preferred, if not the only viable, means employed for moving bauxite-alumina bulk cargoes throughout the world. Over the years, major improvements in the operating efficiencies and shipping infrastructure for exporting the seabulk commodities have been achieved by expanding stockpiling facilities, using faster shiploading equipment, dredging and deepening ports, and employing larger bulk cargo ships. In cases of ocean shipping, transportation costs typically diminish with increasing carrier size and shipping distance. Large carriers, such as the 65,000 dead-weight-tonnage Panamax class, have been found to be the most cost efficient oceangoing vessels for the metallurgical-grade bauxite-smelter-grade alumina cargo trade (Drewry Business Publications 1993). Typical shipping times for nonmetallurgical-grade bauxite to European markets is 6–8 weeks from China and 2–3 weeks from South America, which are in addition to the lead times required to produce the product and move it to port facilities.

In North America and parts of Europe, the use of railroad transportation is typically limited to short-distance haulage because of its normally higher costs. Rail transport is used extensively in China and some African countries, however, for the movement of bauxite ores from mines to processing facilities or ports for export shipment. In other countries, various combinations of both truck and rail transport are used to move bauxite overland to processing plants or markets.

ENVIRONMENTAL CONSIDERATIONS

During the last 25 years, bauxite mining and processing operations have made significant strides in addressing the environmental impacts of their industry. The principal areas of possible adverse environmental impact for both metallurgical- and nonmetallurgical-grade bauxite operations are located at the mines, bauxite beneficiation/processing plants, and Bayer alumina plants.

In 1991, a worldwide survey of 18 metallurgical-grade bauxite mining operations determined that the area mined at these reporting sites ranged from roughly 2 ha to 450 ha, with the average being 76 ha. The total number of hectares per year directly impacted by the mining operations amounted to 1,368 ha (Martyn 1992). The 18 mining locations used in the survey represented 65% of total world bauxite production at the time.

The International Aluminium Institute (2000) conducted a second survey in 1998 covering 27 mining locations representing 72% of the world total bauxite production. The survey found that metallurgical-grade bauxite mining occurs in four major climate groups, and the 1998 distribution was Tropical 48%, Mediterranean 39%, Subtropical 13%, and Temperate 0.5%. The vegetation types impacted by the bauxite mining operations were mainly forests (76%), followed by agriculture and pasturelands (19%) and shrublands (2%). Postmining land use was determined by this second survey to be 70% returned to native forest; 17% to pastureland and agriculture; 7% used for urban and industrial development, housing, and recreational purposes; and 3% to commercial forest. The total area mined per year in 1998 was reported as 1,591 ha, 80% of which was identified as wildlife habitat, and 11% (175 ha) of which was tropical rainforest. The earlier and smaller 1991 survey placed the yearly worldwide total area mined for metallurgical-grade bauxite at 1,368 ha. In 1998, 577 ha of mined area was identified as possessing important fauna species; of these, 527 ha or 91% was to be restored to wildlife habitat by planting of suitable vegetation. It was also reported that the companies responsible for producing 60% of the world's metallurgical-grade bauxite had established their own plant nurseries for the purposes of reforestation and revegetation. In 1998, reclamation plans were in place at 90% of the surveyed mines, compared to 55% in 1991, and the existing reclamation rate was found to be 1,256 ha/year.

The higher value of most nonmetallurgical bauxite, as compared to metallurgical-grade material, usually makes it economically viable for these open-pit operations to be developed to greater depths, so it is often necessary to dispose of larger quantities of overburden. In low-lying swampy areas where there is abundant groundwater, artificial lakes are sometimes constructed and the overburden removed by suction dredge. This has been the case for several mines in Suriname. These lakes or ponded areas must be carefully constructed to avoid large-scale destruction of the native tropical forest. Consequently, owing to circumstances such as these, well-designed mine reclamation programs must be established to ensure that these affected sites are rehabilitated to meet acceptable standards when mining operations cease. This often means replacing topsoil and reforesting the mined areas. In many parts of the world, this is achieved by setting aside and preserving topsoil stripped from active mining sites for later use on reclaimed areas.

Monitoring and controlling the environmental effects of bauxite mining and ore processing operations are continuing responsibilities and generally include monitoring programs for the following parameters: air quality, dust levels, groundwater quality, and liquid effluents. Consideration also must be given to the fauna, flora, and local human inhabitants near these various operations. At the processing site where bauxite is beneficiated by crushing and washing, proper sedimentation facilities are necessary, so that process water can be reused and the tailings may be properly disposed of. The drying and calcining facilities also need to be fitted with dust precipitators to protect air quality and prevent a high level of dust from leaving the plant's stacks. In the production of aluminum chemicals from bauxite, the proper disposal of acidic residue poses an environmental concern at some locations.

A major issue for the alumina and bauxite industry is the disposal of the massive amounts of red and brown mud residues generated from alumina production. The industry has held two major international meetings to address this issue, the first in Kingston, Jamaica, in 1986 and the second in Perth, Australia, in 1992. At the Perth meeting, it was estimated that the world's alumina plants were then producing more than 66 dry Mtpy of bauxite tailings or red mud residues. Depending on the quality of the bauxite and the

technical design of the Bayer plant, between 1.1 and 6.2 t of red mud are generated for each metric ton of alumina produced (Hausberg et al. 2000). This red mud waste stream contains insoluble sodium aluminosilicates, Fe_2O_3 , TiO_2 , and trace amounts of other oxides of metals such as nickel, vanadium, and zinc. The following listing gives some idea of the extremely wide range of chemical composition found in red mud residues from different bauxites: Fe_2O_3 , 30%–60%; SiO_2 , 3%–50%; Al_2O_3 , 10%–20%; Na_2O , 2%–10%; CaO , 2%–8%; and TiO_2 , trace–10%. Apart from the alkalinity imparted by the Bayer caustic leach solution, the waste stream residue is chemically stable and nontoxic (International Aluminium Institute 2000).

Significant research has been devoted to developing methods of drying, handling, treating, and designing storage and containment areas for red mud wastes, plus rehabilitation of the waste ponds. In addition, extensive effort has also focused on developing economic alternative uses for this current waste product. These have included, among many others, the possible use as an agricultural soil conditioner, in ceramics for the manufacture of brick and tile, in water treatment to filter wastewater effluent, in plastics as a filler material, and as iron oxide-based pigments for use in the cement and construction materials industries. To date, efforts have not been highly successful in finding or developing a large-scale, economically workable end use for the alumina industry's red mud wastes.

OUTLOOK AND FUTURE TRENDS

The principal end uses of nonmetallurgical-grade bauxite are directly related to the production and consumption of raw materials for basic heavy industry, such as primary metals, cement, chemicals, ceramics, and so forth (Wright 1990). This serves to make the demand for specialty-grade bauxite cyclical, as it is directly tied to the basic movements of heavy industry—the “smokestack” component of the world economy—a trend that is expected to continue well into the future. An additional concern facing producers of nonmetallurgical-grade bauxite is that most of these markets are mature and neither new nor likely to expand in the foreseeable future.

In the case of refractories, the highest value market for nonmetallurgical bauxite, the outlook for possible future growth lies in the development of more advanced refractories with increased product longevity or greater endurance within very harsh, high-temperature environments (Jain 1994). More sophisticated and demanding applications are being developed throughout the world for refractories, via the modernization of primary metal production processes (iron, copper, etc.), and this driving force will continue to stimulate demand for high-quality calcined bauxite products in the future (Fisher et al. 1993; Moore 2004).

As with all industrial minerals, an intense and persistent competition for markets exists throughout the entire spectrum of nonmetal applications for bauxite. This situation will continue and intensify over time as more sophisticated applications are developed for alumina-based materials. For the top-end and high-quality markets, nonmetallurgical bauxite will remain under sharp market pressure from Bayer-process aluminas.

Relatively new major suppliers of nonmetallurgical bauxite to the world market, such as Brazil and India, will continue to help diversify the sources of world supply and ensure the existence of a stable, long-term raw material resource base for the rest of this century.

A major restructuring and consolidation of the entire aluminum industry occurred toward the end of the twentieth century and start of the twenty-first century, leaving only two or three major integrated world producers, principally Alcoa and Alcan. This has

had and will continue to have only a slight impact on the nonmetallurgical-grade bauxite component of the industry but may result in significant implications for future international markets and sources of supply for alumina products (Crossley 2003a; Anon. 2003). This may be particularly true for the remaining independent, medium-sized (200- to 300-tpy level) producers of alumina trihydrate, which are currently estimated to number fewer than 20 facilities scattered around the world (Table 16).

The chief influence driving future demand for nonmetallurgical-grade bauxite and specialty-grade alumina will remain the continued general strength and vitality of the world's major industrialized economies and their newly developing industrial competitors, such as China with its explosive levels of industrial growth. It is reported that China currently consumes more steel than the European Union (Cole 2001). Hence, China holds a unique place in the future because of its status as both a major consumer of the world's raw materials and its role as a key supplier of nonmetallurgical-grade bauxite to world markets. The expansion or contraction of these nonmetallurgical-bauxite and specialty-grade alumina markets are very closely tied to the world's basic heavy industry, and it will remain so well into the future.

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Beryllium Minerals

Phillip Sabey

BERYLLIUM AND ITS USES

Beryllium (Be), no. 4 in the Periodic Table of Elements, is a naturally occurring element that is generally reported as the 44th most abundant element in the earth's crust. Beryllium is ubiquitous in the environment and is found naturally in soil, surface and groundwaters, coal and oil, wood, foodstuffs, and gemstones such as aquamarine and emerald. The general population has daily exposure to naturally occurring beryllium from ambient air and drinking water, as well as through dietary intake.

Beryllium was discovered in 1798 by the French chemist Louis Nicolas Vauquelin, who originally named the element glucinium. In 1828, the German scientist Friedrich Wohler extracted it in its metallic form and renamed it beryllium. Beryllium has been an essential material in the manufacture of products for the aerospace and defense, automotive, energy, medical, and electronics industries for more than half a century. It is a unique material that exhibits physical and mechanical properties unmatched by any other metal. On a pound-for-pound basis, beryllium is six times stiffer than steel, making it one of the most rigid metals. It also has two thirds the density of aluminum, making it one of the lightest metals. Beryllium possesses high heat-absorbing capability and has dimensional stability over a wide range of temperatures. Because of its unrivaled combination of qualities, beryllium has become an increasingly important material for a wide range of commercial and governmental applications. For example, hundreds of millions of people worldwide enjoy the benefits of keeping in touch, working more productively, or maintaining communications during emergencies with cellular phones and computers manufactured with beryllium-containing materials.

The commercial value of beryllium was recognized in 1926 when a copper-nickel-beryllium alloy was patented. Application of copper-beryllium alloys, beryllium oxide ceramics, and metallic beryllium grew during World War II in the aerospace and defense, automotive, energy, medical, and electronics industries. The estimated global market value for beryllium-containing materials is approximately \$700 million per year.

Beryllium is a strategic and critical material for many industries and poses no special health risk in the solid form, which is most commonly encountered by the public. The beryllium industry produces three primary forms: the greatest production volumes are of beryllium-containing alloys (e.g., copper-beryllium, nickel-beryllium), followed by beryllium metals, with beryllia ceramics

(beryllium oxide [BeO]) taking third place. Metals such as copper, nickel, and aluminum, when alloyed with small additions of beryllium, may be processed to achieve remarkable combinations of physical properties such as high strength, formability, and hardness. Depending on the desired strength and electrical conductivity, copper-beryllium-wrought products typically contain 0.15% to 2.0% beryllium. Copper-beryllium alloys are designed for and specified in highly engineered applications in the electronics, automotive, household appliance, plastic mold, and aerospace industries because of the unique combinations of such properties as strength, electrical and thermal conductivity, magnetic transparency, and corrosion resistance. The three primary forms of beryllium-containing materials are used as critical, high-reliability components in products such as air bag collision sensors, fire suppression extinguisher sprinkler head springs, x-ray windows for mammography, medical equipment laser bores, pacemakers, landing gear bearings, and weather satellites. Beryllium-containing materials are used in automotive electronics, including the ignition control systems of many modern automobiles, to increase gas mileage, thereby reducing air pollution and generation of global warming gases. Copper-beryllium products are integral for both wired and wireless communications, such as cellular phones and pagers. Other applications include computers, oil exploration equipment, and plastic injection molding dies.

Alloys that are high in beryllium (containing 40% to 100% beryllium) are used for aviation and space applications such as advanced electro-optical targeting and infrared countermeasure devices in fighter aircraft, missiles, and radar systems. Many advanced surveillance and extreme performance satellites also contain beryllium structures and electronic components. Because of its nuclear and mechanical properties, beryllium metal is used in commercial nuclear reactor applications including experimental electricity generation projects such as for fusion reactors and in the construction of nuclear devices for defense applications. Because of its unique property of transparency to x-rays, beryllium metal is used in an extremely thin foil form as the transmission window on high-resolution diagnostic x-ray equipment, and for CAT scanning and mammography equipment. In the fall of 2003, optical-grade beryllium metal was selected as the primary mirror material for NASA's \$825 million James Webb Space Telescope, which, once launched, will allow scientists to see 10 to 11 billion light years away. Beryllium ceramics, produced from high-purity beryllium

oxide powder (99.5%), are used in lasers and electronic packaging for high-speed and high-powered integrated circuits.

Over the years, the range of specific products utilizing beryllium-containing materials has expanded in step with the advance of technology. The demand for features such as higher performance, improved reliability, and miniaturization has created new applications for beryllium-containing materials in high-technology devices. There has been no surge, however, in the number of new end-use markets. In fact, beryllium-containing materials were first used in the major markets as follows

- Maritime, 1930s
- Computers, 1940s
- Aerospace, 1940s
- Telecommunications, 1940s
- Appliances, 1950s
- Automotive, 1950s
- Plastics (molds), 1950s
- Recreational, 1950s
- Dental, 1960s
- Oil exploration, 1960s

The United States is the only country other than China and Kazakhstan that is currently producing beryllium products from beryllium ores and concentrates. Bertrandite, which is mined in Utah, is the principal ore source of domestically produced products. Imported beryl, mainly from Brazil, supplements domestic ore supplies. Table 1 shows world production of beryllium in 2002 and 2003 (estimated).

GEOLOGY OF BERYLLIUM DEPOSITS

Although there are more than 50 beryllium minerals (Barton and Young 2002), only bertrandite, beryl, and phenakite are commercially important. Table 2 gives the compositions of some beryllium minerals. Important beryllium resources occur in several different types of deposits worldwide. Locations of some notable resources are shown in Table 3, along with data on size and grade.

Beryllium in Volcanic Rocks

Although significant beryllium deposits in volcanic rocks are rare, one such deposit at Spor Mountain in Utah is by far the most important source of beryllium in the world. The ore mineral bertrandite occurs as nodules and disseminated fine grains in volcanic tuff. Smaller volcanic rock-hosted deposits have been noted elsewhere in Utah and in Arizona (Shawe 1966), and in New Mexico (Hillard 1969). A deposit of metamorphosed tuff in Australia that is enriched in rare metals is also weakly enriched in beryllium (Taylor, Esslemont, and Sun 1995).

Beryllium in Pegmatites

Granitic pegmatites are the world's principal source of beryl. Beryl has been mined from zones, fracture-filling units, and replacement bodies in heterogeneous pegmatites. The principal beryl deposits are in zoned pegmatites. Most beryl-rich zones contain only a few thousand tons of rock, but a few may contain as much as 1 Mt. Beryl occurs in concentrations of approximately 2% in zones containing plagioclase, quartz, and muscovite, from which mica is the principal product. It is also abundant in zones from which spodumene, amblygonite, and feldspar are recovered.

Beryl tends to be finer-grained in outer zones than in inner zones of pegmatites. Much of the fine- and medium-grained beryl of pegmatites in the Black Hills of South Dakota contains abundant

Table 1. World mine production, reserves, and reserve base

Location [†]	Mine Production, t [*]	
	2002	2003
United States	80	100
China	15	15
Kazakhstan	4	4
Russia	40	40
Other countries	1	2
World total (rounded)	140	160

Courtesy of U.S. Geological Survey.

* Estimated.

† Other beryllium-producing countries include Brazil, Madagascar, Mozambique, Portugal, and Zambia.

Table 2. Comparison of some beryllium minerals

Mineral	Chemical Composition	% BeO
Berylite	BaBe ₂ Si ₂ O ₇	15.4–15.8
Bertrandite	Be ₄ Si ₂ O ₇ (OH) ₂	39.6–42.6
Beryl	Be ₃ Al ₂ (SiO ₃) ₆	10.0–14.0
Beryllonite	NaBePO ₄	19.8
Chrysoberyl	BeAlO ₄	16.9–19.7
Danailite	Fe ₄ Be ₃ (SiO ₄) ₃ S	12.7–13.8
Eudidymite	HNaBeSi ₃ O ₈	10.6–11.1
Helvite	Mn ₄ Be ₃ (SiO ₄) ₃ S	10.5–15.0
Herderite	CaBePO ₄ (OH,F)	15.0–15.8
Phenakite	Be ₂ SiO ₄	44.0–45.6

Adapted from Warner et al. 1959.

inclusions of other minerals (Tullis 1952). Large masses of beryl that contain almost no inclusions have been found in inner zones, and these may extend across several zones. Beryl is evenly distributed in some deposits, but in others it is irregularly distributed as rich aggregates in various parts of a zone.

No beryllium minerals in pegmatites other than beryl are of commercial importance because they are exceedingly rare. Chrysoberyl is concentrated in parts of some pegmatites but is much less abundant than beryl.

Beryllium in Quartz Veins

Beryl has been found in quartz veins containing cassiterite, wolframite, molybdenite, scheelite, and other minerals. Such quartz veins may occur in greisen deposits (see section on Beryllium in Greisen in this chapter), and there is considerable overlap between these two deposit types. The concentration of beryl in the outer parts of some quartz veins, just as beryl is concentrated in the outer part of quartz zones in some pegmatites, suggests that these quartz veins are genetically similar to pegmatites. Beryl has been studied in tin veins in South Dakota, England, and elsewhere. Beryl has been reported in quartz veins in Colorado (Adams 1953). Phenakite and bertrandite occur in quartz-scheelite veins associated with beryllium-rich replacement deposits in Nevada (Barton and Young 2002), and bertrandite occurs in quartz-chalcedony veins in Utah (Shawe 1966).

Beryllium in Metamorphic and Replacement Deposits

Metamorphic deposits that contain beryllium are primarily tectites and emerald-bearing schists. Helvite is the chief beryllium mineral

Table 3. Significant beryllium deposits and resources

Deposit(s)	Location	Resource, tons BeO	Grade, % BeO	Source
Volcanic rock-hosted				
Spor Mountain	Utah, United States	72,315*	0.71	This volume
Pegmatite				
Various	North Carolina, United States	122,800	0.05	Griffitts 1954
Various	Brazil	42,000	0.04	Soja and Sabin 1986
Various, Black Hills	South Dakota, United States	13,300	na†	Runke, Mullen, and Cunningham 1952
Tanco	Canada	1,800	0.20	Cerný 1982
Hellroaring Creek	Canada	<1,000	0.10	Barton and Young 2002
Replacement and skarn				
McCullough Butte	Nevada, United States	47,000	0.027	Barton and Young 2002
Sierra Blanca	Texas, United States	11,300	>2.0	Anon. 1986
Ermakovskoe	Russia	>10,000	1.3	Barton and Young 2002
Lost River	Alaska, United States	>10,000	0.3–1.75	Sainsbury 1963
Iron Mountain	New Mexico, United States	<1,000	0.2–0.7	Jahns 1944
Peralkaline rock-hosted				
Strange Lake	Canada	42,000	0.08	Richardson and Birkett 1996
Ilmaussaq	Greenland	>20,000	na	Barton and Young 2002
Thor Lake	Canada	13,300	0.76	Richardson and Birkett 1996
Seal Lake	Canada	6,800	0.35–0.40	Richardson and Birkett 1996
Greisen				
Aqshatau	Kazakhstan	16,000	0.03–0.07	Barton and Young 2002
Boomer	Colorado, United States	<1,000	2.0–11.2	Hawley 1969
Vein				
Gold Hill	Utah, United States	>5,000	0.5	Shawe 1966
Mount Wheeler	Nevada, United States	<1,000	0.75	Shawe 1966

* Remaining reserves 2004.

† na = not available.

of tactites and related rocks, but vesuvianite, grossularite, chlorite, and possibly other minerals also contain beryllium. The most thoroughly documented beryllium deposits in tactites in the United States are in New Mexico (Jahns 1944) and Alaska (Sainsbury 1963), although the Alaskan deposits are of minor significance. At the Ermakovskoe deposit in Russia, the largest skarn-related deposit in the world, early beryllian vesuvianite skarn was overprinted by late phenakite and bertrandite replacement ore with fluorite and carbonates (Barton and Young 2002). Other significant replacement deposits include beryllium-fluorite deposits hosted by carbonate rocks in Texas (Rubin et al. 1990), Nevada (Barton and Young 2002), and Mexico (Griffitts and Cooley 1978).

Beryllium in Greisen

Greisen vein and replacement deposits in and near granitic rocks may contain beryllium minerals in addition to tungsten and tin. Such deposits are typified by the presence of fluorite and topaz. Productive examples include small but high-grade deposits in Colorado (Hawley 1969) and large, low-grade resources in Kazakhstan (Barton and Young 2002). Beryllium minerals have also been found in the classical greisen deposits of Erzgebirge, Germany, and Cornwall, England.

Beryllium in Alkaline Igneous Rocks

Alkaline igneous complexes, some including nepheline syenite and other nepheline-bearing rocks, have been reported to contain as much as 0.76% beryllium oxide. Several large deposits of this type occur in the Northwest Territories and Labrador of Canada (Richardson and Birkett 1996). Beryllium mineral assemblages in such

deposits are complex. The classical peralkaline syenite complex at Ilmaussaq in Greenland contains a large beryllium resource of unknown grade, and alkaline rocks in the Kola Peninsula of Russia also contain beryllium minerals (Barton and Young 2002). Small quantities of beryllium-rich alkaline rock have been found in Arkansas and Colorado (Warner et al. 1959).

Beryllium in Coal

Beryllium also has been found in coal. Sampling of a variety of U.S. coal ashes indicated a significant distribution pattern for beryllium, with an average of 46 ppm for all of the samples (Stadnicko, Zubovic, and Sheffey 1961). Accumulation of beryllium in coal was determined to be a syngenetic process, and the beryllium content of the coal depends primarily on the rocks that contributed material to the coal-depositional sites.

DISTRIBUTION OF MAJOR DEPOSITS

United States

Because of its strategic importance, beryllium mineral occurrences in the United States were studied extensively in the years after World War II, particularly by the U.S. Geological Survey and the U.S. Bureau of Mines. During this period, the United States did not have a reliable domestic supply of beryllium minerals and relied on imports to supply most of its requirements. Most domestic beryllium was recovered from beryl produced as a by-product of mining other pegmatite minerals. After production of bertrandite began in Utah in 1969, providing the United States with a secure beryllium source, little effort was expended to evaluate additional beryllium mineral deposits.

One method of evaluating the importance of individual deposits is to examine the production record of each deposit. Since 1969, nearly all of the U.S. beryllium mineral production has been from one mine in Utah, and production of beryl has nearly ceased. The few beryl-producing mines that operate are almost all family owned, and production from these mines, which exploit pegmatite deposits, is sporadic. In the late 1950s, however, beryl was recovered as a by-product at as many as 200 operations in 12 different states. Quantities produced during this period ranged from a few kilograms to hundreds of tons. Because of the wide variation in beryl concentrations within an ore body, an individual mine may produce by-product beryl for a few years and then cease beryl recovery entirely.

New England

In general, New England beryllium occurrences are either very small or low grade and as such are not economically exploitable. Pegmatitic deposits in New England are grouped into five major districts, with other scattered occurrences. The major districts are Middletown, Connecticut; Keene and Grafton, New Hampshire; and Topsham and Paris-Rumford, Maine. Additional scattered pegmatites containing beryl occur in western Connecticut, western and central Massachusetts, eastern New Hampshire, and Maine. New Hampshire pegmatites were estimated to contain 1,630 t of beryl (Page and Larrabee 1962). Nonpegmatitic deposits in New England include beryl-bearing granite in western Connecticut, central Massachusetts, and eastern Maine; phenakite-danalite-helvite bodies in granite in central New Hampshire; and beryl-bearing quartz veins in northern Rhode Island.

The principal beryllium mineral in all the deposits except one is beryl, sometimes with associated small quantities of hercynite, bertrandite, beryllonite, or chrysoberyl. Because of ionic substitution of alkali metals in the crystal lattice, beryl in New England generally contains about 12.0% to 12.5% BeO and may contain as little as 9%, significantly less than the theoretical BeO content (Barton and Goldsmith 1968).

Beryllium mineral production in New England was limited to the recovery of beryl as a by-product of mica and feldspar mining in New Hampshire, Connecticut, and Maine beginning in the 1800s, and beryl was recovered sporadically from some of these operations until 1963. Most of the beryllium-bearing mines in New England were small open pits, and mining equipment was minimal.

Colorado

Colorado was one of the largest producers of beryllium minerals in the late 1950s. Much of the production was from a nonpegmatite deposit in Park County. Beryllium was found in dumps of the Boomer mine, a lead-silver prospect dating back to the 1890s, and this led to the discovery of high-grade, vein-type greisen beryllium ore in the old workings. Production began in 1956 and continued for a few years. This was most likely the first nonpegmatite ore mined in commercial quantities. The most important minerals present in the Boomer deposits are beryl and bertrandite (Meeves 1966).

South Dakota

During the late 1950s and early 1960s, South Dakota was the largest beryllium mineral-producing state in the United States. Beryl was recognized in the pegmatites of the Black Hills in the late 1800s, but substantial quantities were not produced until 1914. Most beryl was recovered as a by-product of feldspar and mica mining. Minor quantities of beryl continue to be recovered from deposits in Custer County.

The principal minerals in the South Dakota pegmatites are feldspar, quartz, and muscovite. Beryl was reported in all pegmatite

zones; commercial production, however, was predominantly from intermediate zones. Beryl was reported in fair quantities in the wall zones of certain pegmatites, and production was reported from the core. Both fracture fillings and replacement bodies may contain beryl.

Although some deposits in the Black Hills have been investigated, reserve estimates have varied widely because many deposits were not investigated fully or developed. Runke, Mullen, and Cunningham (1952) published reserve estimates of 13,300 t, with 2,400 t in dump material at 75 properties and 10,900 t in unmined portions of the deposits examined. Mining of beryl for beryllium processing from South Dakota ceased in the early 1990s.

Texas

The Sierra Blanca region in the far western part of Texas was investigated in the 1980s by Cabot Corp. as part of a nationwide beryllium geochemical reconnaissance survey. This region is characterized by five rhyolite bodies enriched in beryllium and other rare metals (Rubin et al. 1987) that intrude sedimentary rocks. Mineralization was emplaced as replacement ore in limestone adjacent to the rhyolite. Beryllium is mainly in bertrandite, but also occurs in behoite, phenakite, berborite [$\text{Be}_2(\text{BO}_3)(\text{OH},\text{F})\cdot\text{H}_2\text{O}$], and chrysoberyl (Rubin et al. 1990). Reserve estimates of these deposits were projected to be 11,300 t of BeO contained in deposits grading more than 2% BeO (Anon. 1986). A test mine was excavated and ore samples were evaluated to determine optimum processing methods, but because of a downturn in the beryllium market, a commercial operation was not started.

Utah

The principal beryllium deposit in the United States is bertrandite-bearing tuff that occurs in western Utah. In 1959, beryllium occurrences were discovered in rhyolitic tuff on the lower slopes of Spor Mountain in Juab County. The beryllium is associated with fluorite, lithium, and uranium minerals, and is regionally associated with topaz rhyolite that is enriched in beryllium and other lithophile elements such as niobium and yttrium (Lindsey 1977). Beryl was reported in rhyolite at Topaz Mountain, a few miles southeast of Spor Mountain, as early as 1905 (Davis 1984). The beryllium ore occurs principally in porous, water-laid Tertiary rhyolitic tuff that is overlain by hard, abrasive rhyolite. The tuff rests on a surface of Devonian dolomite and limestone. Drilling in the area indicated that the tuff ranges in thickness from a few meters to more than 80 m.

Montoya, Havens, and Bridges (1962) studied the chemical, mineralogical, and physical properties of the tuff, and found the analyzed tuff to contain from 0.2% to 1.8% BeO. Two beryllium-bearing minerals were found to be present—a hydrated form of bertrandite and a berylliferous saponite. Each of the mineral forms is predominant in certain areas of the district, but the beryllium is distributed erratically throughout the tuff in individual mineralized bodies.

Brush Resources Inc. began mining this deposit in 1969 by open-pit methods. As the company continues to develop new open pits, resource information on this area is updated. In its 2003 annual report, Brush Resource's parent company, Brush Engineered Materials Inc., estimated its proven reserves to be 6.687 Mt of bertrandite ore at year-end 2003, grading 0.267% Be. Probable bertrandite ore reserves were estimated to be 3.519 Mt grading 0.232% Be.

Other Countries

Brazil

Brazil is traditionally the largest beryl supplier in the international market. The principal beryl-producing areas are the Rio Doce Valley and adjacent areas in the state of Minas Gerais, the Campina Grande District in the state of Rio Grande do Norte, the Critais-Berilândia

District in the state of Ceara, and the Jequitinhonha River Province in the state of Bahia. Soja and Sabin (1986) estimated that more than 106 Mt of ore containing more than 15,000 t of beryllium was present in some properties evaluated in these areas, and almost 99% of the contained beryllium is available from the state of Minas Gerais.

All commercially mined pegmatite deposits in Brazil are complexly zoned or heterogeneous pegmatites. The heterogeneous pegmatites are normally composed of three zones, which are progressively coarser grained toward a quartz nucleus. The intermediate zone contains beryl as well as spodumene, columbite-tantalite, cassiterite, and semiprecious gemstones.

Canada

Beryllium occurrences were first noted in the Thor Lake area, near Yellowknife, Northwest Territories, in 1978. Further geological investigations resulted in the definition of a number of unusual mineral assemblages that appear to be products of the somatic replacement of syenitic and granitic types. Beryllium mineralization, primarily as phenakite, is widespread in all the rock types in the area except the syenite (Trueman, Pedersen, and de St. Jorre 1984). In the mid-1980s, Highwood Resources Ltd. began drilling in the Thor Lake area and identified four different zones—the R zone, the S zone, the T zone, and the Lake zone. Much of the beryllium-rich rock was found in the T zone, and reserves were estimated to be 450,000 t of ore grading 1.4% BeO in the T zone and 1.3 Mt of ore grading 0.66% BeO south of the T zone (Anon. 1985). Preliminary studies indicated that recoveries of 80% to 90% could be obtained, producing a concentrate containing 10% to 13% BeO. Because of difficulties in marketing the products, a mine was never opened at this location.

Large concentrations of beryl and euclase have been reported in peralkaline igneous rocks near Seal Lake in Labrador (Table 3), and a larger (although lower-grade) resource occurs in a peralkaline complex at Strange Lake. The Tanco pegmatite near Lac du Bonnet in Manitoba, which has been mined for tantalum and lithium minerals, is a potential source of beryl, with ore reserves estimated at 920,000 t grading 0.2% BeO (Cerný 1982). The Hellroaring Creek prospect west of Kimberley, British Columbia, is underlain by a beryl-bearing pegmatitic body, with indicated ore resources of 500,000 t grading 0.1% BeO (Schiller 1985).

Russia

The Ermakovskoe deposit in Transbaikalia, Russia, has been an important source of beryllium. The deposit has been described as “skarn-related” (Barton and Young 2002). The ore minerals are mainly phenakite and bertrandite, but the deposit also contains a suite of unusual beryllium minerals as well as beryllian vesuvianite. Beryllium enrichment has also been reported in association with alkaline rocks on the Kola Peninsula and in skarn in far eastern Russia (Barton and Young 2002).

Kazakhstan

Kazakhstan has produced beryllium from an unknown source in recent years (Table 1). Barton and Young (2002) reported the occurrence of beryllium-bearing vein, skarn, greisen, and replacement deposits in the country. The Aqshatau tungsten-molybdenum-beryllium greisen deposits in central Kazakhstan have low-beryllium grades but nonetheless constitute a large resource (Table 3).

China

China is currently the third leading producer of beryllium (Table 1), but little information is available about the source. Beryllium-bearing

vein, skarn, greisen, and replacement deposits are known in the country (Barton and Young 2002).

Australia

Beryllium occurs with zirconium, niobium, tantalum, and rare earth elements in the Brockman deposit, Western Australia, as bertrandite-quartz-carbonate veinlets in metamorphosed tuff. The Brockman beryllium reserves are moderate and low grade. Skarn and replacement tin ore has been reported to contain as much as 0.5% BeO as danalite at Mount Lindsay in Tasmania (Kwak 1983).

Other Occurrences

Beryllium has been recovered from small deposits in many countries throughout the world, but production has been sporadic. In the past 40 years, the countries with the largest contribution to world production outside the United States, Brazil, Russia, China, and Kazakhstan, have been Argentina, India, Mozambique, Rwanda, and Zimbabwe. In the 1990s, beryl from Nigeria was marketed, and in recent years, Zambia and Portugal have produced small amounts of beryllium. Because of the nature of beryl mining, production is subject to internal political and social pressures in individual countries, particularly those in Africa. As a result of limited production, deposits in most other countries are not well documented.

Exploration

In many cases, the presence of beryl is visible by the naked eye. It typically occurs as greenish-white crystals, and because it is usually associated with colorless quartz, large crystals are easily distinguished. For other beryllium minerals and finely disseminated beryl crystals, a beryllometer is normally used in the field for detecting beryllium mineralization. The beryllometer uses gamma radiation supplied by an antimony-124 radioisotope to generate neutrons when the radiation field comes into contact with a beryllium-bearing mineral. This equipment is similar to a geiger counter used to detect uranium. Beryllometers can be made with a sensitivity of 0.01% Be or less. Detection of beryllium in ore is usually followed by diamond drilling and assaying to further delineate beryllium deposits.

Mining

Brush Resources mines bertrandite by open-pit methods at Spor Mountain. Unlike beryl, in which the mineral can be identified by color and crystal structure, bertrandite mineralization cannot be recognized by the naked eye. Consequently, Brush Resources conducts geologic and geochemical evaluations on a specific area, followed by a drilling program to determine if an economic ore body exists.

After delineating an ore body, overburden is removed to within 2 m of the ore by a local earth-moving contractor during the winter and spring. This stripping operation usually requires about 9 months for completion. In the 2-m cover remaining, drill benches are constructed on 7.5-m centers to take samples of the ore body at 0.6-m intervals. Information obtained from analyzing the samples allows cross sections and contour maps to be developed. These maps are used to plan the mining and processing operations.

After the maps are prepared, the remainder of the overburden is removed, and the ore is mined, typically with a self-loading scraper. Because of the irregular ore-grade distribution in the ground, the ore is mined from areas defined by drill data and placed in a stockpile in layers to obtain a more homogeneous blend. Further drilling, sampling, and assaying of the stockpiled ore is then performed to generate a map that delineates ore-grade distribution throughout the stockpile. On the basis of the grade distribution, stockpiled ore is selectively trucked to the mill, which is about 80 km away, for further processing.

Table 4. Copper-beryllium alloy specifications

Brush Alloy	Copper Alloy UNS Number	Chemical Composition, wt %						
		Beryllium	Cobalt	Nickel	Cobalt + Nickel	Cobalt + Nickel + Iron	Lead	Copper
25	C17200	1.80–2.00	—*	—	0.20 minimum	0.6 maximum	0.02 maximum	Balance
190								
290								
M25	C17300	1.80–2.00	—	—	0.20 minimum	0.6 maximum	0.20–0.6	Balance
165	C17000	1.60–1.79	—	—	0.20 minimum	0.6 maximum	—	Balance
3	C17510	0.2–0.6	—	1.4–2.2	—	—	—	Balance
10	C17500	0.4–0.7	2.4–2.7	—	—	—	—	Balance
174	C17410	0.15–0.50	0.35–0.60	—	—	—	—	Balance
60	C17460	0.15–0.50	—	1.0–1.4	—	—	—	Balance

Courtesy of Brush Wellman Inc.

Note: Copper plus additions equals 99.5% minimum.

* — indicates constituent not normally present or present below practical reporting levels.

beryllium plate. In impact grinding, a high-velocity stream of air blasts a mixture of chips and oversize powder onto a solid beryllium target. On impact, the chips break into small particles that are removed from the chamber by vacuum conveying. A ball mill is used when extremely fine powder is required. After grinding, the beryllium powder is sized, either with screens or an air classifier. Beryllium powder is formed into billets by vacuum hot pressing, hot-isostatic pressing, or cold-isostatic pressing, depending on the end use of the material. Beryllium metal production flow charts are shown in Figures 2 and 3, and specifications are given in Table 5.

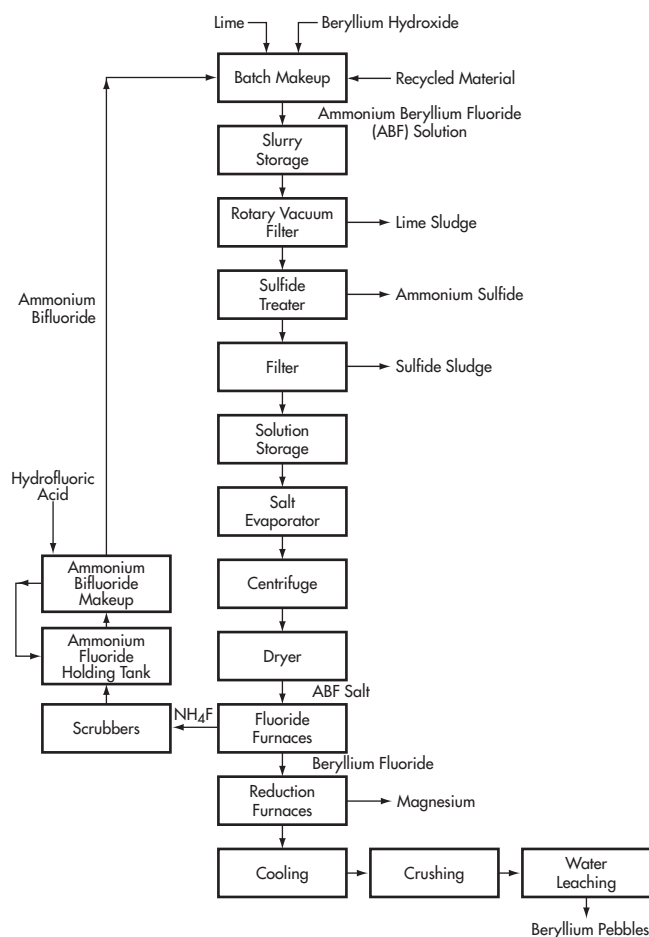
Beryllium Oxide Production

Beryllium oxide powder is produced by dissolving beryllium hydroxide in sulfuric acid. The resulting beryllium sulfate solution is concentrated by evaporation and cooled until the solution is supersaturated. During cooling, beryllium sulfate tetrahydrate crystals are produced. Wet salt crystals are removed from the mother liquor in a centrifuge. Calcining these crystals in a car-hearth furnace at temperatures up to 1,430 °C decomposes the salt to be ryllium oxide, water vapor, and sulfur dioxide (SO₂) and sulfur trioxide (SO₃) gases. The gases are fed through scrubbers, and the beryllium oxide is cooled, screened, and bagged for shipment. Figure 4 shows a beryllium oxide production flow chart.

INDUSTRY STRUCTURE

The United States has the largest demonstrated capacity to process beryllium ore and concentrates into finished beryllium products and supplies most of the rest of the world with these products. As described previously, Brush Resources Inc., a subsidiary of Brush Engineered Materials Inc., mines bertrandite and converts this ore, along with beryl, to beryllium hydroxide at its facility in Delta, Utah. Beryllium hydroxide is shipped to a plant in Elmore, Ohio, operated by Brush Wellman Inc. (another wholly owned subsidiary of Brush Engineered Materials), where it is converted into beryllium alloys and metal. At its Elmore plant, Brush Wellman also produces beryllium oxide, which is further processed into basic ceramic shapes at the Brush Ceramic Products Inc. plant in Tucson, Arizona.

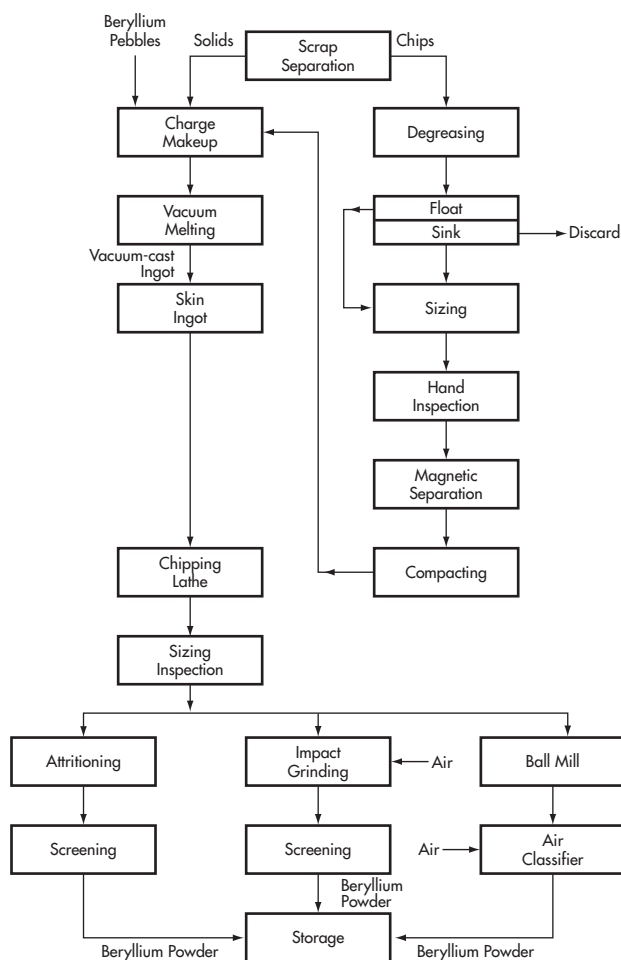
One other company in the United States has the capability to process beryllium alloys. NGK Metals Corp., a subsidiary of NGK Insulators of Japan, produces intermediate forms of beryllium alloys at its plant in Nagoya, Japan. The basic shapes are shipped to a plant in Sweetwater, Tennessee, for further processing and distribution. NGK Metals in Japan reportedly does not have facilities to process the raw materials.



Courtesy of Brush Wellman Inc.

Figure 2. Beryllium pebble production

Ore production from labor-intensive operations outside the United States is sporadic, except for the largest producers in Brazil, China, and some nations of the Commonwealth of Independent States. Before 2000, the majority of the beryl recovered in Brazil was exported to the United States, and Brazil remains the largest



Courtesy of Brush Wellman Inc.

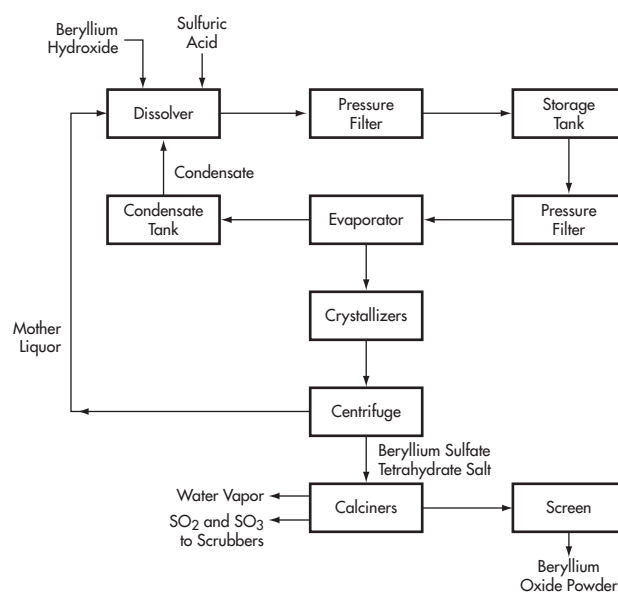
Figure 3. Beryllium powder production

Table 5. Beryllium specifications, wt %

Constituent	Commercial Beryllium Powder SP-200F	National Defense Stockpile Hot-Pressed Powder Billet		
		Grade A	Grade B	Grade C
Be, minimum	98.5	98.0	98.0	94.0
BeO, maximum	1.5	1.5	2.2	9.0
Al, maximum	0.1	0.07	0.10	0.16
C, maximum	0.15	0.10	0.15	0.25
Fe, maximum	0.13	0.12	0.15	0.25
Mg, maximum	0.08	0.08	0.08	0.08
Si, maximum	0.06	0.08	0.08	0.08
Other, each, maximum	0.04	0.04	0.04	0.10

Courtesy of Brush Wellman Inc.

source of beryl imported into the United States. Some beryl ore from China has been imported into the United States in previous years. Recently, China has developed some capability to process beryl and produce some beryllium-copper master alloys. Kazakhstan also has an integrated beryllium industry, based on a stockpile



Courtesy of Brush Wellman Inc.

Figure 4. Beryllium oxide production

of previously mined ores, and has recently restarted operations to market a restricted range of beryllium products.

Beryllium Alloys

Brush Wellman Inc. converts beryllium hydroxide from the Brush Resources mine in Utah into a wide range of alloys of beryllium with copper, nickel, and aluminum at its smelter in Elmore, Ohio. That facility processes the alloys into a wide range of different shapes, such as plate, bar, tube, strip, and wire. Additional strip- and rod-finishing facilities in Reading, Pennsylvania, provide precision finishing capabilities. Currently, Brush Engineered Materials is the only integrated producer of such alloy products in the world.

Copper-beryllium alloys are used in a wide variety of applications and account for approximately 65% of the annual U.S. production of beryllium, on a metal equivalent basis. These alloys, most of which contain between 0.15% and 2% beryllium, are used because of their combination of high electrical and thermal conductivity, high strength and hardness, good corrosion and fatigue resistance, and nonmagnetic properties. Copper-beryllium strip is manufactured into electrically conductive springs, connector terminals, and switches that are used in automobiles, aerospace applications, radar equipment, telecommunications equipment, computers, factory automation devices, home appliances, and instrumentation and control systems. The principal use of large-diameter copper-beryllium tubing is in oil and gas drilling equipment and in bushings and bearings in aircraft landing gear and heavy machinery. Mechanical enclosures and coupling fittings for electronic amplification repeater housings for fiber-optic telecommunications systems represent a significant application for large-diameter copper-beryllium rod and tube stock. Small-diameter copper-beryllium rod and wire is extensively used for the machined miniature sockets that connect integrated circuits to printed circuit boards. Copper-beryllium bar and plate is used in the fabrication of equipment used for the resistance welding of automobile and appliance bodies; for machinery components; for materials handling systems; and for molds used to form metal, glass, and plastic components.

Smaller quantities of beryllium are also used in nickel- and aluminum-base alloys. Electronic connector components that can operate at high temperatures such as those in household cooking appliances and springs used to activate fire sprinklers are leading uses for nickel-beryllium alloys. Aluminum-beryllium alloys are used both in aerospace casting applications and as a master-alloy additive to include small quantities of beryllium in magnesium alloys, which inhibits oxidation during melting operations.

Beryllium Metal

Beryllium metal products, which account for about 20% of the annual U.S. demand for beryllium, are used principally in aerospace and defense applications. The high stiffness, light weight, and dimensional stability over a wide temperature range make beryllium metal useful in satellite and space vehicle structures, inertial guidance systems, avionics, and space optical system components. Because beryllium is transparent to x-rays, it is used in x-ray windows. In nuclear reactors, beryllium also serves as a neutron moderator, in control rods, and as a reflector. Other applications for metallic beryllium include high-speed computer components, audio components, precision electronics processing equipment, and optical scan mirrors. Beryllium metal is used for several applications in NASA's space shuttle, including window and door frames. It is also used to manufacture key components of critical guidance and navigation equipment.

Beryllium Oxide

Beryllium oxide or beryllia is an excellent heat conductor, with high hardness and strength. This material also acts as an electrical insulator in some applications. Beryllium oxide, accounting for about 15% of domestic demand, serves mainly as a substrate for high-power electronic circuits for radio frequency electronics, automotive ignition modules, laser bore components, and radar electronic countermeasure systems. Because it is transparent to microwaves, mobile telephone systems and radar systems also use beryllium oxide.

ECONOMIC FACTORS

Prices

In the past, prices for imported beryl and domestically produced beryllium products were reported by the *American Metal Market*; however, that publication no longer tracks beryllium ores and products. An update on the year-end 2003 prices is not available at this time. After Brush Wellman opened its bertrandite mining operation in 1969, applications for beryllium metal were expanded in the aerospace and nuclear industries. As these new uses were developed, prices remained relatively steady to encourage continued expansion. In the late 1970s, prices escalated rapidly in response to high inflation rates and increased energy costs. At the same time, the U.S. Occupational Safety and Health Administration (OSHA) and the U.S. Environmental Protection Agency (EPA) promulgated new regulations concerning beryllium air emissions. To comply with these regulations, beryllium processing plants were required to install additional pollution control equipment, and the additional costs were ultimately passed on to the consumer. In the 1980s, greater regulation of waste products from beryllium mining and processing increased disposal costs. Again, the increased costs resulted in higher prices for the consumer.

Tariffs and Depletion Allowances

Tariffs for beryl and beryllium products are shown in Table 6. Beryllium ores carry a 22% domestic depletion allowance and a 14% foreign depletion allowance.

Table 6. U.S. import duties*

Tariff Item	HTS No.†	Normal Trade Relations 12/31/03
Ore and concentrate	2617.90.0030	Free
Unwrought beryllium powders	8112.12.0000	8.5% ad valorem
Beryllium, wrought	8112.19.0000	5.5% ad valorem
Beryllium waste and scrap	8112.13.0000	Free
Beryllium-copper master alloy	7405.00.6030	Free
Beryllium oxide or hydroxide	2825.90.1000	3.7% ad valorem
Other	8112.19.00000	5.5% ad valorem

Courtesy of U.S. Geological Survey.

* Ore, metal, scrap, and master alloy: Japan, 28%; Kazakhstan, 24%; Russia, 10%; Brazil, 9%; and other, 29%.

† HTS = Harmonized Tariff Schedule of the United States.

Alternative Materials

Because of its high cost compared with that of other materials, beryllium is used in applications in which its properties are uniquely enabling. Aluminum, magnesium, and titanium alloys, as well as graphite composite materials, may be substituted for beryllium metal in some applications. Many different copper alloys such as phosphor bronzes may be substituted for beryllium-copper alloys. These substitutions, however, can result in substantial loss of performance in some applications, requiring considerable engineering, research, and redesign to compensate for performance loss. Beryllium oxide may, in some cases, be substituted by aluminum oxide or aluminum nitride.

SAFETY REGULATIONS

Beryllium dust and fumes have been recognized as the cause of chronic beryllium disease (CBD), a serious chronic lung disease. The disease was first described by Dr. Harriet Hardy in 1946, before suitable hygienic procedures had been established, among industry employees and their relatives who had handled dusty work clothing. Before modern emission controls came into use, cases of CBD were also reported in the 1940s and 1950s among residents of communities surrounding beryllium-processing plants.

To contract CBD, an individual must be exposed to airborne beryllium in the form of a dust, mist, or fume. This particulate must be small enough (less than 10 µm in diameter) to reach the air sacs deep in the lungs and the individual must be sensitive to beryllium. Not all individuals exposed to airborne beryllium particulate will become sensitized, and of those who become sensitized, not all will develop CBD. Scientists believe that the capacity to develop sensitivity to beryllium is genetically determined and that most people are not susceptible to sensitization.

In recent years, various individuals and organizations have reported that the number of diagnosed cases of CBD has increased since the 1980s. The main factors for this apparent increase are the change in diagnostic criteria for the disease, improvements in medical detection technology, and an increase in the number of workers evaluated for subclinical CBD.

Before the late 1980s, workers were diagnosed with CBD only when they exhibited clinical (observable) symptoms and changes were found in chest x-rays or lung function tests. During the late 1980s and early 1990s, the diagnostic criteria changed, and workers began to be diagnosed without exhibiting clinical symptoms or measurable impairment. Workers diagnosed with CBD in the absence of x-ray or lung function changes or symptoms of disease are referred

to as having subclinical CBD, meaning that they have no clinical symptoms or measurable impairment. This diagnosis became possible through the application of new technology in medical testing and evaluation. Today, workers are typically diagnosed on the basis of sensitization and the presence, on biopsy, of microscopic biological lung formations called granulomas. The biopsy, which uses a procedure called bronchoscopy, is required for obtaining samples of lung tissue. Bronchoscopy with lung biopsy is medically invasive and has its own associated health risks, such as a collapsed lung, bleeding or infection, and a possibility of death.

The natural history of subclinical CBD is not yet known. Workers with subclinical CBD may never develop clinical CBD, or they may develop clinical CBD over time. It is very evident from scientific studies, however, that the incidence of subclinical CBD is higher than the long observed rate of clinical CBD. If most subclinical cases of CBD progressed to a clinical state, historical studies would have shown much higher rates of clinical CBD. It is therefore logical to surmise that in most persons, there is no significant progression of the subclinical disease.

Before the late 1980s, the term "beryllium sensitization" referred to the inflammatory response in the lungs (health effect), which was originally associated with the early stages of clinical CBD. Today, however, the term beryllium sensitization has come into stricter use to describe a positive response to the testing of blood or lung fluid using the beryllium blood lymphocyte proliferation test (BLPT). The BLPT is a laboratory test that measures a level of response when a water-soluble beryllium compound is added to cells isolated from a blood or lung fluid sample. Sensitization does not describe a health effect in the person but rather a response in the blood separate from the person. As detected using the BLPT, sensitization is not an illness or disability, and the test does not detect subclinical or clinical CBD. Competent authorities, such as the American Conference of Governmental Industrial Hygienists, the U.S. Army, U.S. Air Force, and U.S. Navy, have published position papers on use of the BLPT, which recommend that the BLPT not be used for worker screening in the absence of health symptoms.

Although uncertainties related to the cause of the disease still exist, the problem appears to be controlled when established preventive measures are exercised. In beryllium processing plants, harmful effects are prevented by maintaining clean workplaces; requiring the use of safety equipment such as personal respirators; collecting dust, fumes, and mists at the source of deposition in dust collectors; instituting medical programs; and putting other procedures in place to ensure safe working conditions. Control of potential health hazards may add significantly to the final cost of some beryllium products.

OSHA regulates worker exposure to airborne particles containing beryllium. Current OSHA standards limit the 8-hour exposure level to an average of $2 \mu\text{g}/\text{m}^3$ of air, with a peak of $25 \mu\text{g}/\text{m}^3$ not to exceed 30 minutes, and a ceiling concentration of $5 \mu\text{g}/\text{m}^3$. Mine Safety and Health Administration regulations, which are the same as the OSHA standards, affect only the Brush Resources operation in Utah.

Natural and Anthropogenic Sources of Human Beryllium Exposure

The general population is exposed to naturally occurring beryllium from the ambient air, drinking water, and dietary intake on a daily basis. Average ambient concentrations of beryllium in soil range from 2.8 to 5 mg/kg. The average ambient concentration in air in the United States is $0.00003 \mu\text{g}/\text{m}^3$; the median concentration in cities is $0.0002 \mu\text{g}/\text{m}^3$.

Concentrations of beryllium in drinking water range from 10 to 1,220 ng/L with an average of 190 ng/L. The U.S. Agency for Toxic Substances and Disease Registry has estimated that within the United States, about 45% of airborne beryllium results from anthropogenic releases of beryllium. Natural sources such as windblown dust and volcanic activity account for 55% of beryllium released to the atmosphere. Electric utilities generate about 80% of the anthropogenic emissions, and industry and metal mining accounts for about 20%. Beryllium has been measured in rice at $72 \mu\text{g}/\text{kg}$ (fresh weight), lettuce at $16 \mu\text{g}/\text{kg}$, kidney beans at $2,200 \mu\text{g}/\text{kg}$, peas at $109 \mu\text{g}/\text{kg}$, and potatoes at $0.59 \mu\text{g}/\text{kg}$. Beryllium has been found in cigarettes at up to $0.74 \mu\text{g}$ per cigarette. The daily intake of beryllium by nonoccupationally exposed persons from food and water is approximately $0.52 \mu\text{g}$ per day with negligible exposures from ambient air. The average burden of beryllium in nonoccupationally exposed persons is $2.00 \mu\text{g}/\text{kg}$ in the lung, whereas beryllium concentrations in other organs are typically below $80 \mu\text{g}/\text{kg}$.

ENVIRONMENTAL REGULATIONS

Under the Clean Air Act, the EPA has issued standards for certain hazardous air pollutants, including beryllium. Beryllium emissions for plants that process beryllium materials are limited to 10 g of beryllium over a 24-hour period. Plants that machine alloys containing beryllium with less than 4% beryllium by weight are excluded from the hazardous air-pollutant regulations. The EPA regulates beryllium at 4 ppb under the Safe Drinking Water Act.

PROBLEMS AND FUTURE TRENDS

The beryllium industry is rather limited in scale because a single active producer in the United States supplies beryllium-containing materials from its raw material source and processing plants for almost all domestic and most worldwide consumption. Although several other companies have investigated beryllium production as a potential business, it is unlikely that any new plants will be constructed in the United States, primarily because of the significant costs to construct a plant that meets environmental regulations. The commercial outlook for beryllium-containing materials is favorable, especially given their ability to enable end-use products to meet toughening performance demands for weight savings and miniaturization, greater strength, fatigue and corrosion resistance, and thermal and electrical conductivity. Materials producers such as Brush Wellman have continued to work closely with customers in the telecommunications and computer, a automotive electronics, aerospace and defense, oil and gas, industrial components, and appliance industries to ensure new materials are developed in step with advances in end-use product technology. In the past 20 years, for example, Brush Wellman has introduced new proprietary alloys such as Alloy 174, Alloy 60, and most recently, Alloy 390, to serve the market's higher performance requirements. On the metallic beryllium side, the company has introduced AlBeMet, an aluminum-beryllium-metal-matrix composite, to fulfill the unique high performance needs of the aerospace and defense markets.

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Boron and Borates

Steven B. Carpenter and Robert B. Kistler

INTRODUCTION

Boron, element number five on the periodic chart, does not occur alone in nature. Except for a few rare minerals, it is always combined with oxygen. Borates are therefore defined as minerals containing boric oxide or boron–oxygen molecules. These can generally be expressed on the basis of B_2O_3 in combination with a major cation. Borates are sold on the basis of their boric oxide content, and most products and government statistical data are shown in short tons of B_2O_3 (rather than B).

Borates today are used mainly as chemical raw materials in combination with other commodities to produce products used by the ultimate consumers. Fiberglass and glass fibers, glass and ceramics, soaps and detergents, fertilizers and herbicides, and wood preservatives are the major segments of today's market, although more than 25% of the world's borates are used in numerous other consumer products.

Economic mineral concentrations of borates are relatively rare in nature; however, the major deposits now in production are able to adequately supply the existing markets at reasonable prices. Currently, the United States and Turkey supply more than 75% of the world's markets from deposits that are found in Neogene age (<24 million years), continental sediments.

The mineral borax may have been known by ancient civilizations, but the first authenticated use of borates was as a flux for assaying and refining precious metals in the 8th century AD. China was probably the first country to consistently use borates in medicines and ceramics from about 1000 AD (Smith 1997); the borates used were mined from spring deposits and salars or dry lakes in Tibet. Marco Polo claimed to have brought the first borates from China to Europe, and his home port of Venice became the center for fine work in gold, ceramics, and glassware. The use of borates to make these items was a well-guarded Venetian "trade secret" for many years. Elsewhere in Europe, alchemists, and later the medical profession, used small amounts of borates, but the price was high (as late as 1790 the price of refined borax was about \$3/oz in London) and the source of this rare mineral commodity remained mysterious.

Tibet continued to be the source for most borates until the beginning of the 19th century when sassolite was discovered around the fumaroles of Larderello, near Pisa, Italy. Commercial production began there in 1808, and this area soon replaced Tibet as the major western source of borates. The discovery of borates in

the desert marshes of the New World, in both North and South America in the mid-19th century and their subsequent popularization by F.M. "Borax" Smith and others, helped lower the price and expand usage into consumer products, especially soaps and detergents. By 1890, borates were readily available in Europe and the United States at about \$75/t. Finally, the discovery and development of major bedded deposits during the 20th century, first in Death Valley and later at Boron, California, and in Turkey, enabled this once rare mineral to expand into the major, worldwide commodity that it is today.

PRODUCTION AND TRADE

Commercial borate production is centered in southern California, western Turkey, northern Argentina and Chile, southern Bolivia and Peru, eastern Russia, and northeastern and west-central China (Figure 1). The major materials sold are borax pentahydrate (5 mol) and decahydrate (10 mol) and boric acid, followed by colemanite and ulexite mineral concentrates.

The United States is the leader in production of refined borates and boric acid; about half of the domestic production is exported (Table 1). Turkey is the world's major supplier of mineral concentrates and also produces large amounts of boric acid and refined borates. Almost 90% of their production is sold on the export market.

South American production has usually been sold into Brazil and other countries in the southern hemisphere, with sales mainly for agriculture and ceramics. Recently increased production, however, particularly of boric acid, has moved sales into Asia and North America, generally where price is the major consideration.

Russia produces mainly boric acid from their unique borosilicate deposit near the Sea of Japan. Historically, the former U.S.S.R. sent this production by rail as far west as eastern Europe, but with the changing economic climate and their advantageous position near tidewater, some of their boric acid now goes to China, South Korea, and Japan. Chinese borate production is from a number of relatively small mines in both the western and the northeastern parts of that country. Their borate production has yet to equal their internal demand, and most of the Chinese borates are sold within the country; they do, however, export some product to India, Pakistan, Indonesia, and South Korea (Table 2). Figure 2 illustrates current consumption of borates, broken down by end use, in both the United States and the world.

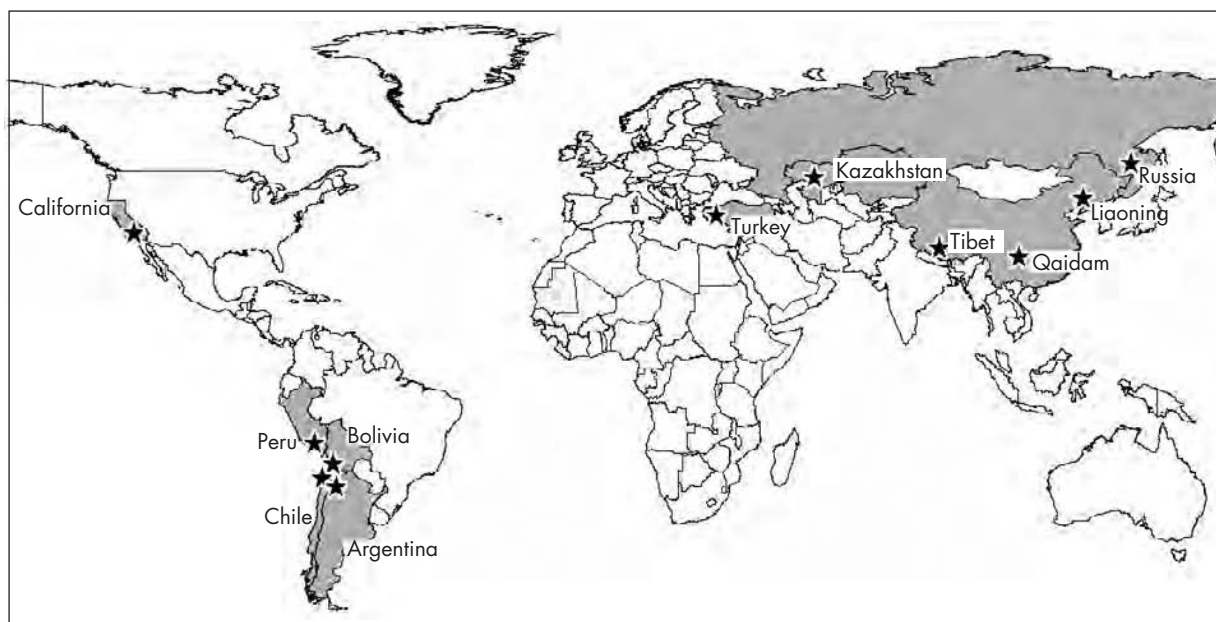


Figure 1. Major world borate deposits

Table 1. U.S. borate production, imports and exports, *kt of B₂O₃*

	1999	2000	2001	2002	2003*
U.S. production	618	546	536	518	536
Imports for consumption, gross weight					
Borax	8	1	1	<0.5	16
Boric acid	30	39	56	49	45
Colemanite	42	26	35	32	14
Ulexite	178	127	109	125	99
Exports, gross weight					
Boric acid	107	119	85	84	79
Colemanite	NA†	NA	NA	5	23
Refined sodium borates	370	413	221	150	142

Courtesy of U.S. Geological Survey (USGS).

* Estimated.

† NA = not available.

Table 2. World borate production—all forms, *gross weight of ore in kt*

Country	2001	2002	2003*
Argentina	500	510	170
Bolivia	34	35	33
Chile	338	330	430
China	150	145	140
Iran	1	4	4
Peru	30	9	9
Russia	1,000*	1,000*	1,000*
Turkey	1,500	1,500	1,500
United States	1,050	1,050	1,060
World total (rounded)	4,600	4,580	4,350

Courtesy of USGS.

* Estimated.

GEOLOGY

Mineralogy

More than 200 minerals contain boron, but only a few are commercially important (Table 3). The majority of borate minerals can be divided into three groups for ease of discussion: sodium and calcium borates, magnesium borates, and borosilicates. In general, sodium and calcium borates are formed under near-surface conditions as a result of volcanic activity and are associated with continental sediments and volcanic rocks. Magnesium borates are most often found with marine sediments, whereas borosilicates are associated with metamorphic and igneous rock and mineral assemblages.

Borates commonly occur with the following elements—arsenic, antimony, calcium, iron, lithium, magnesium, manganese, silica, and sodium—and zeolite minerals. There is also an apparent association with some metals such as gold, iron, and zinc, depending on the geologic setting.

Tests

The early prospectors' test for borate was to wet the sample with sulfuric acid and a little alcohol and light the fumes; "She burns green!" was the result of a successful test. Wetting a sample with specially prepared turmeric or cobalt-nitrate solutions also provides quick positive or negative field test results. Today, most commercial laboratories detect and identify borates using atomic absorption (AA) or inductively coupled plasma (ICP) methods.

Chemical Properties

Boron has the valence state 3+. It forms very strong covalent bonds with oxygen and links with either three oxygen atoms to form triangular planar BO₃ groups or four oxygens to form tetrahedral BO₄ groups (Smith and McBroom 1992). These groups can link together by sharing oxygen atoms to form rings, cages, chains, sheets, and networks. The resulting borate structures possess a negative charge equal to the number of BO₄ groups they contain, because these have a formal 1– charge. As a result, borates form salts and double

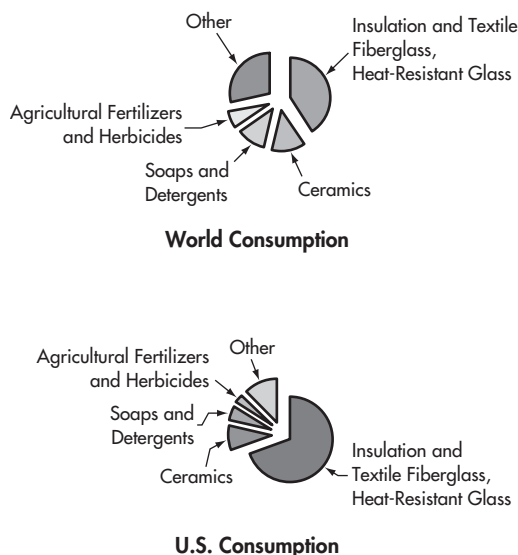


Figure 2. Estimated world and U.S. borate consumption by major end use

Table 3. Commercially important borate minerals

Mineral	Chemical Composition	Wt % B ₂ O ₃
Borax (tincal)	Na ₂ B ₄ O ₇ •10H ₂ O	36.5
Boracite (stassfurtite)	Mg ₆ B ₁₄ O ₂₆ C ₁₂	62.2
Colemanite	Ca ₂ B ₆ O ₁₁ •5H ₂ O	50.8
Datolite	CaBSiO ₄ OH	24.9
Hydroboracite	CaMgB ₆ O ₁₁ •6H ₂ O	50.5
Kernite (rasorite)	Na ₂ B ₄ O ₇ •4H ₂ O	51.0
Kurnakovite	Mg ₂ B ₆ O ₁₁ •15H ₂ O	37.3
Pinnoite	MgB ₂ O ₄ •3H ₂ O	42.5
Priceite (pandermite)	CaB ₁₀ O ₁₉ •7H ₂ O	49.8
Probertite (kramerite)	NaCaB ₃ O ₉ •5H ₂ O	49.6
Sassolite (natural boric acid)	H ₃ BO ₃ 56.3	
Szabelyite (ascharite)	MgBO ₂ OH	41.4
Tincalconite (mohavite)	Na ₂ B ₄ O ₇ •5H ₂ O	47.8
Ulexite (boronatocalcite)	NaCaB ₅ O ₉ •8H ₂ O	43.0

salts with various cations and with interstitial water (Chang 2002). Hydrated borates contain B–OH groups, O[−] groups, or water.

The common borates are slightly basic with a pH of 7 to 10. Their solubility curves are fairly normal from about 50° to 120°C (Garrett 1998). Borax (10 mol) is readily soluble in water and will lose 5 mol of water under summer desert conditions to form tincalconite (natural 5 mol). Ulexite and colemanite are only slightly soluble in water under atmospheric conditions but dissolve rapidly in acid. The Russian borate ore minerals, datolite and danburite, and the principal Chinese borate ore, szabelyite, are acid soluble.

Origin and Modes of Occurrence

Borates are present in low concentrations in most soils and in many rock types. Borates in soil tend to collect on micas and in the molecular lattice of clays in concentrations of <10 to >150 ppm B. The average concentration in surface streams is reported to be about 0.1 ppm, and in seawater averages about 4.6 ppm (Sprague 1972).

Borate deposits throughout the world are found in tectonically active, extensional terrains near subducted plate boundaries. They are associated with calc-alkaline extrusive rocks, tuff, tuffite, limestone, marl, claystone, gypsum, and continental silts and sands; the ultimate source of the boron, however, is still under discussion. The boron may be leached from marine sediments in the mio- or eugeo-synclinal continental margins or from earlier granitoids and brought to the surface by volcanic activity associated with the subduction of plate margins (Kasemann, Erzinger, and Franz 2000). Others suggest that the B₂O₃ may be leached from the surrounding rocks; local ignimbritic volcanism is considered the source for the Kirka deposit in Turkey (Floyd, Helvacı, and Mittweide 1997). Limited field investigations by the authors indicate that rocks surrounding and down-dip from known deposits are usually low in boron and show no signs of having been leached, which casts some doubt on local, near-surface crustal sources for most North American borate deposits.

Most of the commercial-grade borate deposits worldwide are associated with continental sediments. These can be divided into spring and spring-apron deposits, playa or salar accumulations, and lake deposits, although there is a gradation between these categories.

All the major “world class” deposits in North America and Turkey are found within Neogene lake sediments that are associated with contemporaneous faulting and volcanism. The borates within these lake sediments appear to be chemical precipitates that formed as the concentration of boron in the lake waters reached temporary saturation levels, either because of changes in the evaporation rate or from periodic influxes of boron-rich waters from nearby springs. Precipitation of the primary borate minerals appears to be controlled by pH. Borax precipitates at a higher pH than ulexite and colemanite forms as a primary mineral at a slightly lower pH and warmer temperature (Helvacı and Orti 1998).

The Searles Lake brines, a major borate source in the United States, are unusual in that they have resulted from the progressive concentration and decanting of salts from springs quite a distance from the lake (Smith 1979). A local spring source associated with the tuff cones within the lake itself may, however, also have furnished at least some of the salts, including the borates.

Neogene to Recent age salar or playa borate deposits, mainly ulexite, are an important borate source in South America and China. The Recent age deposits have near-surface water tables, fed by springs that appear to furnish the borates. Depositional control is related to spring outflow, borate concentration of the water, pH, and possibly changes in pressure. These deposits are within currently active volcanic belts associated with plate subduction boundaries.

Some accumulations of borates are directly associated with active hot springs or fumaroles. Larderello in Italy and Clear Lake in California are examples; others such as Antuco in Argentina and many of the Tibetan sources are formed from spring waters cool enough to be frozen during part of the year. It is clear that surface water temperatures are not as important as borate content.

Borate deposits associated with marine sediments appear to form in near-shore bays, possibly enhanced by borate springs. The borate-enriched seawater is concentrated during desiccation and compaction of the sediments, resulting in the deposition of the primary borates. Some accumulations of marine borates are further concentrated during uplift, by erosion or dissolution of the associated salts.

Igneous and metamorphic borate concentrations are formed from hydrothermal solutions that accompany granitoid intrusions. There is no universal agreement on whether the borates are in the magmatic fluids or if the fluids act on and incorporate borate-containing calcareous sediments.

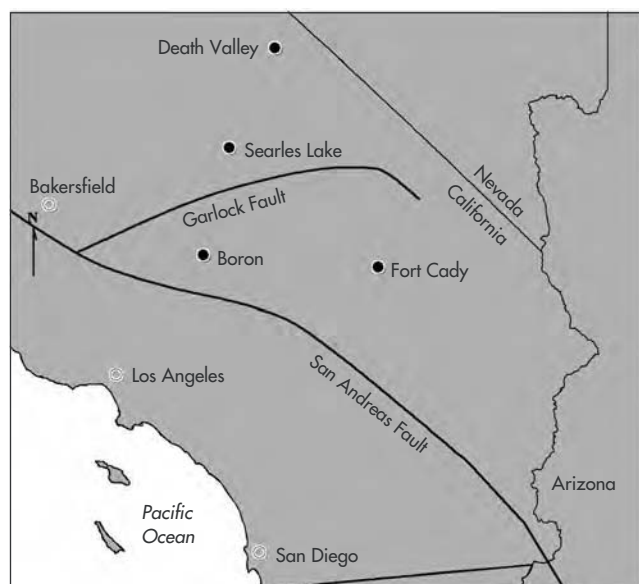


Figure 3. Major U.S. borate deposits



Courtesy of Courtesy of U.S. Borax Inc.

Figure 4. U.S. Borax's open-pit operation at Boron, California

The Paleoproterozoic borates of Jilin and Liaoning provinces in eastern China appear to be sedimentary borates that have been metamorphosed by the intrusion of later granitic plugs (Peng and Palmer 1995). Other investigators subscribe to a granite-related metasomatic source for these deposits (Wang and Xu 1964).

In the Bor deposit in Russia, the source is clearly of magmatic origin (Ratkin and Watson 1993). The calcareous host sediments were further altered by later brines heated by a second series of intrusions (Malinko 1992; Hamet and Stedra 1994), resulting in a relatively high-grade borate skarn. Sullivan, B.C., Canada, where a high-boron tourmaline skarn is associated with a large zinc deposit, might be an example of either metamorphic or magmatic action.

Distribution of Major Deposits

North America

Almost all of the known borate deposits in the United States are found in southern California and adjacent portions of Nevada (Figure 3). The only other known North American borate deposit is in the northern part of Sonora, Mexico. All of these deposits are of Neogene age and are associated with continental sediments and volcanic rocks.

United States. United States production is dominated by the Kramer borax and kernite deposit located at Boron, California, midway between the towns of Barstow and Mojave, and by the borate-

containing brines of Searles Lake, which is located about 65 miles north of Barstow.

U.S. Borax, Inc. (Rio Tinto) mines the large Kramer deposit at Boron by open-pit methods (Figure 4). The ore body consists of lake sediments containing up to 90% borax, some of which has been converted to kernite by the pressure of burial. The borates are within a thick sequence of Miocene-age continental sediments, protected from dissolution by a surrounding series of greenish marls and clays. The deposit is underlain by olivine trachybasalts and overlain by up to 300 m of Miocene-age silts and arkosic fanglomerates. Faulting, some of which was penecontemporaneous with mineralization, has offset portions of the ore body. The ore is refined in an adjacent plant where a full range of sodium borate and boric acid products are produced. Specialty borate products are made at Borax's Wilmington plant and shipping facility located at the Los Angeles harbor.

Searles Lake, a Holocene salar (approximately 40,000 years old), contains both bedded salts and brines that reach thicknesses of more than 40 m and extend over several tens of hectares. Searles Valley Minerals, Inc. selectively pumps the brines from several of the salt layers and refines them in the ir plants near the town of Trona on the west side of the lake. These brines supply other commercial salts in addition to sodium borates and boric acid.

Death Valley continues to produce limited amounts of colemanite and ulexite/probertite concentrates from a relatively small underground mine located on the east side of Death Valley National Park. The American Borate Company (ABC) operates this mine, the Billie. None of the other small borate deposits in or around the park is currently being mined. These deposits are all dated at between 5 and 8 Ma.

Fort Cady Minerals Corporation maintains a small acid-solution mining project at Hector, about 30 miles east of Barstow. This Neogene-age colemanite deposit is injected with sulfuric acid that is pumped to a nearby plant, and calcium meta-borate is precipitated. As of 2004, this plant was on standby status. No other borate deposits are in production in the United States.

Mexico. U.S. Borax and Vitro MEX discovered a small colemanite deposit near the town of Magdalena, Sonora, in 1972 (Aiken and Kistler 1992). It is not currently in production.

South America

At least 30 borate sources in South America are producing or have produced borates. These are all located on the high Andean *altiplano* or *puna* near the common borders of Argentina, Bolivia, Chile, and Peru (Figure 5). South American borate producers have historically sent much of their production to Brazil, with smaller amounts going to other countries within the Latin American economic trade zone. Most of this production has been borax and ulexite concentrates. Within the last 10 years, however, many of the larger producers have constructed boric acid plants and expanded their markets to include Taiwan, China, Japan, and portions of the United States and Europe.

Argentina. All of the known Argentine borate deposits are located in northwestern Argentina. For many years, South American borate production has been dominated by the Tinicalaya open-pit borax mine of Borax Argentina (Rio Tinto). This Late Neogene, tectonically deformed, playa deposit (5 to 6 Ma) is located in Salta Province near the Salar de Hombre Muerto. Borax Argentina also mines Neogene-age ulexite, hydroboracite, and colemanite at Sijes, close to Salar Pastos Grandes, and Holocene ulexite from several salars in Salta and Jujuy provinces. Their main processing plant and new boric acid facility are located at Campo Quijano, near the city of Salta.

Procesadora de Boratos Argentina (PBA) operates a Neogene borax and ulexite deposit at Loma Blanca near Coranzuli in Jujuy Province and their plant is located at Palpala, near the city of Jujuy. At least seven other active borate mines are on the Argentine *puna* in Salta and Jujuy provinces, all based on Holocene-age salar ulexite deposits; none of them furnishes large amounts of production.

Bolivia. The borate industry in Bolivia centers on several salar deposits in the southern portion of the country and on the southern edge of Salar de Uyuni (Figure 6). Ulexite is the ore mineral in these deposits. The major producers are Cia Minera Tierra Ltda. with salar operations at Laguna Capina, Chalhvi, and Pastos Grandes, and two companies that operate on the southern edge of Uyuni, Minera Rio Grande and Non Metallic Minerals, the latter a venture between D. Moscoso and the Chilean borate producer Quimica y Industrial del Borax (Quiborax). Non Metallic is currently the largest borate producer in Bolivia with production capacity of 100,000 tpa. At this time there is no production from the brines of Salar de Uyuni itself. Most of the ulexite mined in Bolivia is exported as a mineral product. Tierra is the only Bolivian producer of boric acid. Their 15,000-tpa plant located at Apacheta uses geothermal heat from the nearby Laguna Colorado hot springs.

There have been a number of stories about the local borate industry in the past decade or so. In 2001, the Bolivian government temporarily shut down Tierra's boric acid facility for supplying acid to the cocaine trade. In mid-2004, the government revoked the mining concessions of Non Metallic Minerals for evading customs taxes. The latter charge is being fought in the courts. Both instances indicate a heightened interest in this long-neglected corner of the country by the central government and are a sign that borates are becoming a more significant Bolivian export.

Chile. The Chilean borate producers are all located in the northern portion of the country. The largest, Quiborax, produces a number of products, including boric acid, from their plant outside Arica and their newly purchased boric acid plant in Antofagasta. Their main resource base is Salar de Surire near the Bolivian border. Other smaller operations are located on Salars Ascotan and Pajonales.

Sociedad Quimica y Minera de Chile S.A. (SQM) produces boric acid from their large brine deposit on Salar de Atacama as a by-product of their lithium and potassium sulfate production. There is also a small, independently owned boric acid plant located at Iquique.

Peru. There is one major producer of borates in southern Peru, Industrias Bitossi S.P.A., which is based in Arequipa; Laguna Salinas is their ulexite source. They produce ulexite concentrates, much of which is shipped from the port of Matarani to Lardarello in Italy under the Inkabor label. They also produce boric acid.

Eurasia

Turkey is the world's major borate producer outside of the United States. Their borate sources include the world's largest known deposits of borax, colemanite, and ulexite. These are all Neogene age, continental lake-bed deposits located in the northwestern part of Anatolia.

Chinese production is from Paleoproterozoic metasediments and metavolcanics in Liaoning and Jilin provinces, northeast China, and from Holocene-age salars in Qinghai and Xizang provinces, western China. Russian production comes from Bor, a unique metamorphic deposit located near the Sea of Japan. The borate production in Kazakhstan, north of the Caspian Sea at Inder, ceased in 2003.

Turkey. All Turkish borate production is currently under the control of Eti Holdings, a state corporation. They produce from five distinct areas: Kirka, the Emet Valley, Kestelek, Sultancayiri, and the Bigadic Basin (Figure 7). The deposit at Kirka consists of



Figure 5. South American borate deposits



Courtesy of Robert Kistler.

Figure 6. Ulexite mining at Rio Grande, Bolivia

borax, up to 145 m thick, with light green to white intercrystalline carbonates and clays; the deposit is capped by a porcelaneous limestone (Helvacı et al 1993; Kistler and Helvacı 1994). Mining is by open-pit methods. The ore is processed locally and sent by truck and train to the port of Bandırma.

Eti also produces from two large colemanite deposits in the Emet Valley north of Usak, where the ore is interbedded with limestone, and from two smaller colemanite deposits at Kestelek and Sultancayiri, south of the Sea of Marmara. These deposits are mined mainly by open-pit methods. The large bedded ulexite-colemanite deposits in the Bigadic Valley south of Balıkesir occur in two distinct geologic units separated by a thick tuff (Helvacı and Yagmurcu 1995). These deposits are mined by both open-pit and underground methods. All the Turkish deposits currently being mined range in age from 16 to 19 Ma.

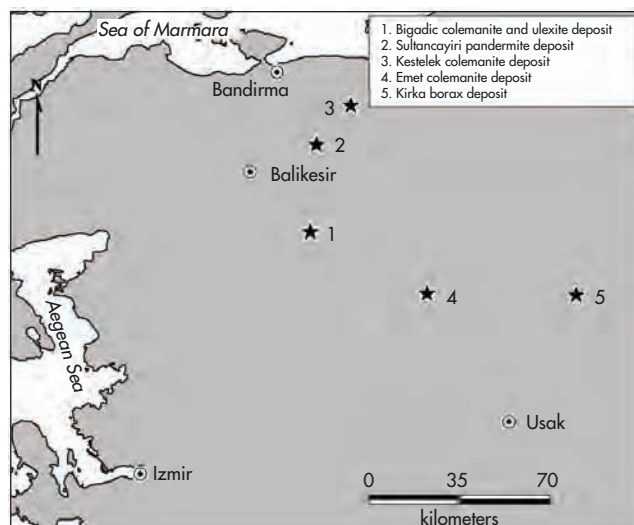


Figure 7. Borate districts of Western Turkey

Eti has constructed boric acid plants at both Emet and Bigadic, but their main processing plants are at the shipping port of Bandirma on the Sea of Marmara. They sell a full range of borate products, including both colemanite and ulexite concentrates as well as sodium borates and boric acid; more than 90% of their production is exported.

Europe. There is no reported borate production from Europe at this time. Historically, borates were recovered as a by-product of potash mining from the Zechstein Group in eastern Germany but they are no longer being produced. The borates discovered in the Jarandol Basin of Serbia and held by Electropriroda Srbije, the state electric company, are not yet in production because of continuing political problems in that part of the world. Larderello, near Pisa, Italy, no longer reclaims commercial borates from fumaroles, although the facilities there continue to produce boric acid from imported material.

Asia

China and Russia are the major suppliers of borates from Asia (Figure 8). Kazakhstan, Iran, India, Tajikistan, and North Korea all have reported borate occurrences; some of these countries may produce very limited amounts of borates for internal consumption.

China. Chinese borate production originates from two geologically and spatially distinct areas. Paleoproterozoic sequences of metasediments and metavolcanics in Liaoning and Jilin provinces, northeast China, are the source of more than 94% of China's current borate production. These deposits contain magnesium and magnesium-iron borates that are mined by underground methods. More than 20 plants convert these borates into borax and boric acid, which is sent, mainly by rail, to the major manufacturing centers. Most of this production is near the cities of Yingkou, Fengcheng, and Dandong. It is mostly consumed internally, although there are some exports to the neighboring countries of Pakistan, Indonesia, North Korea, and India. The glass and porcelain enamel industries are the main consumers of borates in China.

Lake terrace and salar-type lake-bed deposits of kurnakovite and borax are mined in Xizang (Tibet) Province, and lake-bed ulexite and pinnoite is mined in Qinghai Province. Mining is by labor-intensive methods and on a relatively small scale. These



Figure 8. Current Asian borate producers

borates are shipped to manufacturing centers in eastern China by truck and rail.

Russia. The only major source of borates in Russia at this time is the unique Bor deposit, a large skarn accumulation with datolite and danburite as the major borate minerals, located at Dalnegorsk near the Sea of Japan. The two distinct stages of borate skarn mineralization have been loosely dated at 55 and 35 Ma (Malinko 1992) and >64 Ma (Ratkin and Watson 1993). This deposit, which is mined by open-pit methods, is now under the ownership of JSC Energomash-Bor. Their major product is a high-grade boric acid, much of which is railed to western Russia, although some is shipped to China, South Korea, and Japan.

Russian scientists have identified a number of small skarn borate deposits, many near the Ural Mountains (Alexeev and Chernyshov 1997), which produced sporadically until the late 1970s. These are apparently not in production at this time.

Kazakhstan. The marine borates at Inder, located just north of the Caspian Sea in the far western part of Kazakhstan, are associated with a series of large, Permian-age salt domes. These deposits, consisting mainly of nodular ulexite and hydroboracite, were at one time the major source of borates for the former U.S.S.R. The shallow, easily recovered reserves are exhausted, and, as of late 2003, there was no borate production from Inder. A deposit in a similar geologic setting has been identified by drilling about 100 km to the north at Satimola, but it is not currently in production.

Other Areas. There are no known borate deposits on the continent of Africa, in Australia, or in Indonesia, although hot springs with elevated boron values have been identified in New Zealand. Borate-rich springs have long been known in the Puga Valley of India, but they are too low grade to permit commercial exploitation at this time. The borosilicate deposits in the high mountains of southern Tajikistan are very remote, and the danburite ore would be difficult to refine economically. North Korea has reported low-grade ludwigite bodies southwest of Pyongyang. Iran has several small colemanite showings that are handpicked for a few tons each year, which are consumed by local ceramic manufacturers.

TECHNOLOGY

Exploration Techniques

The search for undiscovered borate deposits continues in many parts of the world. Governmental geologic surveys, major corporations, and prospectors are involved in this search, some using the latest in

scientific methods and data searches. Others, particularly in the less developed areas of the Far East, continue with the time-tested methods of outcrop evaluation that have been used for hundreds of years.

The borates of commerce (borax, ulexite, and colemanite) are the most commercially valuable and are the exploration target of choice in areas where the geology is permissive. These are usually buried under protecting layers of associated sediments and volcanics. As a result, the more recent borate exploration techniques concentrate on indirect detection of buried targets.

Satellite imagery can detect surface and near-surface exposures of clays, limy sediments, and salts as well as borates themselves. These surveys are most useful in areas with little vegetative cover, such as Death Valley, where these studies have been pioneered (Crowley 1993). Geophysical methods, including seismic, magnetic, and gravity surveys, are used as indirect indicators of borate deposits, generally in areas with known structures or deposit controls.

Geochemical methods for indicating borates have been used for some years. Boron is a relatively mobile element and can be detected in soil and rock samples to <10 ppm, and to <1 ppm in water. Typical indicator elements include arsenic, antimony, beryllium, fluorine, lead, lithium, magnesium, and strontium, but boron values usually provide the best indication of a nearby borate deposit. Geochemical prospecting methods utilize concentrations and ratios of the more mobile elements in combination with boron values.

Basic geologic evaluations of permissive areas and outcrops by mapping and sampling followed by drilling remains the best, but most time consuming, exploration technique. Drilling methods vary by area, target and target depth, and drill availability.

Evaluation of Deposits

Borate deposits are evaluated on the basis of their B₂O₃ grade, mineralogy, mineral recovery, and projected sales targets. As previously noted, most of the borate deposits that remain to be discovered in the western hemisphere are buried under protecting layers of sediments and volcanics. Evaluating these deposits usually requires drill testing followed by bulk sampling. Because these borates are susceptible to leaching, drill-sampling procedures using air recovery or larger diameter core are preferred to small-diameter coring methods.

In some areas, surface trenching and channel sampling of anomalous sediments are a cost-effective method of evaluation. For more deeply buried deposits, large-diameter core samples are used to obtain bulk samples for initial tests. Limited underground work or small-scale open-pit tests then provide the bulk samples for final mine and mill design.

Mining

Most of the major borate deposits in the world are now mined by open-pit methods, generally using truck and shovel or backhoe equipment. In the United States, only ABC in Death Valley operates underground at this time. Several mines in Turkey and all of the ones in eastern China are mined underground using labor-intensive methods. A few of the South American and Chinese salars continue to use hand-mining methods to recover the thin borate layers. Searles Valley Minerals in the United States and FMC in Chile produce borates by pumping and refining complex brines; Fort Cady Minerals, also in the United States, uses acid dissolution of in situ colemanite as their mining method.

United States

The boron open-pit mining operation of U.S. Borax operates a fleet of 260-st unit-rig trucks and several P&H 4100 electric shovels with 58-yd³ buckets as their main mining equipment. Mining

benches are 17 m high. The ore is currently trucked to a surface primary crusher.

In Death Valley, ABC mines colemanite and probertite from depths of 230 m to more than 300 m below the desert surface using conventional drill-and-blast methods and backfilling of stopes.

Searles Valley Minerals pumps brines from several salt layers, up to 100 m deep, in Searles Lake, and then injects spent plant liquor back into the formation to improve recovery. At Hector, Fort Cady Minerals injects weak sulfuric acid into various levels of their bedded colemanite deposit, which is more than 300 m deep, and recovers calcium metaborate from the solution.

South America

Borax Argentina and PBA both mine their borax deposits by open-pit methods, using relatively small front-end loaders and 24-st trucks. All the major operators (Borax, Quiborax, Tierra, and Bitossi) use tracked backhoes to strip and mine their salar ulexite deposits. The ulexite is then transported by small trucks, or wagons pulled by farm tractors, to drying areas off the salars. Smaller operators continue to use hand methods to mine, turn, and sun-dry the wet ulexite recovered. The major producers also have adopted mechanically aided drying methods. The dried ulexite is then trucked, or in some cases railed, from the salars to processing plants that are generally located near major towns where water and power are available. SQM pumps brine from Salar de Atacama and concentrates the salts by solar evaporation before introducing them into their plant. They produce other commercial products in addition to borates.

Turkey

Eti Holdings mines the large Kirka borax deposit by open pit, using truck-shovel methods for both mining and overburden removal. Similar methods are used for their colemanite mines in the Emet Valley. The smaller colemanite deposits at Sultançayırı and Kestelek have been mined by both open-pit and underground methods, using relatively small equipment. The major ulexite/colemanite deposits in the Bigadic Basin also are mined by both open-pit and underground methods.

China

Privatization of the Chinese borate industry has resulted in production from a large number of relatively small deposits. The hard-rock deposits in Liaoning and Jilin provinces are mined by underground methods. These underground mines use conventional drilling and blasting with some hand tramming, and many use rail declines from the surface. Almost all of these mines have nearby mills where the ore is converted to borax or boric acid, which is then shipped mainly by rail to the manufacturing centers of eastern China.

The salar deposits in Qinghai and Xizang provinces are worked mainly by hand, although a few now use small backhoes. Production from this area moves by truck to centralized railheads and then by rail to processing plants in eastern China.

Russia

The Bor deposit in far-east Russia is mined by open pit. During the last visit by the authors, it was observed that older model Russian trucks and shovels were still being used. The ore is trucked to an adjacent boric acid plant. Much of Russia's boric acid production is still shipped by rail to the Moscow area; exports are shipped from the small, nearby port of Rudnaya Pristan.

Processing

The basic processing steps used to convert most borate ores into either sodium borates or boric acid, the main products consumed by

Table 4. U.S. borax typical product grades and specifications, ppm

Type	% B ₂ O ₃	SO ₄	Cl	Fe	As	Insol
Anhydrous borax (AB)	68.5	<150		<40		
Pentahydrate (5 mol)	49.3	<100	<120	<10		<400
Decahydrate (10 mol)	38.3	<600	<700	<30		
Boric acid, technical grade	59.1	<3.0	<0.4	<2.0	<0.2	<10

other industries, are as follows: (1) crushing the ore; (2) dissolving the ore mineral in either heated water if borax or kernite is the ore, or in acid if ulexite, colemanite, or other borate mineral is the ore; and (3) precipitating the product, either boric acid or sodium borate. The wet recovered product is then dried, screened, and prepared for shipment in either bag or bulk (Table 4). Most of the South American salar ulexite producers sun-dry their ore before processing, and SQM in Chile uses the sun to concentrate their brine before plant processing. Almost every major processor has a plant design specific for that ore and that location; these processing plants are discussed in some detail in works by Garrett (1998).

Marketing

Marketing is tied to the consumer with products specifically designed for the needs of major customers. Price and service after the sale are becoming an increasingly important part of the business.

Borates are an essential component of many items. Without borates, many products would be inferior, and some could not be produced in their current form. The principal uses are in insulation-grade glass fibers, textile-grade glass fibers, heat-resistant glass, soaps and detergents, fertilizers and herbicides, enamels, frits and ceramic glazes, wood preservation, and cellulose insulation. The many other uses include fire retardants, metallurgy, specialty paints, nuclear applications, taxidermy and embalming, sports products, batteries, high-intensity magnets, and specialty chemicals.

Competitive products have eroded some markets in the soap and detergent field, in lower-grade ceramics, in some types of glass fibers and in some fire retardants. These losses have been more than recouped by the many new uses.

Product Pricing

Prices for borates (Table 5) have been flat for the past few years, reflecting competition in the marketplace and a balance between supply and demand. Prices for the various products reflect the energy cost of refining and drying.

Transportation and Distribution

United States

Borates are a lightweight, low-bulk-density commodity, and thus sales are usually made in carload lots. Because of the purity specifications and solubility of manufactured borate products, both major U.S. producers have their own fleets of railcars dedicated to the exclusive shipment of product. For U.S. Borax, unit trains transport refined borates from Boron to their facility at Wilmington in the Los Angeles harbor, where they are transferred into several special ships that make regular runs to company export terminals at Rotterdam, Nules (Spain), and Singapore. Unit trains are also used to supply major customers in the United States. Smaller shipments are packed in 2,000-lb super sacks or in special bags that are then plastic-wrapped on pallets for distribution by truck or rail. Searles Valley Minerals ships by rail from its plant at Trona.

Table 5. Typical prices per metric ton (May 2005)

Product	Price, US\$
Bulk, f.o.b.* California	
Anhydrous borax (AB)	840-900
Pentahydrate, refined (5 mol)	400-430
Decahydrate, technical (10 mol)	340-380
Boric acid, technical (BA)	900-925
Lump colemanite, Turkey, f.o.b. U.S./Japan	270-290
Ulexite, f.o.b. Lima, Peru	250-300

Adapted from *Mineral PriceWatch* 2005.

* f.o.b. = free on board.

Turkish and South American imports enter the United States principally through the ports of Charleston, South Carolina, and Houston, Texas.

Other

In Europe, barges are used for distribution to most of the major consumers that receive their borates from the port of Rotterdam. Shipments from Spain move by rail and truck in both bag and bulk. South American shipments are usually made in bags, some of which move by rail, but most shipments are by truckload lots. Most of the Asian distribution of refined borates is bagged, and much of it is railed in open hopper cars.

ECONOMIC FACTORS

Borates are an essential ingredient in many products and are treated as a commodity. Supply and demand have kept prices stable for most major consumers for the past 10 years. Several years ago, U.S. Borax and some other companies decided to exit the consumer market and concentrate on selling to other large manufacturing companies. Although small boxes of Borax 10-mol still appear on supermarket shelves, usage is small and the market shrinking. Bulk shipments and consumer-driven specifications have tailored the current market to major corporations who utilize borates in their end products. In many cases, borates lower the temperature of manufacturing (of, for example, glass, glass-fiber, and enamels) and thus offset a portion of their cost with energy savings.

GOVERNMENT REGULATIONS

Sodium borates on federal lands are currently covered under the provisions of the Mineral Leasing acts of 1917 and 1920. Much of Searles Lake consists of alternating federal sections that are covered under these regulations, as is much of the prospective area of the Mojave Desert. Borate minerals have a 14% depletion allowance. A portion of the Mojave Desert is listed as prime habitat for the desert tortoise (*Xerobates agassizii*), a threatened species. U.S. Borax has purchased more than 5,000 acres near their Boron operation as mitigation for loss of tortoise habitat.

Although there are no reported cases of borate toxicity, a permissible exposure limit (PEL) of 10 mg/m³ of sodium borate dust has been adopted by the Occupational Safety and Health Administration (OSHA). No cases of industrial intoxication or exposure to inorganic borates have been reported. Ingested boric acid is excreted rapidly, and there is no evidence of carcinogenic or mutagenic activity (Smith and McBroom 1992).

OUTLOOK FOR THE FUTURE

Borates currently have a vital role in producing glass fibers and heat-resistant glass by reducing energy costs and improving

strength. Both of these markets are relatively new and are projected to continue well into the future. Continued development of specialty fertilizers containing borates, targeted to specific agricultural crops, is increasing, as is the use of zinc borates in flame and fire retardants in plastics and wiring. Treating wood products to prevent termite damage is also an important and continuing use. Boron-fiber-reinforced plastics are finding increased roles in the construction of parts for air and spacecraft, automobiles, and military uses.

Soaps and detergent use is decreasing in total volume, especially in Europe, although special beauty aids continue to be an important niche market. Fiberglass insulation has gone through a cycle of borate use and reduction but remains a major end product. Boron-nitride coatings find use in cutting tools and grinding processes and in special technologies where resistance to wear and high heat are important considerations. Boron carbide control rods remain the major controlling devices for nuclear reactors. Minor but important uses are in the encasement of spent nuclear waste, special optical fibers, high-gloss paints for the auto industry, and high-intensity electromagnets.

To reduce chemical waste, U.S. Borax has introduced a borate autocauticizing process into the kraft paper industry. A possible major new use is in automotive fuel cells using sodium borohydride, which is recyclable. Many electronic items use liquid crystal displays that require minute amounts of boric oxide, again, a niche market that only borates can fill. Research continues into boron esters and polymer substances, with many potential new uses in the field of superconductors and electrolytes. Medical research into the use of borates shows promise in cancer treatment where borates target cancer cells for absorption of thermal neutrons (called BNCT, or boron neutron capture therapy).

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Bromine

Ron Frim and Shmuel D. Ukeles

INTRODUCTION

Bromine, a heavy, mobile, reddish-brown liquid with an intensely irritating odor, is the only non-metallic element that is a liquid at normal room temperatures. Bromine belongs to Group 17 (VIIA)—the halogen group of elements—in the periodic table. It is a diatomic molecule with the chemical formula Br_2 . Its place in the periodic table is between chlorine (a gas) and iodine (a solid). The atomic number of the bromine atom is 35 and its atomic weight is 79.904. Within wide limits, both the liquid and vapor are diatomic (Br_2).

Carl Lowig, a young chemistry student, originally prepared bromine the summer before beginning his first year at the University of Heidelberg. Winter exams and holidays delayed the continuation of his work long enough for another chemist, Antoine Jerome Balard, to publish a paper in 1826 describing the new element that he had discovered in seawater bitterns. Balard was thus credited with the discovery of bromine, and the French Academy of Science named it after the Greek *bromos*, meaning stench.

The first commercial production of bromine in the United States was from salt brines in 1846 at Freeport, Pennsylvania. In Germany, the first commercial production plant began operation in 1865. This German plant used solutions from the Stassfurt potash factories in its bromine production. Contrary to the method used by Balard to obtain bromine—oxidizing the bromide ion with chlorine—the German process was based on oxidation using manganese dioxide with the aid of sulfuric acid.

Bromine, which occurs naturally in sea water and brines, is extracted using a number of processes. Herbert Dow invented the *blowing out* process for use on Midland (Michigan) brines in 1889. A very small plant in Canton, Ohio, and then a second plant only a little bigger than the first used the blowing out process. Brine electrolysis liberated bromine for a certain period, and then was replaced by the use of chlorine to reduce the bromide to bromine.

Bromine has a number of industrial uses including in flame retardants, drilling fluids, agricultural chemicals, and water treatment.

PRODUCTION AND TRADE

World bromine production capacity in 2003 was estimated to be >563,000 t (Lyday 2003). Two countries and three companies maintain most of this production capacity: the United States (Albemarle Corporation and Great Lakes Chemical Corporation) and Israel (Dead Sea Bromine Group). Of the almost 548,000 t of bromine produced in 2002, the United States accounted for approximately

39% of this amount and Israel accounted for 38%. The three companies also accounted for the majority of the world trade in bromine derivatives.

Principal Producing Countries

China

Official figures indicate that China produces an estimated 40,000 tpy of bromine. This is believed to be a conservative estimate: the Ocean Chemicals Group (OCG) is reported to have a production capacity of 50,000 tpy at facilities north of Laizhou Bay.

Commonwealth of Independent States (CIS)

The U.S. Geological Survey (USGS) estimates that Azerbaijan produced about 2,000 t of bromine in 2002; Ukraine produced about 3,000 tpy; and Russia produced about 3,000 tpy. Kazakhstan and Turkmenistan apparently hold considerable promise for future production based on brines associated with massive natural gas reserves.

France

Overall production estimated for France in 2001 and 2002 was 2,000 tpy. This production rate has been constant since 1996. Elf Atochem SA produces this amount of bromine in southeastern France in its Port-de-Bouc plant, which has a capacity of 12,000 t. The company is investing about \$12.8 million in a specialty brominated derivatives plant based on the bromine from the Port-de-Bouc plant. The derivatives production is destined for the pharmaceutical industry. Albemarle Corporation operates a flame retardant plant at Port-de-Bouc in addition to a bromine derivatives plant at Thann.

India

Although no detailed production figures were found for India, the little information available indicated production levels of about 1,500 tpy, produced from salt production bitterns. Solaris Chemtech Ltd. (formerly BILT Chemicals, Gujarat) is planning to expand yearly production to 10,000 t in the near future.

Israel

Dead Sea Bromine Group (DSBG) produces bromine and bromine derivatives for applications in air conditioning, batteries, cleaning solvents, flame retardants, mineral separation, oil-well drilling, photography, and water treatment. From 1998 through 2002, more

Table 1. DSBG production, 1998–2002, kt

Bromine	1998	1999	2000	2001*	2002*
Elemental	185,200	181,000†	210,000	206,000	206,000
Compounds*	247,000	247,000†	250,000	250,000	250,000

* Estimated numbers.

† Revised numbers.

than 90% of its sales were from exports. Table 1 shows production figures for DSBG during that time period (Yager 2002).

Japan

The Tosoh Corporation, Japan's largest bromine producer, extracts bromine from sea water. It has a reported production capacity of 24,000 tpy (Davenport 2003).

Jordan

The bromine production capacity of the recently constructed Jordan Bromine Company plant at Safi is 50,000 tpy. The plant also produces 35,000 t of calcium bromide and 50,000 t of tetrabromobisphenol for Asian and European markets.

United Kingdom

Until the end of 2003, when the Great Lakes Chemical Corporation closed its plant at Amlwch, Wales, about 28,000 tpy of bromine was extracted from seawater in the United Kingdom.

United States

Current U.S. production of bromine is from inland brines, which are in plentiful supply. The most concentrated domestic brines (up to 5,000 ppm bromide) are in Arkansas and less-concentrated brines (about 2,500 ppm bromide) are in Michigan. An advantage of the Arkansas brines is that they come to the surface at approximately 96°C, a temperature favorable for bromine extraction.

According to USGS data, the quantity of bromine sold or used in the United States from three companies operating in Arkansas and Michigan was equal to production and had a value of \$155 million in 2002. In 2003, the estimated U.S. bromine production was 216,000 t; in 2002 production was 222,000 t (Lyday 2004).

The apparent consumption of bromine in the United States during 2002 was 216,000 t, an increase from 214,000 t in 2001 (Lyday 2004). The estimated bromine consumption for 2003 was 211,000 t. U.S. bromine usage is divided into the following categories and percentages: fire retardants (40%); drilling fluids (24%); brominated pesticides (12%); biocides/water treatment chemicals (7%); and other products (17%). The other products are photographic chemicals, rubber additives, dyes, pharmaceuticals, brominated intermediates (used to manufacture products and bromide solutions used alone or in combination), and gasoline additives. The brominated gasoline additives and halon markets have virtually disappeared because of environmental considerations and legislation. Unofficial sources predict that other markets will show either modest growth or decline in the coming years, except for water treatment applications, which should demonstrate good growth.

Overall, demand for bromine in the United States was estimated to grow at a modest yearly rate of about 1% to 2% from 2001 through 2006. This estimate was based on the assumption that no new, major legislative restrictions would be placed on bromine chemical use during that period.

The USGS maintains bromine production data. The apparent consumption of elemental bromine in the United States has been defined as production plus imports minus exports. Table 2 gives the

Table 2. U.S. supply and demand data for elemental bromine, 1995–2004, kt*

Year	Annual Capacity	Production	Imports	Exports	Apparent Consumption
1995	259	218	2.22	3.22	206
1996	290	227	0.42	2.92	225
1997	337	247	1.65	2.33	249
1998	337	230	1.19	1.49	235
1999	337	239	1.97	2.11	239
2000	349	228	5.47	1.87	238
2001	715	212	5.61	3.71	214
2002	261	222	2.02	6.07	216
2003†	262	216	1.92	2.28	210
2004†	No data	222	No data	No data	220

* Data compiled from various USGS sources.

† Data based on preliminary estimates.

Table 3. U.S. imports of bromine chemicals, 1995–2003, kt*

Year	Inorganic Chemicals		Organic Chemicals		Total	
	Gross Weight	Bromine Content	Gross Weight	Bromine Content	Gross Weight	Bromine Content
1995	3.81	2.64	5.85	4.88	9.66	7.52
1996	15.17	11.61	6.52	5.09	21.69	16.70
1997	38.84	6.75	8.91	6.90	47.75	13.65
1998	6.98	5.00	8.99	6.77	15.97	11.77
1999	8.74	6.36	7.40	0.78	16.14	7.14
2000	61.37	13.96	7.76	5.86	69.13	19.82
2001	67.16	11.00	5.95	4.30	73.11	15.30
2002	21.36	4.52	4.92	0.18	26.28	4.70
2003	51.87	7.66	3.28	0.25	55.15	7.91

* Data compiled from various USGS sources.

supply and demand data for elemental bromine from 1995 through 2002, and estimates for 2003 and 2004.

Most bromine trade involves bromine derivatives rather than elemental bromine. The United States imports a wide range of bromine-containing chemicals, including bromide salts such as ammonium bromide, calcium bromide, potassium bromide, and sodium bromide, as well as sodium bromate and potassium bromate. Other imported bromine chemicals were mainly organics, largely brominated fire retardants from Israel. Table 3 lists U.S. imports of bromine chemicals for 1995 through 2003.

Exports of bromine chemicals from the United States to other countries have been estimated to be about 49,000 to 51,000 t (gross weight). The major portion of this quantity was flame retardants, estimated to be about 30,000 t.

Principal Producing Companies

Albemarle Corporation

The Albemarle Corporation, headquartered in Richmond, Virginia, was spun off as a separate company from the Ethyl Corporation in 1994. The company has two operating divisions: the Fine Chemicals Division, which produces performance chemicals, pharmaceuticals, and agricultural products; and the Polymer Chemicals Division, which produces fire retardants (brominated and non-brominated), catalysts, and adhesives. Total annual sales of about

Table 4. World production of bromine, 1995–2003, kt*

Year	China	France	Israel	Japan	United Kingdom	United States	CIS†	Other	Total
1995	32.7	2.3	130	15	26.2	218	5.6	1.8	432
1996	41.4	2.0	160	15	30.6	227	5.1	1.9	483
1997	50.1	2.0	180	20	35.6	247	5.1	1.9	542
1998	40.0	2.0	185	20	30.0	230	5.2	1.9	514
1999	42.0	2.0	181	20	55.0	239	5.2	2.4	547
2000	42.0	2.0	210	20	32.0	228	5.2	2.4	542
2001	40.0	2.0	206	20	35.0	212	5.2	2.4	523
2002	42.0	2.0	206	20	35.0	222	5.2	7.4	540
2003‡	42.0	2.0	206	20	35.0	216	5.2	22.4	549

* Data compiled from various USGS sources.

† CIS here includes Azerbaijan, Turkmenistan, and Ukraine.

‡ Estimated figures.

\$980 million have been reported. Bromine is critical to many of the company's products. Aside from manufacturing brominated fire retardants, Albemarle also produces other products containing bromine, including metal alkyls, inorganic bromides, and a number of fine chemicals. Albemarle's bromine-based operations are in the United States and France. In 1999, Albemarle Holdings (an Albemarle affiliate) established a joint venture with Arab Potash/Jordan Dead Sea Industries to construct a bromine and bromine derivatives complex at Safi, Jordan, on the Dead Sea. Phase one, which opened in October 2002, was a bromine unit and a production facility for inorganic bromides and hydrogen bromide. The second phase involves the construction of a Sayytex CP-2000 (tetrabromobisphenol) flame-retardant plant.

Dead Sea Bromine Group

DSBG, headquartered in Beer Sheva, Israel, is the world's largest producer of elemental bromine. Total annual sales are more than \$500 million (Y. Gramse, personal communication). The company's elemental bromine plant is on the shore of the Dead Sea, and an affiliated company, Dead Sea Works (a producer of potash and other inorganic chemicals), supplies the raw material for its bromine production. Israel Chemicals, which has its headquarters in Tel Aviv, owns both companies. DSBG—through subsidiaries such as Bromine Compounds (Ramat Hovav, Israel)—produces a broad range of organic and inorganic bromine compounds.

In addition to elemental bromine and bromine derivatives in Israel, DSBG also produces bromine derivatives in the Netherlands at its Eurobrom facility. DSBG and its subsidiaries are grouped into eight business units that produce elemental bromine, flame retardants, biocides, agrochemicals, oil-field chemicals, industrial chemicals, organic intermediates, and fine chemicals.

In 2003, DSBG and Manac of Japan signed an agreement for long-term cooperation to produce and market a flame retardant for engineering plastics. Also in 2003, DSBG entered into a long-term strategic sourcing agreement for elemental bromine and certain bromine derivatives with the Great Lakes Chemical Corporation.

Great Lakes Chemical Corporation

Great Lakes Chemical Corporation (GLCC), with headquarters in Indianapolis, Indiana, has total yearly sales of more than \$1.5 billion. It has four operating units: water treatment, polymer additives, performance chemicals, and energy services and products. All these units generate bromine-containing products. The polymer additives unit produces flame retardants and polymer stabilizers. The flame retardant segment uses brominated and nonbrominated compounds.

The performance chemicals unit uses elemental bromine, methyl bromide, and other bromine products. GLCC's elemental bromine production is primarily from brines in Arkansas, but it also operates a plant in the United Kingdom (Associated Octel) that extracts bromine from seawater.

Brominated compound production, especially flame retardants, is focused in the United States, but there is also production in the United Kingdom. GLCC has formed a joint venture for tetrabromobisphenol with DSBG at Ramat Hovav, Israel. In 2003, GLCC and the ICL Industrial Products Division (Israel) announced a global agreement whereby the latter would supply bromine and bromine compounds to GLCC.

World Production Statistics

In 2002, the United States continued to maintain its leading position in bromine production, which was estimated at about 222,000 t that year. Israel was second with 206,000 t. These two countries accounted for about 78% of the world's elemental bromine production of 550,000 tpy. Other leading producers accounted for the remaining 22%, including China, France, India, Japan, the United Kingdom, and CIS members.

Table 4 gives production data for the world's largest producers of bromine for 1995–2003. Harben (2003) presented slightly different figures that reflect data not available through USGS.

OCCURRENCE

Distribution in Nature

Bromine is distributed widely in nature as bromide salts and as organobromine compounds, which are produced by various marine organisms. Bromine is present in the hydrosphere, mainly as soluble bromide salts in seawater, salt lakes, inland seas, natural brine wells, and in evaporite chloride minerals. Concentrations vary from 65 mg/L in seawater up to 6.5 g/L in the southern basin of the Dead Sea. Its abundance in igneous rocks is 0.00016% by weight, whereas seawater has an abundance of 0.0065% by weight.

The only minerals that contain bromine are some silver halide ores: bromyrite (AgBr), embolite [Ag(Cl, Br)], and iodobromite [Ag(Cl, Br, I)]. H.E. Boeke (1908) determined the distribution of bromine in marine evaporite minerals, and in the solutions from which they crystallize.

Terrestrial plants contain an average of about 7 ppm bromine. The highest bromine content in animal life is found in marine animals (e.g., fish, sponges) and crustaceans. Animal tissues contain 1 to 9 ppm bromide whereas animal blood has a content of 5 to 15 ppm bromine.

Table 5. World bromine reserves, 2005 estimate, kt

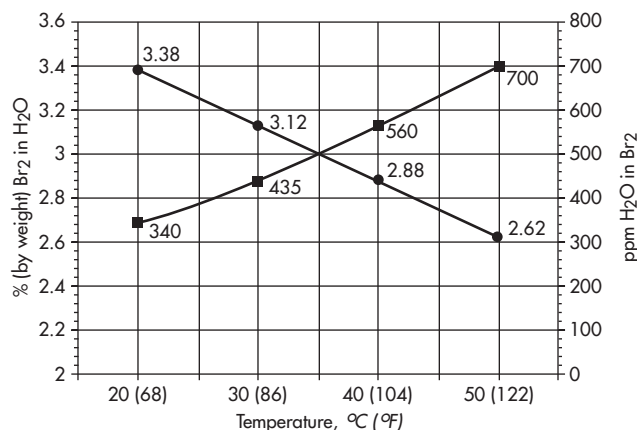
Country	Reserves	Country	Reserves
Azerbaijan	300	Japan	Unlimited*
China	Unlimited*	Spain	1,400
France	1,600	Turkmenistan	700
India	Unlimited*	Ukraine	400
Israel/Jordan	1,000,000	United Kingdom	Unlimited*
Italy	Unlimited*	United States	11,000

Adapted from Lyday 2005.

* Available from waste bitters associated with solar salt.

Table 6. Physical properties of bromine

Property	Value
Freezing point	-7.25°C
Boiling point	58.8°C
Density of liquid	
(20°C)	3.1226 g/mL
(25°C)	3.1055 g/mL
(30°C)	3.0879 g/mL
Density of vapor, 0°C, 101.3 kPa	7.139 g/L
Refractive index, 20°C	1.6083
Heat of fusion, -7.25°C	66.11 J/g
Heat of vaporization, 50°C	187 J/g



Adapted from Great Lakes Chemical Corporation, undated.

Figure 1. Mutual solubility of bromine and water

Commercial Sources and Reserves

The Dead Sea is today the richest commercial source of bromine; its brines contain 5 g/L bromine in the open sea, 6.5 g/L in the southern basin (near Ein Bokek, Israel), and up to 12 g/L in the end brine from potash production. This end brine serves as an almost unlimited source of raw material for Israeli and Jordanian bromine production. Other important bromine sources are underground brines in Arkansas (3 to 5 g/L) and Michigan (2 to 3 g/L) (United States), Russia, China, and the United Kingdom; bitters from mined potash (France and Germany); and sea water or sea water bitters in France, India, Italy, Japan, and Spain.

Table 5 gives a breakdown of the estimated world bromine reserves by country (Lyday 2005). The Dead Sea is estimated to contain about 1 billion t of bromine. The bromine content of underground brines in Poland has been estimated at 36 Mt.

Analytical Methods for Bromine and Bromides

The analysis for liquid bromine and bromine is based on its reaction with an aqueous potassium iodide solution to form molecular iodine, followed by its titration with a standard sodium thiosulfate solution. Bromine vapor can also be determined by absorption into aqueous potassium iodide solution and subsequent iodometric titration of the liberated iodine. Impurities in bromine (e.g., chloride, iodide, sulfur, water, organic compounds, and heavy metals) can be determined quantitatively.

Other methods for determining bromine are the Mohr, Volhard, and Fajans methods, silver nitrate titration using a silver indicator electrode, and a gravimetric method (silver bromide). Some methods used for determining trace amounts of bromide quantitatively are

- the van der Meulen method, which is useful in the presence of large chloride concentrations;
- constant-current and constant-potential coulometry, which can determine fractions of a milligram to several grams of bromide;
- ion chromatography;
- polarography for microgram quantities; and
- a spectrophotometric method, which is useful for microgram quantities in the presence of chloride.

Bromine in organic compounds can be determined by chemical methods following their oxidation and the reduction of bromine to bromides. The bromine content in the organic compounds can be determined subsequently by one of the following methods: neutron activation, x-ray fluorescence (XRF), infrared spectroscopy, or atomic emission spectroscopy.

PROPERTIES OF BROMINE

Physical Properties

Bromine liquid volatilizes readily at room temperature into reddish vapor, which is highly corrosive to many materials and human tissues. The liquid and vapor are diatomic (Br_2) up to about 600°C. Table 6 gives some of bromine's most important physical properties (Grinbaum and Freiberg 2002).

Bromine is fairly soluble in water, having the following solubilities at the corresponding temperatures: 3.41 g/100 g solution at 20°C; 3.35 g/100 g solution at 25°C; and 3.33 g/100 g solution at 40°C. The solubility of bromine increases in the presence of bromide or chloride ions from complex ion formation (e.g., formation of tribromides and pentabromides). Bromine is also soluble in nonpolar solvents (e.g., carbon tetrachloride, chloroform, carbon disulfide, and ether) and polar solvents such as methyl alcohol and sulfuric acid. Figure 1 shows the mutual miscibility of bromine and water.

Chemical Properties

Bromine, as other halogens, has a tendency to accept an electron to form either a negative bromide ion (Br^-) or a single covalent bond ($-\text{Br}$). Except for helium and neon, the other elements of the periodic table are able to form halides with the halogens, including bromine. The bromides that are primarily ionic in nature tend to have high conductivities in the fused state and high boiling points, and are not susceptible to hydrolysis if they are soluble bromides. The predominantly covalent bromides that can form are volatile and nonconductive in the liquid state, and usually undergo hydrolysis. The nonmetallic bromides generally hydrolyze to hydrogen bromide and an oxy-acid containing the other element.

Reactions with Hydrogen and Metals

Bromine reacts with hydrogen at elevated temperatures to form hydrogen bromide. Heated charcoal and finely divided platinum

metal are used as catalysts for this reaction, which is the basis for the commercial production of hydrogen bromide. Bromine reacts with all metals except tantalum and niobium; elevated temperatures are sometimes necessary to accomplish this conversion. The reaction of bromine with lead, magnesium, nickel, and silver forms a surface coat of bromide that resists further attack. This protective coating permits the use of lead and silver as linings in bromine containers. Metals corrode more rapidly from bromine in the presence of moisture than in its absence, probably because of the formation of hydrobromic acid (HBr) and hypobromous acid (HOBr).

Reactions in Water

When bromine dissolves in water, it undergoes partial disproportionation to form hypobromous acid, hydrogen ions, and bromide ions. The hypobromous acid is relatively stable only in solution and decomposes under the influence of heat, light, or copper catalysis to produce HBr and oxygen. In the dark, hypobromous acid decomposes to bromic acid (HBrO_3) and bromine. Bromic acid is relatively unstable and slowly decomposes to form bromine and oxygen (Grinbaum and Freiberg 2002).

In basic solution, bromine reacts rapidly to form bromide (Br^-) and hypobromite (OBr^-) ions. It is necessary to maintain this reaction below 0°C to limit the disproportionation of hypobromite to bromate and bromide.

Reactions with Organic Compounds

Bromine can react with organic compounds in various ways (Ioffe and Kampf 2001). Typical of such reactions are the addition of bromine to unsaturated hydrocarbons and the substitution of hydrogen on an organic substrate, with corresponding release of hydrogen bromide. It is possible to carry out reactions both in the liquid or vapor phases and in the presence or absence of solvents or catalysts. Some of the solvents used are chloroform, carbon tetrachloride, acetic acid, and hydrobromic acid. Lewis acid catalysts (e.g., aluminum chloride) are used frequently for the bromination of aromatic compounds, whereas light or peroxide catalysts are used in the bromination of aliphatic compounds.

The indirect reaction of other functional groups with bromine derivatives is the preferred method for the preparation of some organic compounds. An example is the preparation of methyl bromide (an alkyl bromide), which is best prepared by the reaction between methanol and hydrogen bromide. An alternate preparation of alkyl bromides is by the reaction of hydrobromic acid to an olefinic compound.

TECHNOLOGY

Processing Methods

Current methods for bromine production use chlorine to oxidize bromide to bromine. The principal processing steps follow:

1. Oxidize bromide to bromine.
2. Strip bromine from the aqueous solution.
3. Separate the bromine from the resulting vapor.
4. Purify the bromine.

Differences between various processes generally are manifested in the stripping and purification steps.

The two principal processing variations are the *steaming-out process* and the *blowing-out process*.

Steaming-Out Process

The current process used for producing bromine from bromide-containing brines (1 to 5 g/L Br^-) is based on the *hot* or *steaming-out* process first described by Konrad Kubierschky in 1906 (Jolles

1966). It consists of simultaneous chlorination and steam blowing. The brine is preheated, usually to $75^\circ\text{--}80^\circ\text{C}$, before its introduction into the Kubierschky tower, and then heated inside the tower by live steam to near boiling. The bromine is steam-distilled as it is being set free by the chlorine. The distillation steam is a small fraction of the live steam supplied to heat the brine. The steaming-out process requires heating the brine to near boiling and reducing the partial pressure of bromine (and chlorobromide) in the effluent brine to nearly zero to improve the stripping of the bromine from the brine. Drying the brine usually is achieved with sulfuric acid.

The advantage in the steaming-out process is that bromine is condensed directly from the steam, as opposed to the air blowing-out process, in which the bromine is trapped in an alkaline or reducing solution to concentrate it.

Blowing-Out Process

The blowing-out process uses air rather than steam. (The cost of steam to heat ocean water, with its very low bromine content of 65 mg/L, is prohibitively expensive.) In this process, bromide-containing water is pumped to the top of blowing-out towers. Sulfuric acid and chlorine are added above the pumps to ensure that mixing occurs in the brine during its ascent. An excess of about 15% chlorine is used over the theoretical amount required. Air is drawn through the towers, thus sweeping out a mixture of bromine and chlorine (or bromine chloride) from the descending water. The bromine-laden air is drawn next through the absorber towers in which it is scrubbed countercurrently with a sodium carbonate solution. To remove the spray from the air, small packed chambers are interposed between the absorber towers and the fans. When the alkalinity of the scrubber solution is nearly depleted, the solution is transferred to a storage tank and then to a reactor where it is treated with sulfuric acid and steamed to release bromine. Subsequently, the bromine is condensed.

Production from Wastes

An increasing amount of bromine is being produced from wastes. Hydrogen bromide, which is emitted as a by-product in many organic reactions, is a major source for this kind of bromine production. Part of the hydrogen bromide comes from incinerating organic wastes in a bromine recovery unit (BRU). The emitted flue gases from the BRU contain hydrogen bromide and molecular bromine, which are usually separated before the hydrogen bromide processing. The process used to recover bromine is similar to that used for producing bromine from bromides, that is, by oxidation with chlorine gas or another oxidant.

Another approach tested recently is recovering bromine from hydrogen bromide waste streams using electrolytic membranes to decompose the hydrogen and bromine. This process apparently has not yet been commercialized.

Product Specifications

Table 7 lists the American Chemical Society (ACS) specifications for reagent grade bromine and typical product specifications for purified bromine. The bromine content (by weight %) represents a minimum value, whereas the water and chlorine contents are maximum values (Grinbaum and Freiberg 2002).

MARKETS

Uses of Bromine

The synthesis of a wide range of brominated organic compounds involves the direct or indirect consumption of bromine. For the majority of brominated flame retardants (BFRs), bromine reacts with a suitable starting material to form the flame retardant (FR) along with one molecule of hydrobromic acid for each atom of

Table 7. Specifications for elemental bromine

Parameter	ACS Specification	Product Specification
Bromine content, %	99.5	99.9
Specific gravity, 20/15°C	na*	3.1
Water, ppm	na	30
Chlorine, ppm	500	100
Organic halogen compounds, ppm	Must pass ACS test	80
Nonvolatile matter, ppm	50	30
Iodine, ppm	10	Must pass ACS test
Sulfur (as S), ppm	10	Must pass ACS test
Heavy metals (as Pb), ppm	2	Must pass ACS test
Nickel, ppm	5	Must pass ACS test

* na = not available.

bromine contained in the end product. The hydrobromic acid produced is further reacted (e.g., with an alcohol to form an alkyl bromide) or neutralized to form a bromide salt.

Before describing uses, a few words should be devoted to the use of bromine in ethylene dibromide (EDB) as a gasoline additive. Bromine demand for this use steadily declined each year after the U.S. Environmental Protection Agency (EPA) issued regulations in the 1970s to reduce and eliminate lead in gasolines. (The EDB acts as a lead scavenger by converting lead oxides to lead bromide, which then escapes along with the engine exhaust.) An EPA mandate to eliminate all the lead from motor vehicle gasoline formulation by 1996, therefore, decreased EDB consumption drastically. Some lead is still used in aviation fuel formulations, although most of the small amount of U.S. production is exported to countries still having less-strict environmental legislation.

Flame Retardants

BFRs are still a growing market. The total global FR market has an estimated annual volume of approximately 2.0 billion lb (about 909,000 t), valued at about \$2.2 billion. Halogenated materials, which include halogenated phosphorous FRs, make up about 35% to 40% of this volume and are 55% by value. BFRs alone account for 25% of the volume and 35% of the value (Tullo 2003). Brominated polymers are used in FR applications and bromine-containing epoxy sealants are used as FRs in semiconductor devices.

The BFRs (which are typically brominated aromatic or cyclic aliphatic compounds), can be the additive type, where the FRs are incorporated as a constituent in mixtures with polymers before, during, or more likely after polymerization; or the reactive type, where the FR is bonded chemically to the polymer itself. The BFR slows down or stops flame generation in polymer systems by interfering with the chain reaction mechanism of combustion, that is, by extinguishing radicals that serve to propagate oxidation. Synergists such as antimony trioxide, antimony pentoxide, or zinc borate add to the effectiveness of BFRs as do halogens when they are present in the polymer.

The consumption of bromine in FRs has risen steadily over the last several decades, mostly because of increased use of electronics and communications products. Because of the significant economic downturn in 2001, however, consumption fell drastically to its lowest level in many years.

Drilling Fluids

The oil and gas drilling industry uses calcium, zinc, and sodium bromides to prepare high-density, clear drilling, completion, packer,

and workover fluids (Ukeles and Freiberg 2002). These brine fluids are used in deep, high-pressure oil and gas wells; they do not plug the formation in workover and completion operations, as conventional drilling muds can do. Such bromide salt brine usage has led to higher production rates and longer production lifetimes. For such applications, calcium bromide is the largest volume bromide salt in use, followed closely by zinc bromide and sodium bromide. Sodium bromide finds use in specialized situations where calcium or zinc brines could cause a minimal amount of swelling, or in carbon dioxide-containing strata where there is a danger of calcium carbonate precipitation.

The bromine-based completion fluids are used in both of offshore and onshore drilling operations. Recent expansion in drilling activity and in the type of activity—namely deep, high-pressure wells—has contributed to the rapid growth of this market.

The inorganic bromides used in this application are prepared by neutralizing hydrobromic acid, which represents one of the two largest uses for this acid.

Brominated Agricultural Chemicals

Methyl bromide is currently the major bromine-containing pesticide used worldwide, but its use is declining. It is a broad-spectrum pesticide used to control pest insects, nematodes, weeds, pathogens, and rodents. About 25,000 t of methyl bromide were produced in the United States in 1999 for both domestic and foreign markets; much of it was produced as a by-product of BFR manufacture. Applications include soil fumigation, commodity and quarantine treatment, and structural fumigation. Global production in 1999 was estimated to be about 52,000 t.

When used as a soil fumigant, methyl bromide usually is injected into the soil at a depth of 30 to 60 cm before a crop is planted. This effectively sterilizes the soil, killing most soil organisms. After injection, the soil is covered with a tarp for 24 to 72 hr to slow the movement of methyl bromide from the soil to the atmosphere.

The three major manufacturers of methyl bromide—Albemarle Corp., GLCC, and Israel's DSBG—account for 75% of global production.

Biocides/Water Treatment

Even with continued dominance of chlorine in most of the water treatment sector, brominated compounds continue to make inroads into that market. This is probably due in part to environmental restrictions that chlorine has experienced in recent years. Among the advantages that bromine enjoys over chlorine in some water treatment areas are the following:

- Brominated compounds are less likely to form undesirable, halogenated organic compounds.
- Bromine has been found to be more efficient at higher temperatures than unstabilized chlorine.
- Brominated compounds are more effective at lower concentrations and at a higher pH than chlorine, thus allowing for greater throughput in waste treatment plants and cooling towers.
- Debromination of treated effluent streams is unnecessary, and any bromamines that are formed degrade more rapidly than the corresponding chloramines.
- Brominated products are estimated to be three times more effective than chlorine at controlling algae in cooling towers.

Bromine (e.g., bromochlorodimethylhydantoin [BCDMH]) has also made gains in the consumer water conditioning market as a

biocide for spas, pools, and hot tubs. The brominated hydantoin releases both hypochlorous and hypobromous acid in solution, where the latter is more effective at higher pH.

Brominated Intermediate

Brominated compounds are frequently used as intermediates in the production of other organic chemicals such as agrochemicals, pharmaceuticals, and dyes. For such applications, no bromine is present in the end product. Some of the bromine released during production processes that use these intermediates may be recovered and recycled (generally as hydrobromic acid or as a bromide salt); there are losses, however, that result when the by-product becomes too dilute or too contaminated. Some examples of chemicals that are used as intermediates are bromoacetyl bromide (cefotetan, labetalol), n-hexyl bromide (a building block for fragrances and dyes), 4-bromoaniline (meto bromoron, resorantel), and 2-bromopropionic acid (naproxene, prilocaine).

Other Uses

A number of pharmaceuticals are prepared in the form of bromides or hydrobromides. One example is the antitussive (alleviates or prevents coughs) dextromethorphan hydrobromide. Bromide salts also find use in some rechargeable batteries.

More than 5,000 t of bromine are used in the United States in the production of bromobutyl rubber for the inner linings of automobile tires. The majority of tire manufacturers prefer the improved performance of the bromine derivative over the chlorine-containing compound (i.e., chlorobutyl rubber).

Bromine is capable of desulfurizing fine coal (Grinbaum and Freiberg 2002). Bromine and its salts are known to recover gold and other precious metals from their ores by serving as an oxidant and complexant of gold.

Zinc-bromine storage batteries are being developed as load-leveling devices for use in electric utilities. In addition, photovoltaic batteries have been made from selenium or boron doped with bromine. Bromine also is used in quartz-halide light bulbs.

Product Pricing

Data from USGS indicated that the average price of purified elemental bromine was 99 cents/kg (44 cents/lb) during 2002. This was an increase from 67 cents/kg (30 cents/lb) for 2001. The price cited for 2001 represents a sharp decrease from the 2000 price, which was listed as 90 cents/kg (41 cents/lb) (Davenport 2003). According to Lyday (2005), prices peaked again in 2002 at 99.2 cents/kg (45.1 cents/kg) before declining to 72.0 and 70.0 cents/kg (32.7 and 31.8 cents/lb) in 2003 and 2004, respectively.

Packaging

Bromine is generally supplied as a liquid in drums or portable tanks (isotanks), depending on the quantities required by the customer. Hazardous Materials Regulations (HMR) are based on the recommendations of the United Nations Economic Commission for Europe (UNECE; 2005). Known as the "Orange Book," the UNECE directory provides an extensive list of dangerous goods and their control in transport by air, rail, road, sea, and inland waterways. It covers classifications and definitions of all dangerous substances; packaging, labeling and relevant shipping documentation; and training of transport workers.

In the United States, bulk quantities of bromine are shipped in lead-lined pressure tank cars or nickel-clad pressure tank trailers (filled to 92% of capacity). International shipments made by DSBG are in 15.2 to 23.3 t (5,300 to 8,000 L) lead-lined tank containers (isotanks). For smaller quantities of bromine, lead-lined

tanks ("goslars") of 3.5 t (4 t packed on one isoframe) and 400-kg (140-L) drums are used. Packaging is designed according to UN recommendations for Packing Group I.

Problems may be encountered in shipping and storage because of the relatively high freezing point of bromine (i.e., -7.25°C). If bromine freezes in a tank car, warm water—below 54°C —must be circulated through the car's heating coils.

Engineering Materials

Because bromine is highly hygroscopic, improper handling may cause its water content to increase to >300 ppm. When water content and organic matter content of bromine increase, the probability that it will corrode engineering materials increases. Therefore, bromine must be stored under dry nitrogen or dry air. Bromine with <30 ppm water content is noncorrosive to many nonferrous metals, including lead, nickel, tantalum, Hastelloy B, Hastelloy C, and Monel.

Some of the points previously mentioned are amplified below:

- Lead and lead-lined steel are commonly used in process equipment and storage containers when bromine is dry. The protective layer of lead bromide formed on the interior of a storage vessel allows it to be used with bromine with a water content up to 75 ppm.
- Glass has excellent resistance to wet or dry bromine corrosion.
- Nickel and nickel alloys such as Monel 400 and Hastelloys B and C are corrosion resistant to dry bromine (<30 ppm water) but are attacked rapidly by wet bromine.
- Tantalum and niobium both have excellent resistance to corrosion to either wet or dry bromine and can be used at temperatures up to 149°C .
- Steel and stainless steel are not recommended as construction materials because of corrosive bromine and bromine vapors.
- Fluorinated plastics such as Kynar, Kalrez, Halar, and Teflon (polyvinylidene fluoride [PVDF], perfluoroelastomer parts, ethylene-chlorotrifluoroethylene [ECTFE], and polytetrafluoroethylene [PTFE], respectively) are resistant to bromine corrosion and are used in valves, piping, gaskets, and linings.
- It is not recommended to use other types of polymers if contact with bromine is imminent.

Storage

Bromine for laboratory or pilot use generally is purchased in glass bottles. It is poured or pumped into small glass, ceramic, or lead-lined vessels that are equipped with PTFE stopcocks. The bottles are stored in their cartons in a dry, cool location away from direct sunlight. The storage temperature should not fall below the freezing point of bromine, -7°C .

Drum, tank truck, or carload quantities of bromine are stored in lead, lead-lined steel, or glass-lined steel storage tanks, which feed into a particular process or reaction. When using larger storage tanks (where bottom outlets cannot be used), the bromine should be pumped out of the tank with nickel, PVDF, or PTFE pumps.

Drums should be stored empty or full in an upright position, in a cool (above -7°C), dry place. Exposure to heat will cause a dangerous pressure buildup to develop. Protection from moisture and humidity is extremely important. GLCC offers bromine in non-returnable 120-gal steel cylinders that hold about 2,800 lb of bromine. The precautions previously outlined for drum storage also apply to cylinders.

Storage tanks also should be protected from moisture or humid air, because bromine will absorb moisture. When bromine is exposed to air having a normal summer dewpoint of 5° to 10°C , it

will equilibrate with about 70 to 80 ppm water. Wet bromine can severely corrode many metals. A slight positive pressure (0.1 in. of water) should be maintained in storage tanks by purging with dry air or dry nitrogen.

Transport of Bromine

A number of options are available for the transport of bromine. For example, GLCC ships bromine in bulk, using lead-lined, double-barrel tank trailers with a capacity of about 600 gal. Another option offered by GLCC is bromine in bulk either in 2,400 gal (56,000 lb) or in 4,400 gal (110,000 lb) lead-lined tank cars. The liquid bromine supply configurations used by DSBG (e.g., drums, goslars, or isotanks) were previously described.

Because bromine is a very corrosive and toxic material, regulations mandate which materials can be placed in proximity with, or require separation from, bromine. These regulations are available in the International Maritime Dangerous Goods (IMDG) code that covers regulations for international shipping.

U.S. Department of Transportation (DOT) regulations allow the transport of bromine within the United States, although it must be packaged, marked, labeled, placarded, stowed, segregated, and certified in accordance with the IMDG code, provided that part or all transportation is by vessel (Gilmour 1998). The total quantity in one tank may not be less than 88%, or more than 92% of the tank volume.

HEALTH AND SAFETY FACTORS

Effects of Exposure

Bromine has a sharp, penetrating odor. Bromine exposure—by liquid contact or vapor inhalation—is a considerable hazard with potential risk for serious injury and even death (Reineke 1978). The liquid rapidly attacks skin and other tissue to produce irritation and necrosis. Vapor concentrations of about 1 ppm are unpleasant, can cause eyes to water, and are highly irritating to the entire respiratory tract; 10 ppm becomes intolerable, even for more than a few moments.

If 10 ppm or more of toxic bromine are inhaled, severe burns and serious inflammation in the respiratory tract result, and these are frequently followed by pneumonia (Grinbaum and Freiberger 2002). Some symptoms of overexposure include coughing, nosebleed, feeling of oppression, dizziness, headache, and possibly delayed abdominal pain and diarrhea.

Skin contact with liquid bromine produces an initial mild cooling sensation, followed by a heating sensation. If bromine is not removed by washing the area affected with water, the skin will turn red, then brown, and the resulting deep burn is slow to heal. Contact with concentrated bromine also results in burns and blisters. Small areas in the laboratory that have become contaminated with bromine can be neutralized with a 10% solution of sodium thiosulfate. Such a solution should be kept readily available when working with bromine.

Vapor concentrations of 500 to 1,000 ppm by volume are dangerous to life at exposures for 0.5 to 1.0 hr. With respect to respiratory exposure, the Occupational Safety & Health Administration (OSHA) threshold limit value—time weighted average is 0.1 ppm in air for an 8-hr working day and 40-hr workweek. Monitoring devices are available for determining bromine concentrations in air.

Protective Equipment for Bromine Handling

Processes incorporating bromine should use totally enclosed systems. The minimum safety equipment requirements for handling bromine in the laboratory are chemical goggles, rubber gloves

(Buna-N or neoprene rubber), laboratory coat, and fume hood. For handling bromine in a manufacturing plant, personal protective equipment should include hard hat, goggles, neoprene full-coverage slicker, Buna-N or neoprene rubber gloves, and neoprene boots. When evacuating from an area where a release of bromine has occurred, a full-face respirator with an organic vapor-acid gas canister is desirable.

Fire Precautions

In case of fire, personnel should wear a self-contained breathing apparatus when working in an area containing bromine compounds. Bromine does not burn, but it is a strong oxidizer and reacts violently with aluminum, titanium, sodium, and potassium. Wood, paper products, fabric, petroleum products, plastics, and other organics may combust spontaneously in the presence of liquid bromine.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Methyl Bromide

Methyl bromide, which is a known toxic substance to human beings that damages the central nervous and respiratory systems, also may contribute significantly to the destruction of the Earth's stratospheric ozone layer. In September 1997, at the Ninth Meeting of the Parties to the Montreal Protocol, participating members agreed to a schedule for the reduction in the use of this fumigant. In developed countries, most uses were slated to cease in 2005 except for certain exemptions, and developing countries would have until 2015 to phase out methyl bromide.

Methyl bromide was listed as a Class I ozone-depleting substance in the 1990 Clean Air Act Amendments in the United States, which previously had instituted a ban that would take effect in 2001. The U.S. Congress extended the phaseout of methyl bromide to coincide with the 2005 ban set by the Montreal Protocol. To avoid any trade differences that might arise between U.S. growers and those in countries that still would have access to methyl bromide after 2005, the EPA has stated that in the absence of alternatives for methyl bromide, it would support limited, essential uses of this material.

Recently, a UN body (the Technology and Economic Assessment Panel) approved a U.S. request for exemptions from a ban on methyl bromide. This panel recommended exemptions for methyl bromide on U.S. crops such as strawberries, raspberries, eggplant, and tree seedlings. These exemptions have been the focus of objections from the Natural Resources Defense Council.

Flame Retardants

The polybrominated diphenyl ethers (PBDEs) are the BFRs that have been under the most scrutiny because of their apparent persistence in the environment and concerns for bioaccumulation. Recently, GLCC announced a voluntary U.S. phaseout of two PBDEs. The two flame retardants—pentabromodiphenyl ether (penta-BDE) and octabromodiphenyl ether (octa-BDE)—were phased out by the end of 2004 (Hogue 2003). (The phaseout of these two PBDEs is not considered to be as critical as would be any exit from deca-BDE [a styrenics additive], which is produced in the highest volume of the PBDEs.)

Because of environmental regulations, many polymer fabricators are now trying to avoid BFRs altogether. BFR suppliers themselves are diversifying their product offerings to include nonbrominated FRs. Thus, although both Albemarle's and Great Lakes' flame-retardant businesses were 100% bromine-based less than a decade ago, the situation has changed significantly. Through acquisitions and internal developments, roughly 35% of their sales now come from nonbrominated FRs.

OUTLOOK AND FUTURE TRENDS

Unofficial growth estimates for the bromine industry have been placed at about 2% per year throughout 2008. Bromine production from seawater is becoming an expensive process and will eventually become infeasible. No new areas of growth are expected in the near future, so the majority of bromine will continue to be consumed by FRs, intermediates, oil drilling, and biocide applications. The bromine industry has a negative image, which it feels is unjustified. The results from upcoming risk assessments of BFRs (e.g., tetrabromobisphenol A [TBBA], deca-BDE, penta-BDE, and hexabromocyclododecane [HBCD]) will be crucial to the future of the industry. Lobbying activities and industry panels will play an important part in the future of the bromine industry.

The price of elemental bromine and the prices of bromine compounds and derivatives are correlated. The current lower prices of the major brominated products, along with regulatory pressures, threaten the industry's reinvestment capabilities in new R&D and production facilities and thus its long-term viability. In addition, the geographical shift of major industrial chemical activities from the West to China will continue to influence this industry along with others.

China

Approximately 80% of Chinese bromine is produced from saturated brines in Shandong Province (Bohai Bay). The remaining 20% is produced from seawater. Bromine reserves in Shandong are estimated to be 1.0 to 1.5 Mt. Many of the big Chinese producers are also in the process of going downstream to produce brominated compounds, and their relocation to bromine resources is being observed. Also of note is the trend of consolidating smaller bromine plants into one large company. The Chinese bromine industry has the ability to produce new products and improve the quality of existing products (e.g., FRs, dyestuffs, pharmaceuticals, and bromides) rapidly. Many of the bromine industry customers are either producing or in the process of establishing a production base in China. Chinese markets are going to adopt the European regulations (Restrictions of Hazardous Substances, or RoHS) for chemicals such as FRs.

Israel

Of the approximately 548,000 t of global yearly bromine production in 2002, approximately 206,000 t (almost 38% of the total) are produced in Israel. A slightly larger quantity is produced in the United States. The overall estimated global growth of about 2% is also true for Israel. The sole Israeli producer of bromine is DSBG, which is part of the ICL Group. DSBG also produces bromine derivatives that have a wide range of applications. DSBG produces bromine from the Dead Sea, where its concentration ranges between 6.5 g/L in the southern basin and 12 g/L in the liquors remaining after potash production from the Dead Sea.

As previously stated, more than 90% of DSBG's sales are from exports. Therefore the current situation of lower prices for the main brominated products, along with regulatory pressures, threatens the main business of the company and its status as a major producer. DSBG is also a major manufacturer of the fumigant methyl bromide, which is being phased out. Therefore, DSBG, as well as other major producers, are seeking environmentally safe "green" products using bromine and bromine-containing chemicals.

Jordan

Because Jordan is situated on the eastern shores of the Dead Sea, it was only a matter of time before bromine production from Dead Sea brines began. A 25,000-tpy bromine plant was commissioned

in 2003. At full production capacity of 50,000 tpy, this plant would be able to replace the Albemarle production facilities in the United States. The production of brominated compounds (e.g., TBBA) will be able to commence very shortly after that time.

United States

It is difficult to find data on any definitive future demand estimates for bromine in the United States. Unofficial sources have predicted a modest yearly growth rate of about 1% to 2%. This prediction is based on the assumption that no new, major legislative restrictions will be placed on bromine chemical use in the foreseeable future. Bromine production from wells in Arkansas is diminishing at 2% to 3% per year, and higher production costs are anticipated. The major U.S. bromine chemical compounds companies (Albemarle and GLCC) are succeeding in finding alternative bromine sources. Albemarle finalized an agreement with a Jordanian partner to build the bromine plant previously described, with a maximum capacity of 50,000 tpy. GLCC completed an agreement with the Israeli company DSBG for the supply of bromine and brominated products. GLCC is developing alternative flame-retardant products based on tetrabromobenzoate esters as an alternative to the ecologically problematic penta-BDE FR used in the polyurethane sector. Albemarle is enlarging its TBBA (a leading BFR) production capacity. Both companies also have diversified their flame-retardant product lines by moving into nonhalogenated FRs through acquisitions.

OUTLOOK ACCORDING TO MAJOR USE

Flame Retardants

Over the last 10 years, the FR industry has been growing 3% to 5% annually (Chemical Products Synopses 2003). Unofficial figures from reliable sources indicate that the brominated section of the industry is growing at a similar pace. One of the reasons given for continued growth of the brominated segment is the increasingly stringent fire safety standards in place in Europe and the United States as a result of increasing fire-safety awareness. California, the most populous state in the United States, requires fire retardants in polyurethane foam mattresses, and proposed federal laws (e.g., American Home Fire Safety Act) would require similar actions.

Industry observers claim that there are about 50 different major BFRs. All major FRs (e.g., deca-PBDE, HBCD, TBBA, and penta-BDE) are currently undergoing risk assessments to see if they are in accord with the PBT (persistent, bioaccumulation, toxicity) criteria. Increasing efforts are being made to replace these with nonhalogenated FRs or with more environmentally friendly BFRs; that is, reactive ones that will not leach to the environment during use. Thus far, many of the introduced replacements have been different BFRs from the PBDEs that they were to replace. The strategy used by producers of brominated products is to shift from products under attack to products that are considered less environmentally problematic and are recyclable.

Drilling Fluids

The forecast for the clear brine fluids market depends on the general oil and gas drilling business climate, which itself is a highly fluctuating market. The mercurial behavior of this industry is illustrated by the steep decline in drilling activity between 1990 and 1993, followed by a significant increase in activity between 1994 and 2000. The market for calcium bromide in 2003 was approximately 90,000 t with a price of \$400 to 500/t; the market for zinc bromide brines was about 50,000 t. The market exhibits price erosion during periods of low demand, and competition from brine production from effluent hydrobromic acid.

The drilling fluids market is threatened by several factors:

- Consumption of brine fluids on a per-well basis will decline because of the expansion in reuse and recycling of brine fluids.
- Emerging ecological requirements are expected to have an accompanying new demand for “green” drilling fluids.

Biocides

The worldwide bromine-based biocide market is estimated to be about \$1.80 billion with an annual growth rate of 4% to 5%. Approximately half of this is from industrial water treatment applications (cooling towers, paper mills, and so forth.) where the major products are bromine (hypobromous acid); bromochlorodimethylhydantoin (BCDMH); sodium bromide; ammonium bromide; 2,2-dibromo-3-nitropropionamide (DBNPA); 2-mercapto benzothiazole (MBT); and 1,4-bis(bromoacetoxy)-2-butene (BBAB). This market is divided as follows: North America and Canada, 50%; Europe, 25% to 35%; and the rest of the world, 15% to 25%. The other half goes mainly to the swimming pool and spa business as BCDMH and sodium bromide. In this case, the North American fraction is about 75% whereas the rest goes to southern Europe and Australia. The latter market fluctuates according to weather and the mood of the public.

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Chemicals

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INTRODUCTION

This chapter discusses the relationship between industrial minerals and chemical manufacturing. It supplements rather than duplicates the commodity chapters in this volume. Particular emphasis is given to the pertinent chemical elements and to market factors.

Condensing this broad subject into a few pages of this book permits treating only the most important elements derived from industrial minerals. Hydrocarbons, which quantitatively dominate as raw materials for the chemical industry, are omitted, as are the metallic elements and minerals covered in other chapters in this volume, such as phosphorous, potassium, and nitrogen for fertilizers, and titanium dioxide for pigments. The remaining six elements of major importance covered here are boron, bromine, chlorine, fluorine, sodium, and sulfur.

Table 1 affords an overview of the main industrial minerals, the chemical products derived from them, and end uses of the products.

Salt brines have particular importance as raw material sources for the chemical industry. Table 2 is a chart of the chemical compounds derived from four types of brines: (1) Owens Lake-type brines, which are sources of boron and sodium compounds; (2) Midland-type brines, from which bromine, iodine, and chlorides of calcium, magnesium, potassium, and sodium are derived; (3) Searles Lake-type brines, yielding boron, bromine, lithium, magnesium, potassium, and sodium compounds; and (4) Silver Peak-type brines, produced mainly for lithium.

MARKET ATTRIBUTES

Some of the important market traits common to industrial minerals used by the chemical industry are as follows:

1. They are international commodities (e.g., fluorspar, many of which move in foreign trade).
2. Grade and freedom from deleterious elements are important factors affecting their usability in chemical processes. An example is salt (NaCl) used in electrolysis where ultrapure evaporated salt is required to meet rigid specifications.
3. Purified products take on the characteristics of specialty items and command a distinctly higher price than the basic commodity from which they are derived.
4. In practically all cases, chemical users require some sort of purification or beneficiation of the naturally occurring mineral to bring it to specification, and individual specifications may vary from user to user for essentially the same use.
5. In some instances it is necessary to strike a balance between what the vendor can supply and what the buyer requires, with the result that specifications have to be eased to afford the needed materials in marginal cases.
6. Because they tend to be bulk commodities, low cost for handling and transportation is important; so cost may limit the area from which a chemical user can draw its supply.
7. Shipments are usually in bulk and frequently in multiple-car, full-trainload, or full-shipload lots to reduce transport costs, which in turn may require large investment in terminal facilities.
8. Purchases are generally by contracts of 1 year or longer term, with spot buying playing only a minor role.
9. Contract prices are usually fixed in short-term commitments but can vary according to assay, with premiums and penalties for content above or below the norm; general practice, however, is for specifications to be fixed in the contract with minimums set for the desired material and maximums for undesired elements. In longer term contracts, prices are often prorated on labor, fuel, and other vendor processing costs.
10. Suppliers of individual commodities to the chemical industry tend to be few and are generally medium- to large-size producers supplying a few major consumers.
11. The bulk of the mineral volume is for basic chemical uses; sulfur suppliers to sulfuric acid producers and fluorspar for hydrofluoric acid producers are typical examples. These basic chemical products then are used for the manufacture of other products.
12. Shortage of a supply of adequate quality leads consumers to seek substitute sources. For fluorspar, much work is being done on recovery of fluorine from phosphate rock. Success in the form of fluoro-silicic acid or hydrofluoric acid production could, in time, affect the hydrofluoric acid chemical industry.
13. Markets tend to be characterized by cycles of shortage followed by oversupply, with attendant wide price fluctuations.
14. Barriers to international trade can have an adverse effect on the movement of industrial minerals needed by the chemical industry. Antidumping laws, quotas, and tariffs can disrupt or dislocate normal markets.

Table 1. From industrial mineral to inorganic chemical

Commodity	Chemical Formula	Reaction Type	Reagents	Product Formula	Product Name	Uses for End Products
Spodumene	LiAl(SO ₄) ₃	Acid decomposition	Sulfuric acid	Li ₂ SO ₄	Lithium sulfate	Ceramics, glass fluxes, flame colorant, pharmaceuticals, cement additive
		Alkali decomposition	Limestone	LiOH	Lithium hydroxide	Absorption refrigeration, greases, high-strength glass, dyes, wood preservatives
Rock salt	NaCl	Electrolytic	Electricity, water	NaOH	Caustic soda	Miscellaneous chemicals, rayon, pulp and paper, metals, soap, water treatment
				Cl ₂	Chlorine	Miscellaneous chemicals including organics, pulp and paper, water treatment, pharmaceuticals
				H ₂	Hydrogen	Ammonia synthesis, miscellaneous chemicals, metallurgy, hydrochloric acid
		Ammoniation	Ammonia, lime, carbon dioxide	Na ₂ CO ₃	Soda ash	Miscellaneous chemicals, glass, metallurgical, soaps
				CaCl ₂	Calcium chloride	Road treatment, dust suppression
Sylvite	KCl	Electrolytic	Electricity, water	KOH	Potassium hydroxide	General chemicals, fertilizers, detergents, agriculture, batteries, foodstuffs
				Cl ₂	Chlorine	General chemicals, fertilizers, detergents, agriculture, batteries, foodstuffs
				H ₂	Hydrogen	Gas: Petroleum refining, reducing agent, production of high-purity metals
						Liquid: Coolant and propellant, fuel for rocket engines and cryogenic research
Beryl	3BeO•Al ₂ O ₃ •6SiO ₂	High-temperature fluorination	Sodium fluoroferrate	Be(OH) ₂	Beryllium hydroxide	Fluorescent tubes, glass, ceramics, Cu-Al-Ni alloying chemical feedstock
Limestone	CaCO ₃	Calcination	Heat	CaO	Quicklime	Flue-gas desulfurization, fluxes, caustic soda manufacture, effluent treatment, water treatment
				CO ₂	Carbon dioxide	General chemicals, soda ash
Seawater	MgCl ₂	Precipitation	Dolime	MgO	Magnesium oxide	Refractories
Magnesite	MgCO ₃	Calcination	Dolime	MgO	Magnesium oxide	Refractories
Brine	MgCl ₂	Steam decomposition	Dolime	MgO	Magnesium oxide	Refractories, general chemicals, fertilizers, cements
			Not applicable	HCl	Hydrochloric acid	Miscellaneous chemicals, metal pickling, organic chemicals, pharmaceuticals, environmental
Celestite	SrSO ₄	Carbothermic reduction	Coal	SrCO ₃	Strontium carbonate	Glass, ceramics, pyrotechnics
Barytes	BaSO ₄	Carbothermic reduction	Coal	BaCO ₃	Barium carbonate	Glass, ceramics, pyrotechnics, drilling muds, oxygen source, ferrite magnets, medicine, pigments, bricks, metal soaps, superconductors, flux

Adapted from Fulton 1994 and Harben 2002.

(Table continued next page)

Table 1. From industrial mineral to inorganic chemical (continued)

Commodity	Chemical Formula	Reaction Type	Reagents	Product Formula	Product Name	Uses for End Products
Basinacsite Monazite Xenotime	Ce, La(PO ₄)	Acid decomposition	Sulfuric acid	Ce,LaO	Rare earth oxides	Glass colorants, polishing powders, lighter flints, arc carbons, catalysts, phosphors, ceramic stains, camera lenses
Zircon	ZrSiO ₄	Chlorination	Chlorine, coke	ZrOCl	Zirconium oxychloride	Metal production, special chemicals
Rutile (natural and synthetic)	TiO ₂	Reductive chlorination	Chlorine, coke	TiCl ₄	Titanium tetrachloride	Pigments, titanium metal, waterproofing agents, glass, ceramics, pharmaceuticals
Chromite	Fe ₃ CrO ₄	Alkali decomposition	Soda ash	Na ₂ CrO ₄	Sodium chromate	Chromium chemicals, oxidants, metallurgy, drilling mud, fanning, pigments, wood preservatives
Pyrolusite	MnO ₂	Acid decomposition Carbothermic reduction	Hydrochloric acid Coal, nitric acid	MnCl ₂ Mn(NO ₃) ₂	Manganous chloride Manganous nitrate	Dry batteries, fertilizers, glass, enamels, catalysts, chemical feedstock, flux
Colemanite	Ca ₂ B ₄ O ₁₁ •5H ₂ O	Alkali decomposition	Soda ash	NaBO ₂	Sodium borate	Detergents, fluxes, bleaches and dyes, pharmaceuticals, glass, water treatment
Bauxite	Al ₂ O ₃ •2H ₂ O	Alkali solution Acid decomposition	Soda ash Sulfuric acid	Al(OH) ₃ Al ₂ (SO ₄) ₃	Aluminum hydroxide Aluminum sulfate	Water treatment chemicals, flocculants, dye mordants, refractories, catalysts
Quartz, silica	SiO ₂	Alkali reaction	Soda ash	Na ₂ SiO ₃	Sodium silicate	Adhesives, cements, deflocculants, soaps, inks, cosmetics
Caliche	NaNO ₃	Reductive chlorination	Chlorine, coke	SiCl ₄	Silicon tetrachloride	Organic chemicals (silicone fluids and rubbers), silicon metal, plasma etching
Phosphate rock	Ca ₅ F(PO ₄) ₃	Acid decomposition	Sulfuric acid	HNO ₃	Nitric acid	Fertilizers, general chemicals, metals and ore processing, urethane, explosives
Brimstone	S ₆	Electric furnace reduction	Silica, coke	H ₃ PO ₄	Phosphoric acid	Fertilizers, detergents, foodstuffs, organic chemicals, water treatment, tanning, refractories
Iron pyrite	FeS ₂	Burning	Air	P	Phosphorus	See phosphoric acid
Fluorspar	CaF ₂	Catalytic oxidation	Air	SO ₂	Sulfur dioxide	Fungicide, insecticide, reducing agent, solvent, chemical feedstock
Seawater, brines	NaBr	Oxidation	Chlorine	H ₂ SO ₄	Sulfuric acid	Fertilizers, chemicals, petroleum refining, pigments, metallurgical
Seawater, brines, caliche	NaI	Oxidation	Chlorine	H ₂ SO ₄	Sulfuric acid	Fertilizers, chemicals, petroleum refining, pigments, metallurgical
				HF	Hydrofluoric acid	Chemicals, fluxes, etchants, metallurgy, isotope separation, semiconductor manufacture, catalyst
				Br ₂	Bromine	Organic synthesis, pharmaceuticals, petroleum additives, water purification, pesticides, batteries
				I ₂	Iodine	Foodstuffs, sanitizers, organic chemicals, dyes, medical, catalysts, metals

Adapted from Fulton 1994 and Harben 2002.

* See corresponding chapters in this volume for detailed discussions.

Table 2. Salt brine derivatives*



* See corresponding chapters in this volume for detailed discussions.

15. Chemical industry consumers may back-integrate for security of supply or for favorable economics by joint ownership, often with experienced mining partners.
16. Conversely, industrial minerals producers may forward-integrate into chemical production.
17. Governmental regulation can affect the usage of chemicals derived from industrial minerals, as is the case of the prescribed phaseout of brominated products under the Montreal Protocol.

ELEMENTS OF MAJOR IMPORTANCE

Boron

Boron is used by the chemical industry mainly as borax (disodium tetraborate decahydrate). It is derived principally from desert evaporite deposits. Major commercial boron minerals are tincal, or native borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$); colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$); tincalconite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$); ulexite ($\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$); and kernite ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$). Commercially, sodium borates predominate and are supplied by refineries in a variety of grain sizes in either the purified borax form or as fused, crushed, anhydrous borax. Boric acid and boric oxide are also available. The industry defines boron content in terms of B_2O_3 : for example, granular borax decahydrate contains 36.5% B_2O_3 ; 69.1% anhydrous borax; and 56.3% boric acid. These products are sold at 99.5% purity. Raw and semiprocessed ores also are sold. Major world production is in the United States, Turkey, and Russia, each with a million or more tons per year.

Borates are used as fluxes in metal processing, in ceramics, as a constituent of heat-resistant glasses, as an aid in glass fiber manufacture, as cleaning agents, and in textile manufacture. Boron is being used as sodium borohydride in development of hydrogen fuel cells in a public-private project in connection with \$150 million funding by the U.S. Department of Energy (O'Driscoll 2002). Borates are used to suppress forest fires, typically dispensed from aircraft. Borax and boric acid are used as extenders in dye making. In elemental form, boron acts as a neutron absorber in shielding against radioactivity in electricity generation. High level nuclear wastes can be vitrified using boron compounds for shielding radiation (Loft 2002). Organic boron compounds are used as gasoline additives, in insecticides, and in pharmaceuticals. Trifluoroborate is used for manufacture of fluorinated hydrocarbons and in production of antiknock compounds for gasoline. Boron nitride has extreme hardness and stability at high temperature, up to 1,600°F in oxidizing atmosphere. It is used for molten-metal pump parts, transistor and rectifier mounting wafers, and heat-resistant fibers for military composites. Fuels containing boron and hydrogen are outstanding for high energy yield but have not been widely used because of pollution effects and high cost. Table 3 describes boron starting materials and end products.

According to the U.S. Geological Survey (USGS; Lyday 2002a), U.S. production of boron minerals and compounds in 2001 was 1.05 Mt gross weight compared to 1981 at 1.342 Mt, and 1991 at 1.24 Mt, illustrating a continuing decline. Approximate year-end free on board (f.o.b.) prices, quoted per ton in bulk for 1990 and 2001, are as follows:

	1990, \$	2001, \$
Boric acid (99.9%, technical grade)	775–784	788
Pentahydrate borax (technical grade)	321	376

Opportunities for wider applications of boron compounds, in addition to the growth in established fields of use, include in glass fibers for reinforced plastics for weight reduction in automobiles, in fuels, and as a possible replacement of fluorspar as a fluxing agent in steelmaking. Boron's capability of forming a large number of

coordination compounds offers a venue for investigation through which a variety of diverse products would result.

Bromine

Bromine compounds are used in flame retardants (40%), drilling fluids (24%), pesticides (12%), water treatment chemicals (7%), and others (17%) (Lyday 2002b). A variety of organobromides are used in agriculture as fumigants for controlling nematodes in soil and insects in grain and seed storage. Elemental bromine is consumed in disinfectants and bleaching agents. Sodium, potassium, and ammonium bromides have minor uses in textile fiber manufacturing, photography, and medicines. Bromine compounds are used in small amounts in making dyes, resins, leather, and rubber products as well as in producing textile intermediates and finishing agents. Expanding uses are in flame retardants and extinguishing agents and for gas- and oil-well completion fluids as calcium, sodium, and zinc bromides. Biocides containing bromine used in industrial cooling are replacing those based on chlorine for environmental considerations.

According to the USGS (Lyday 2002b), U.S. refinery production of bromine in 2001 was about 212,000 t compared to 230,000 t in 1998. Current U.S. production compares to production capacity of about 260,000 t p.y. Israel was the second largest producer in 2001 at 206,000 t. Total production worldwide in 2001 was about 543,000 t.

Average value of bromine sold or used in 2002 was 75 cents/kg, compared to about 88 cents/kg at year-end 1990; it had increased from 45 cents in the mid-1960s to about 60 cents in the early 1980s. The price is expected to increase mainly because of the increased cost of process energy. The reader is referred to the chapter on bromine in this volume for further information.

Chlorine

A number of principal chlorine consumers in the chemical industry are situated in the producing regions and in many cases are back-integrated with obvious advantages. Consumers who are not back-integrated purchase either chlorine or chlorine compounds such as hydrochloric acid, chloroform, ethyl chloride, ethylene dichloride, carbon tetrachloride, perchlorethylene, and the like, depending on process requirements and economics. Choice of purchase mix is determined by relative costs, for example, buying either carbon tetrachloride or chlorine and hydrocarbons for in-house production of the chlorocarbon. This choice has ramifications, such as the internal generation of HCl produced as a by-product of hydrocarbon chlorination and of fluorination. The internally produced HCl can then be oxidized back to chlorine in a closed circuit, thereby reducing the intake of purchased chlorine and reducing costs.

Similarly, manufacturers of polyvinyl chloride (PVC) can choose to buy ethylene dichloride or, if they have chlorine and ethylene available, they can elect to make it themselves. Recycling by-product HCl from vinyl chloride monomer plants is widely practiced with use of HCl in oxychlorination to make ethylene dichloride.

Principal chemical industry uses for chlorine are for intermediates and for synthesis of organic and inorganic chlorides used in plastic solvents, agricultural chemicals, automotive fluids, sanitation products, and so forth. Another use of ethylene dichloride is for making solvents, such as trichloro- and perchloroethylene. Ethylene dichloride also is a less expensive, though less effective, lead scavenger than ethylene dibromide used in fuels as antiknock compounds; lead, however, has been eliminated almost entirely from gasoline intended for spark-ignition engines, although small amounts of lead still are used in automotive fuels and in aviation gasoline.

Table 3. Boron minerals and chemicals

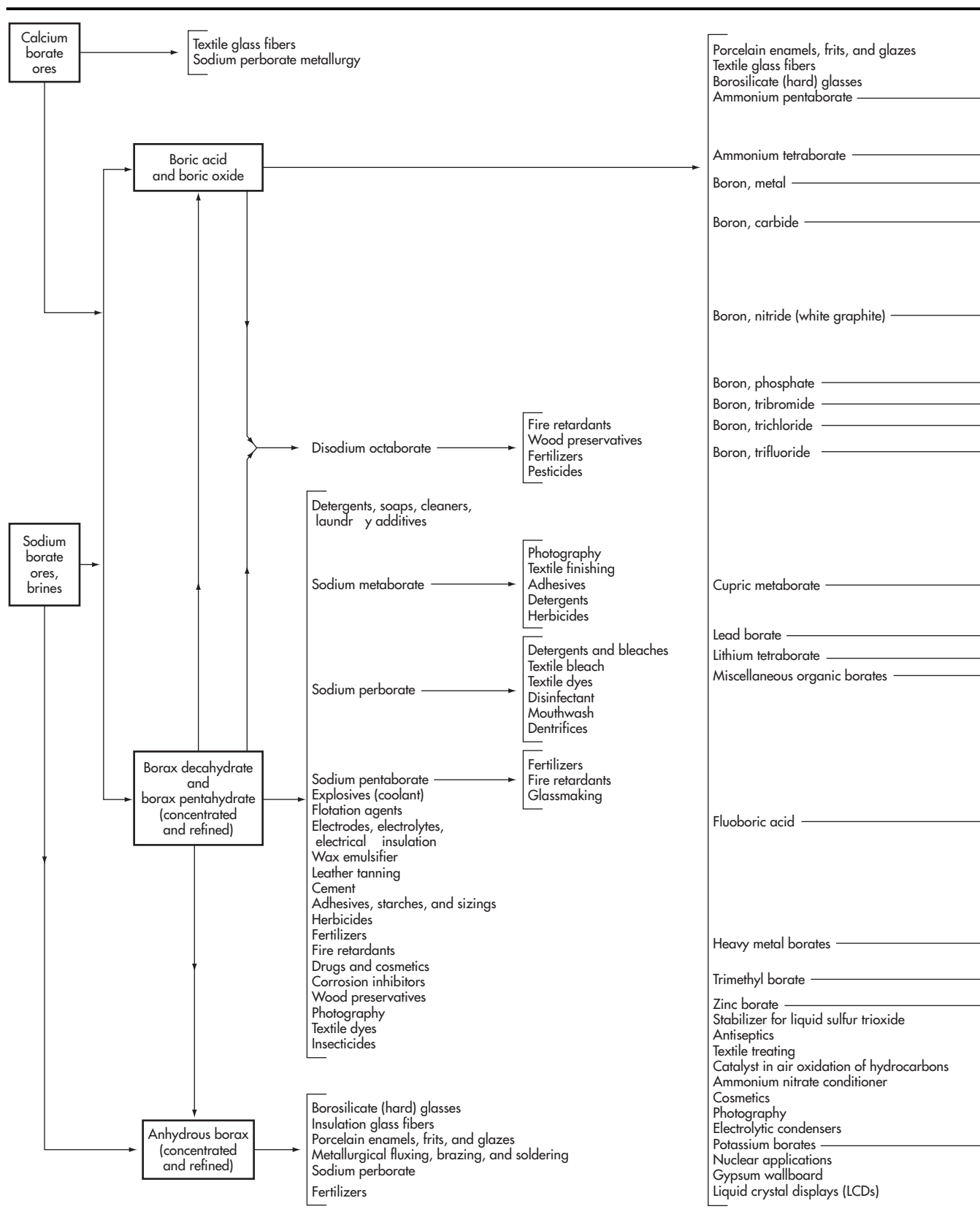


Table 3. Boron minerals and chemicals (continued)

Electrical condensers Fireproofing Paper coating	Delay fuses Flare ignitors Boron phosphide	High temperature transistors
Neutralizing agent Fireproofing	Hexaboron silicide Tetraboron silicide	Refractory material
Abrasives Steel refractories Control rods for nuclear reactors	Getter in manufacture of vacuum tubes Abrasives Grain refiner in aluminum manufacture Nuclear shielding Coating material for solar batteries Semiconductors Laser technology	Pentaborane High energy fuels
High-temperature lubricant Refractory Fibers Cosmetics Abrasives Thermionic devices	Boron trifluoride Diborane	Higher boron hydrides Polymerization catalyst for ethylene Copolymerization of styrene and butadiene
Ultra-low-loss dielectric Diborane	Organo-boron compounds Trichloroborazole Depolymerization of paraldehyde	Gelling agent Catalyst
Neutron analysis Catalyst	Flux Polymerizing agent for driers Stabilizer for liquid sulfur trioxide Lightweight, high performance products	
Fireproofing agent for wood Fungicides Oil pigments Pigments for ceramics	Wheat rust compounds	
Ceramics	Paint and varnish driers Lead glass	Glycol borates Alcohol borates
Ammonium fluoborate	Molding sand additive in magnesium casting	Jet fuel deicer Epoxy resin curing agents Nuclear shield via neutron-detecting Bactericide in fuels Trimethoxyboroxine
Cadmium fluoborate Cupric fluoborate Lead fluoborate Nickel fluoborate	Electroplating baths	Extinguishing metal fires Epoxy foams
Potassium fluoborate	Binder and cooling agent in abrasive wheels Electrolytic brightening of aluminum	
Sodium fluoborate		Electrochemistry Heat treating magnesium alloys Nonferrous flux
Stannous fluoborate Zinc fluoborate	Electroplating baths	Lithium borohydride Potassium borohydride Pharmaceuticals Reduction of aldehydes and ketones
Fireproof and mold resistant paints		Vat dyes Blowing rubber and epoxy resin foams Paper bleach and pulp brightener Hair waving formulations
Sodium borohydride		
Ceramics Medicines Fire-retardant Fungicides		
Inorganic boron compounds Photography Casein solvent Metallurgical welding and brazing Diazotype developer solutions Fluxes		

An important inorganic intermediate used in the manufacture of titanium dioxide (TiO_2) pigment is titanium tetrachloride, which is manufactured by the so-called chloride process that now supplants the older sulfate process.

Chlorine also is required for the manufacture of organic intermediates such as adiponitrile from butadiene. Adiponitrile is a feedstock chemical used in the production of Nylon 6,6. In this case, both chlorine and caustic are consumed, fortunately, in the same ratio as produced by electrolysis of brine. This ratio, known industrially as one electrochemical unit (ECU), consists of 1.0 t of chlorine to 1.1 t of caustic soda and requires 1.75 t of salt to produce one ECU.

Growth of elastomeric products, made using chlorine, butadiene, and caustic or using hydrochloric acid and acetylene, has contributed significantly to world demand for chlorine.

Product obsolescence can play an important role in the chlorine market, as in the case of by-product chlorine from metallic sodium manufacture. The amount of chlorine available from sodium production decreased as demand for leaded gasoline declined; lead was amalgamated with sodium as a step in the manufacture of lead antiknock compounds.

Phosgene is another chlorine chemical important to chemical processing, for example, in the production of agricultural chemicals, isocyanates, and other fiber intermediates and elastomers.

Overall domestic growth is generally flat or slightly declining because of (1) nonchlorine-based processes supplementing some of the chlorine requirements; (2) slackened growth in cyclic organic detergents and chlorinated solvents, which have been criticized on environmental grounds; (3) leveling off in growth of other major products containing chlorine, such as vinyl chloride; (4) the problem with dioxin poisoning and its negative influence on the bleaching of pulp and paper; and (5) curtailment of chlorofluorocarbon manufacture and use. An exception is PVC, where growth is currently positive because of increased building construction in a growing economy and relatively low interest rates.

Environmental issues profoundly affect the chlorine business. Discontinuing use of lead additives and curtailing carbon tetrachloride production are prime examples. The generally accepted thesis that chlorine in the upper atmosphere is responsible for a chain reaction destroying the Earth's protective ozone layer eventually may lead to reductions in manufacture and use of chlorine compounds.

Chlorine-caustic market pricing provides insight into the pricing mechanism at work. Chlorine pricing is characterized by vendor willingness to make long-term contracts at a set price. Such contracts, with terms of 5 to 7 years, provide the seller with an adequate, though modest, return on investment. ECU prices are generally equally divided between chlorine and caustic. The chlor-alkali manufacturers can find advantage by raising caustic prices, thus compensating for any weakness in chlorine and giving a slight increase in overall profitability. Industry return on investment is not so great as to give strong incentive to accelerate expansion.

Since most of the chlorine produced in the United States is for captive use (about 60%), the manufacturers have used merchant sales to achieve high rates of operation, thereby minimizing unit costs of their captive requirements. These merchant sales are largely influenced by proximity of vendor to purchaser. The overall market demand must be viewed in terms of chlorine chemicals; some of the ostensibly captive chlorine requirement of manufacturers is truly just one move downstream along the route to a final product. For chlorinated hydrocarbons, the chlorine manufacturer takes the next step of treating hydrocarbons and selling the chlorinated compound.

An interesting change of technology in chlorine manufacture is the decline of mercury cells in favor of diaphragm cells because of environmental measures to control mercury, even though diaphragm cells cost more to operate but require less initial investment. Before this restructuring, the trend was toward increasingly larger mercury cells that produced 20 t of chlorine per day. The emphasis has changed so that the majority of chlorine produced by brine-electrolysis comes from diaphragm cells. The development of the dimensionally stable electrode eliminates the problem of gradual chlorination of the organic binders used in graphite anodes that resulted in inefficient cell operation as the anodes disintegrated. An electrode made of titanium metal, protected by a film of inert metal oxide, permits construction of larger cells with higher current densities and results in a 3- to 5-year electrode life compared to 3 to 6 months for graphite electrodes. Diaphragm cells with a production capacity of 3 tpd of chlorine have a life of 9 months to 1 year and are limited only by problems with the diaphragm itself. Solving difficulties with the diaphragm is centered on new materials and construction techniques.

A further cell modification is a bipolar cell in which anodes are connected directly to adjacent cathodes to reduce voltage drops now experienced in busbar connections between cells. Development of bipolar membrane cells will permit higher concentrations of caustic in the cell, thereby eliminating subsequent costly evaporation.

In 2002, percentages of chlorine produced in the three types of electrolytic cells were diaphragm (78%), mercury (14%), and membrane (6%); the balance of chlorine and caustic production (2%) is by-product from magnesium and sodium metal production (Kostic 2002b).

The long-range market outlook is continued modest, steady growth in chlorine use by the chemical industry despite the adverse factors cited.

Fluorine

Fluorine in the chemical industry is used mainly as a constituent of fluorocarbons and in organic fluorides. Hydrofluoric acid is the intermediate for practically all fluorine chemicals. It is produced by reacting fluor spar with sulfuric acid to yield hydrogen fluoride gas and calcium sulfate. The gas usually is liquefied as anhydrous hydrogen fluoride, but it may be adsorbed in water to make aqueous hydrofluoric acid, usually 70% HF. In commercial practice, about 2.2 t of acid-grade fluor spar (97% CaF_2) are required to make 1 t of hydrofluoric acid. Contaminants found in commercial, acid-grade fluor spar are calcium carbonate, silica, and sulfur; maxima are usually set by the consumer. Other objectionable constituents, for which maxima may be set, include arsenic, chloride, and phosphate. Grain size and moisture content are also specified.

The fluorocarbons are a large family of useful compounds. The first to obtain commercial acceptance were refrigerants; they still constitute a major part of the market. They are used in the manufacture of plastics that are characterized by chemical inertness, toughness, and electrical resistivity. Other fluorocarbons are used as fire-extinguishing agents, dielectrics, surfactants, anesthetics, and pharmaceuticals.

Concern for the ozone-depleting potential of chlorofluorocarbons has led to the development of alternatives that contain less or no chlorine in the molecule and do not deplete ozone in the stratosphere. Because of environmental concerns, the United States ended chlorofluorocarbon use in aerosol propellants. In other applications, substitutes (i.e., "not in kind" substitutes) are sought. Most alternative fluorocarbon molecules contain a higher percentage of

fluorine atoms than the chlorofluorocarbons they replace. Depending on the amount of the market captured by not-in-kind substitutes and the amount gained by the new, higher fluorine-containing alternatives, fluorspar usage by the chemical industry may stay about level or even increase moderately.

Inorganic fluorides are produced by reacting hydrofluoric acid with the appropriate base or basic salt. Principal uses of inorganic fluorides are outside the chemical industry, such as (1) the use of synthetic cryolite (Na_3AlF_6) in the production of aluminum metal; (2) the relatively minor uses of sodium and potassium silicofluorides for fluxes and as constituents of enamels and glass; (3) the use of aluminum fluoride as brazing flux; (4) the use of sodium-aluminum-fluoride in resin-bonded grinding wheels; and (5) the use of sodium silicofluoride in water supply systems to control human tooth decay.

Hydrofluoric acid is a source of fluorine in reactions with uranium to produce gaseous uranium hexafluoride from which U^{235} is diffusion separated from the more abundant U^{238} . Hydrofluoric acid is also widely used as a catalyst in the alkylation of petroleum during high-octane gasoline production. A minor use of hydrofluoric acid is for etching glass, such as electric light bulbs.

The reader is referred to the chapter on fluorspar in this volume for further information.

Sodium

Caustic soda, soda ash (sodium carbonate), and salt cake (sodium sulfate) are useful to the chemical industry mainly as sources of alkalinity and the sodium ion. Supply of caustic is entirely dependent on chlorine production (see section on Chlorine in this chapter).

Demand for caustic is related, in part, to chlorine, but caustic is unrelated to chlorine in many of its applications. For example, the organic intermediate adiponitrile, mentioned previously, is produced from butadiene. Where chlorine and caustic are related in direct proportion (see section on Chlorine in this chapter) to the ECU, a price advantage for the total ECU is possible because the vendor has no surplus of either commodity. Generally, however, the pricing of the two is independent.

Various sodium raw materials may be used for the manufacture of certain sodium compounds such as bicarbonate, cyanide, perborate, nitrate, and silicate. In making sodium bicarbonate and sodium silicate, soda ash is the usual starting material, but caustic is sometimes used for silicate.

Caustic is used in making such diverse products as cellophane, nylon intermediates, and pigments. It has important applications in waste treatment processes and in pulp, paper, and alumina manufacture. Increased demand for these applications led periodically to tight supply and rising prices, partly because chlorine demand failed to keep pace with demand for caustic. On occasion, environmental concerns adversely impacted chlorine use in its principal markets, including pulp and paper, chlorofluorocarbons, chlorinated solvents, and PVC, whereas caustic soda demand continued its steady, though moderate, growth. As a result, the price of chlorine dropped and caustic rose. The discrepancy between weak caustic supply, dependent on chlorine production, and steadily growing demand can create a gap, causing instability in the market on an ECU basis.

Shortages or noncompetitive prices for caustic push users to buy soda ash for alkalinity requirements. An example is trona (sodium sesquicarbonate), which can be used by itself or converted to caustic. Six companies in the United States produce soda ash, which is used principally in the manufacture of glass (49%); in chemicals, including caustic (26%); in soaps and detergents (11%);

in pulp and paper (2%); in flue-gas desulfurization (2%); and in miscellaneous uses. In 2002 U.S. production was 10.5 Mt, compared to world production estimated at 37.1 Mt. (Kostic 2002a).

Sulfur

Sulfur's usefulness is so widespread and pervasive in the chemical industry that its consumption closely follows the pattern of industrial activity. Tables 4 and 5 provide a clear condensation of the role of sulfur and sulfuric acid derivatives in organic and inorganic reactions and process applications.

Frasch process sulfur was formerly a strong factor in meeting sulfur supply requirements, but the last Frasch mine in the United States closed in 2000. No new, important supplies of sulfur are coproduct sulfur from natural gas and petroleum and, increasingly, sulfur obtained as the by-product of pollution control.

Marketing of sulfur reflects the well-established preference of bulk consumers for deliveries in liquid form. High labor and energy costs for remelting, together with environmental aspects, continue to stimulate the preference for transport and use of liquid sulfur.

U.S. sulfur production in 2002 was about 9.27 Mt, of which recovered elemental sulfur was 8.5 Mt and other (mainly as by-product sulfuric acid) was 770,000 t. Imports were 2.9 Mt. Comparative figures for 1998 were 11.7 Mt of production consisting of 1.8 Mt Frasch, 8.3 Mt of recovered, and 1.61 Mt of other, with imports the same at 2.9 Mt. Average prices in 2002, free on board (f.o.b.) producing plant, were \$11.84/t, compared to \$29.14/t in 1998, when high-cost Frasch was a factor in the pricing.

The outlook is for increased sulfur supply coming from pollution control. For additional information, the reader is referred to the chapter on sulfur in this volume.

ENVIRONMENT

As an example of industrial sensitivity to environmental concerns, U.S. Borax, Inc., a major producer, is acting to ensure that its activities promote sustainable development, including low environmental impact at its operations and enhancement of standards of living by its products and their contribution to economic development. In line with these objectives, the Industrial Minerals Association—North America (IMA—NA) was formed in 2002, and U.S. Borax is a member of its soda ash and borates section. The aim of IMA—NA's 38 member organizations is to coordinate industrial minerals producers' actions in governmental affairs, safety and health, environmental concerns, operations, and engineering (Industrial Minerals Association—North America 2003).

Sustainable development has become the catchword of the chemical industry. Goals in the pursuit of sustainable development are economic, environmental, and social to maximize effective use of resources, to minimize environmental impacts of operations, and to protect the health and safety of employees and of the public.

The toxicology branch of the U.S. Centers for Disease Control and Prevention has about 50 studies in progress to assess safe and unsafe levels of certain chemicals and has released a survey of 116 chemicals measured in blood and urine samples collected nationwide. Findings to date have focused on exposure to lead, organophosphate pesticides, dioxin and related chemicals, and other selected chemical compounds (Hileman 2003).

The United States approved the Montreal Protocol limiting the production, trade, and use of chemicals associated with destruction of ozone in the stratosphere; this affected mainly chlorofluorocarbons. An amendment in 1997 added methyl bromide to the list of controlled substances and requires licensing for the export and import of all substances controlled under the Protocol. Another

Table 4. Sulfur derivatives

Ammonium hydrosulfide	Ammonium polysulfides Photographic developer Textile industry Coloring brasses	Insect sprays	Chlorine dioxide Hydrochloric acid (Hargreaves process) Hydroxylamine sulfate Potassium bisulfite
Ammonium sulfite Ammonium thiosulfate	Reducing agent Hair waving formulations Photographic fixer Liquid fertilizer additive	Naphthylthiourea (antu) Rodenticide Thiourea Guanidine sulfoxyante Fertilizers Photography Freezing solution (liquid rocket propellant) Weed killer/defoliant Electroplating	Potassium hydrosulfide
Ammonium thiocyanate			Potassium sulfate (Hargreaves process)
Barium sulfate	Barium sulfide Paint pigment Plastics Rubber Medicine X-ray indicator	Depilatory Vulcanizing	Potassium thiosulfate
Calcium polysulfide		Sodium hydrosulfide Agricultural fungicide	Sodium bisulfite Sodium persulfate
Carbon disulfide	Viscose rayon Cellulose film Ferbam Fluorocarbons Carbon tetrachloride	Fungicide	Sodium sulfate (Hargreaves process)
Hydrogen sulfide	Ammonium sulfide Mercaptoethanol Sodium sulfide Sodium hydrosulfide Purify hydrochloric and sulfuric acid Vulcanize synthetic rubber	Textiles Photo developer Color brass/bronze Dye solvent Pharmaceuticals Insecticide Flotation agent	Sodium sulfite
Mercaptans	Methyl mercaptan Methionine Dimethyl sulfide Dimethyl sulfoxide Pharmaceuticals Propyl and butyl mercaptans Dodecyl mercaptan	Protein food additive Insecticides Synthetic rubber Fungicides Surfactants	Sodium thiosulfate
Molybdenum disulfide	Molybdenum pentachloride Solid lubricants		Sulfur trioxide
Mercaptobenzothiazole (Captax)	Rubber vulcanizing accelerator	Lube oil additive Rubber additive Flotation agent Insecticides	Sulfuric acid (chamber process)
Phosphorus pentasulfide			Sulfurous acid
Phosphorus sesquisulfide	Matches		Sulfuryl chloride Thionyl chloride Zinc sulfide Zinc hydrosulfite
Potassium thiocyanate	Thioures Aminothiazole Photography Rubber accelerator Freezing mixtures Dyeing textiles	Sulfa drugs	Zinc sulfoxylate
Sodium polysulfide	Electroplating Dye Petroleum additive Polysulfide polymers (thiokol compounds)		Alkyl chlorosulfonates Isoamyl chloride Sulfonyl chlorides Thioyl bromide Antihistamine compounds Fatty acid chlorides Organic acid anhydrides Organic acid chlorides Dyes Nitrites Pharmaceuticals Catalyst (chlorobenzene from sulfuryl chloride) Dessicant to remove water of hydration from Synthetic pyrethrum
Sulfur dioxide			Sodium sulfate Sodium sulfide Mineral decomposing flux Disinfectant Dyeing Carbonizing wool Magnesia cements Soap
Sulfur hexafluoride	Dielectric insulating gas for transformers, coaxial cables, and other high-voltage electrical equipment		
Sulfur monochloride	Chlorinating agents Complexes with polyvalent metal chlorides Mustard gas Organic acid anhydrides Sulfur dichloride Thionyl chloride Catalyst (chlorobenzene from benzene) Rubber vulcanizing Purifying sugar juices Textile finish Vulcanized oils	Chemical warfare agent Sulfur tetrachloride Thionyl chloride Chlorine carrier Vulcanize rubber Purify sugar juices Organic chemicals Insecticides	
Sulfuric acid Sulfur dyes Sulfur nitrides Agricultural fungicide Polymerization inhibitors Rubber vulcanizer	Hydrochloric acid Nitric acid	Sodium bisulfate Styrene Vinyl acetate	

Chemical	Uses
Caprolatum	Reduce organic compounds Antiseptic Food preservative Flour bleach Tanning
Separation of heavy metals	Bleach Antiseptic Pharmaceuticals Synthetic rubber polymerizer
Potassium persulfate	Dimethyl sulfide Dilipatory Medicine
Potassium sulfide	Sodium hydrosulfite Dye Perfume Wood pulp Food preservative Medicine Pesticide Fermentation industry
Alum manufacture Fertilizer Medicine	Dimethyl sulfoxide Polyacrylonitrile solvent Industrial cleaner Paint stripping Hydraulic fluid Pesticides Wool felt treatment
Fat/oil bleach	Odor donor natural gas Catalyst impregnator
Sodium thiosulfate Dyes Organic chemical Textile bleach Reducing agent Latex treating Food preservative Photographic developer	Sulfamic acid Reducing agent Dye stripping Bleaching sugar, soap, minerals
Ammonium sulfamate	Flameproof textile paper Weed killer Electroplating
Chlorosulfonic acid Dioxane sulfotrioxide Dodecylbenzene sulfonate	Cyclamates Sulfated surfactants Saccharin Poison gas Sulfamic acid
Fluosulfonic acid Lauryl sulfate	Organic catalyst Electropolishing
Oleum	Synthetic detergents Anthraquinone-disulfonic acids Dimethyl sulfate Naphthalenetrisulfonic acids Sulfamic acid Sulfanilic acid Sulfonic acids of saturated paraffin hydrocarbons Thionyl chloride Naphthylamine sulfonic acid Naphthylamine disulfonic acid Synthetic processes Naphthalenesulfonic acid
Pyridiniumsulfonic acid Pyrosulfuryl chloride Sulfur dioxide (high purity) Sulfuric acid (contact process) Thionyl chloride Thioxane sulfotrioxide	Dyes Methylating amines and phenols Dyestuffs Organic synthesis Medicine Sodium alkane sulfonates Emulsifying agents
Organic synthesis Bleach straw, paper, textile Wine, food, beer preservative	Dyes
Brighten paper pump Sugar juices Bleach textiles, oils, straws Dye stripping Alkyl chlorides Dialkyl sulfites	Disinfectant soaps Alkyl sulfonyl chlorides Aryl sulfonyl chlorides Benzal chloride Benzyl chloride Chlorobenzene Chlorophenols Rayon Zinc sulfoxylate Military poison gas Pharmaceuticals Solvent for chlorination or bromination of dyes and dye intermediates Dye stripping
Surfactants Peroxides	Surface active agents
Aluminum chloride Magnesium chloride Titanium trichloride	Leather dipilatory Organic chemicals Dyes Rayon Flotation process Engraving/printing Photographic reagent
Corn starch	Natural glues
Pulp wood digestion (semichemical and sulfite process)	Annaling of glass
Antichlor	Kraft pulp bleaching Water purification
Bleach	Beet sugar solutions Crude straw Silk Wool
Fertilizer	Grain Silage
Fumigant	
Heat treatment of magnesium alloys	
Ore flotation agent (depressant of zinc blende during flotation of copper ores)	
pH control	Beer Fresh and dried fruits Meat Wine
Preservative	
Refrigerant	
Solvent extraction of lubricating oils	
Solvent for aromatic and sulfur compounds in petroleum feed stocks (Edeleanu process)	
Soybean protein	
Sterilizing fermentation equipment (citric acid)	
Tanning	
Manufacture of	Activated carbon Bromine Iodine from oil well brines Selenium from copper slimes
Cutting oils Fungicides Insecticides Lubricating oil additives Paper Polishes Textiles	Oil-soluble petroleum sulfonate, barium salt Oil-soluble petroleum sulfonate, calcium salt Oil-soluble petroleum sulfonate, sodium salt

Table 5. Sulfuric acid derivatives

Inorganic Reactions			
Aluminum sulfate		Sizing paper Water purification Dye mordant Sewage treatment	
Iron free aluminum sulfate		Fire fighting Fat/oil clarifier Aluminum sodium sulfate	Textile waterproofing Tanning Paper precipitant Sugar refining
Ammonium bisulfite	Ammonium persulfate		
Ammonium sulfate (from coke-oven gas)	Fertilizer	Hydrogen peroxide	
Ammonium sulfate (from synthetic ammonia)		Ammonium chloride	Dry cells
Antimony sulfate	Explosives	Cobaltous ammonium sulfate Nickel ammonium sulfate	Electroplating
Barium sulfate (synthetic blanc fixe)	Barium oxide White pigment for paints	Fertilizer Flame retardant in fabrics Industrial ethyl alcohol from molasses (nutrient for yeast culture)	
Beryllium sulfate	Beryllium oxide	Viscose rayon	Cadmium electric cells Medicine Vacuum tube manufacture
Boric acid			
Cadmium sulfate			
	Sulfamic acid Sulfonated oils Sulfuryl chloride o-Toluene sulfonyl chloride Sulfated surfactants	Textile finishing agents Saccharin Dyestuffs	Zinc chromate Anodizing aluminum and aluminum alloys Ceramic glaze Chrome plating baths Copper stripping Dyestuffs Metal surface treatment Pharmaceuticals Rubber pigment
Chlorosulfonic acid			
Chromic acid			
Chromic sulfate	Green paint/varnish Leather tanning Textiles	Ceramics Pigments Glass Plating	
Cobaltous sulfate			
Copper sulfate	Fungicide	Aluminum etching Pigment Soil amendment Coagulant in water and sewage treatment	
Ferric sulfate			
Ferrous sulfate			
Fluoboric acid	Electroplating		
Fluosulfonic acid	Aryl sulfonyl fluorides	Lubricating oil additives	
Hydrochloric acid (from sodium chloride)	Catalyst (alkylation of isoparaffins) Electropolishing Wood preservative	Acrylonitrile Acylates Adiponitrile Dyes Fumigants Rubbers Plastics Chelating agents	
Hydrofluoric acid (from fluorspar)			
Hydrocyanic acid (from sodium cyanide)			
Hydrogen sulfide	Ceramics Leaded zinc oxide Pigment Stabilizer in vinyl plastics	Mineral water Magnesium tungstate Fireproofing formulations Leather tanning Medicine Paper sizing	Luminescent paint
Lead sulfate, basic	Pharmaceuticals		
Lithium sulfate			
Magnesium sulfate	Medicine Gold/silver extractant Galvanic batteries	Nickel-ammonium sulfate Nickel catalyst Nickel plating Printing textiles	Electroplating
Mercuric sulfate	Laboratory batteries		
Mercurous sulfate			
Nickel sulfate			
Oleum	Monoammonium phosphate Enriched superphosphate Triple superphosphate	Diammonium phosphate	Fertilizer
Phosphoric acid (wet process)	Rust proofing metals Soft drinks Sugar refining Water treatment		Fertilizers
Potassium bisulfate	Food preservative Tartrates	Potassium aluminum sulfate (potash alum) Potassium bisulfate Potassium persulfate Potassium sulfide Antiflash agent in smokeless powders Fertilizers Manufacture of gypsum wall board	Medicine Dye mordant Baking powder Medicine Depilatory
Potassium dichromate			
Potassium sulfate (from potassium chloride)			
Silica gel			
Silicon tetrafluoride (by-product of phosphate rock acidulation)	Fluosilicic acid Metallurgical flux Pickling metal Leather bleach Cleaning agents		
Sodium bisulfate			
Sodium dichloromate			
Sodium sulfate			
Sulfamic acid			
Sulfuryl chloride			
Titanium dioxide		Pigment for Delustering synthetic fibers Single crystals for transducers Filler for Welding rod	Lacquers Paint Printing inks Varnish Coated fabrics and textiles Floor coverings Paper Rubber
Tungstic acid	Tungsten, metal Textiles Plastics		
Vanadyl sulfate	Mordant Aniline black Ceramic coloring		
Zinc sulfate			

* Varying strengths of sulfuric acid are used as processes require (sulfuric acids = 100% H₂SO₄, or oleum 100% H₂SO₄).

	Organic Reactions	Process Applications
Acridine → Dyes Anthraquinone → Dye Chloroanthraquinone → Medicine Benzene (from coke-ovens) Benene sulfonic acid	Phenol Resorcinol Organic synthesis Detergent hydratropes	Additive to sodium peroxide baths for bleaching groundwood pulp Alumina silica catalysts Assistant in dyeing wool with acid dyes Catalyst in manufacture of Chlorine drying Coagulant for styrene butadiene rubber (SBR) elastomers Corrosion inhibitor in phosphoric acid Cracked gasoline treating Creeping agent for cotton Deodorizing tall oil Desulfonation Dessiccant in manufacture of Desulfonation Electrolyte in lead-acid storage batteries Kraft pulping Mixed fertilizers Oat hulls → Furfural Ore flotation agent (pH modifier) Parchment paper Production of electrolytic copper and zinc Pickling of iron and steel Polymerization Regenerating bath for cellulose Sec and tert butyl alcohol Synergist for phenolic antioxidants Textile finisher Treating kerosene Water treatment/clarification Rubber catalyst
Chloral → Dichlorodiphenyltrichloroethane (DDT)	Beverage Pharmaceuticals Effervescent salts	Acrylic esters by alcoholysis Amyl acetate from amyl alcohol Butyl acetate from butyl alcohol Caprolactam Cellulose acetate from cellulose by acetylation DDT from chloral Diakyl phthalates from phthalic anhydride Diphenylethane Ethyl acetate from ethyl alcohol Petroleum alkylate from petroleum feed stocks Vinyl acetate from acetylene
Citric acid → Creosote Disinfectant Lube oil additive	Solvent for cellulose acetate Paint/lacquer Dye dispersant Cosmetics Fumigant Glues	Chlorine from sodium chloride Nitric acid
Cresols and cresylic acid → Dicyandiamide	Fungicide Dermatological applications Veterinary medicine	
Dichlorophene → Diethyl sulfate Diethyl sulfate Dimethyl sulfate Dioxane	Organic solvent Anesthetics Medicine Smokeless powder Organic synthesis Fumigant	
Dodecylbenzene sulfonic acid Ethyl hydrogen sulfate (from ethylene)	Alkyl sulfates → Anionic detergents	
Fatty alcohols → Alkyl sulfates	Formate esters Dyeing Laundry sour Fumigant Food preservative Rubber coagulant Ore flotation Electroplating	
Formic acid → Reducing agent Condensation reactions Acetate fiber catalyst Blood tests Metal and mineral analysis Fungicide In adhesive	Acetone Solvent Deicing agent Lacquers Perfumes Preservative	Acetic anhydride Diacetone alcohol Methyl isobutyl ketone
Lacquers Isopropyl alcohol Ketoglutaric acid Lactic acid Mannitol hexanitrate (MHN) → High explosive Methyl methacrylate Naphthalene sulfonic acids → β-naphthol Naphthol sulfonic acids Naphthylamine sulfonic acids Oxalic acid (from calcium oxalate) Phenol (from coke-ovens, petroleum, and sodium phenolate) Phenanthroline Phenol sulfonic acid → Picric acid	Naphthionic acid → Dye intermediate	
Salicylic acid Stearic acid Tall oil Toluene sulfonic acid, sodium salt Xylene sulfonic acid, sodium salt	Dipentaerythritolhexanitrate (DPEHN) Nitrocellulose Nitroglycerin Pentaerythrioltetranitrate (PETN) Trinitrotoluene (TNT)	Guncotton → Single-base propellant Double-base propellant Pyrocotton → Coating material Pyroxilin → Low-energy propellant High explosives Bromine dinitrobenzene → Trinitrobenzene
Vanillin Mixed acid (nitric and sulfuric) Synthetic petroleum sulfonates Manufacture of	Kraft paper production Lead sulfate → Storage batteries Molybdate chrome orange Ceramic glaze Assistant in dyeing wool with acid dyes Synthetic detergents diluent Freezing mixture Glass Nickel smelting Spinning baths for viscose rayon Tanning Wool pulp (sulfate process) Ammonium sulfamate → Fire retardant Ceramic cleaning Electroplating Fire retardant Formaldehyde Metal pickling Plasticizer Weed killer	

amendment in 1999 added bromochloromethane to the list for phaseout of production, consumption, and trade (*Chemical Marketing Reporter* 2002).

OUTLOOK

The role of these industrial minerals in the chemical industry ensures their vitality in U.S. and world economies. As noted, each fills significant human needs and will continue to be drawn upon to fulfill their roles in chemical production.

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Chromite

John F. Papp and Bruce R. Lipin

INTRODUCTION

Chromite ore is mined mostly for metal content; it has useful properties, however, for the refractory and foundry industries. Louis Nicolas Vauquelin first isolated chromium from the mineral crocoite in 1797. He called the new element chromium because its compounds had a wide variety of colors. *Χρῶμα* is Greek for color, which is *chroma* in Latin. One of these compounds was a yellow pigment that became popular; as a result, paint was the first commercial application of chromium. Soon thereafter chromium was discovered in chromite (FeCr_2O_4), a much more common mineral, from the Ural Mountains.

On the periodic table, the element Cr has many name variations: *chromium* is the American name of the element, *chrome* is the British and French name, *chrom* is the German name, and *xpom* (in the Cyrillic alphabet) or *krom* (in the Latin alphabet) is the Russian name.

CHROMIUM IN THE 20TH CENTURY

The United States started the 20th century both producing and consuming chromite, but today it is solely a chromium consumer. In 1900, “chromic iron ore” described what is now called chromite ore. At that time, it was used as an alloying element, in chemical compounds, and in refractory materials. The United States produced 142 t of chromite in 1900, 0.27% of world production. U.S. production had averaged 2,200 tpy from 1880 through 1896, and there was no production from 1897 to 1899. Production increased during World War I and World War II, and ended in the mid-1960s.

Chromite consumption peaked in 1943 as a result of World War II mobilization, but did not reach maximum consumption until 1977. The United States was the major world chromite consumer until after the war. Chromite consumption in the chemical industry grew in the years from 1900 to 2002. Metallurgical industry consumption peaked during 1956 and 1957. Chromite-containing refractory production grew until the mid-1960s and then declined because of technological developments and environmental concerns.

Isaac Tyson Jr. (1792–1861) was responsible for starting U.S. chromite production and chromium chemical manufacturing. He studied geology, mineralogy, and chemistry in France, and subsequently developed the first chromite ore mines in the United States. He also established the first U.S. chromium chemicals plant, the Baltimore Chrome Works, in Baltimore, Maryland, in 1845. The plant closed in 1985. Some of Tyson’s mines are preserved today in the Soldiers Delight Natural Environmental Area northwest of Bal-

timore. Tyson was inducted into the National Mining Hall of Fame and Museum in 1996.

The United States no longer accounts for significant chromite production, but continues to be a major consumer of chromium. Ferrochromium was once produced in the United States from imported chromite, but now nearly all ferrochromium is imported. Ferrochromium is consumed predominantly by the stainless steel industry, a sector that has continued to show significant growth.

Chromium is important in metallurgy as an alloying element. Chromium and tungsten were alloyed with iron to make tool steel. Chromium also was used to harden armor plating. These uses, and chromite use as a refractory in steel-producing furnaces, made material containing chromium strategically critical material World War I. Stainless steel was first produced in France, Germany, the United Kingdom, and the United States between 1910 and 1920 when chromium was alloyed with iron. Once the role of chromium, nickel, and other alloying elements was understood, stainless steel became an integral part of the steel industry. In 2002 stainless steel accounted for more than 2.4% of U.S. steel production, averaging 2.2% between 1998 and 2002. Stainless steel production has been growing and that growth is expected to continue. Stainless steel accounted for 75% of U.S. chromium consumption in 2002. Superalloys are engineering alloys of chromium and nickel for demanding applications in aggressive environments that were unknown in 1900. They are used in the internal workings of jet engines, an important strategic use of chromium, and in stationary turbine electrical power generation, another important critical use.

The term *chromite* is used in many different ways. Terminology is not consistent throughout the industry or among academic disciplines that study chromium. For this chapter, the *mineral chromite* describes the mineral itself. *Chromite ore* refers to rock in the ground that is economically minable for the mineral chromium content and run-of-mine ore (i.e., material removed economically from the ground). *Chromite* refers to products made from chromite ore and supplied to the marketplace. For trade purposes in the Harmonized Tariff System, chromite is called *chromite ore and concentrate*, which is made from chromite ore. This description frequently is shortened to chromite ore, chromium ore, chromite, chrome ore, or chrome. The terms are used synonymously and may appear confusing to the general readership. Historically mines supplied minimally processed material, so there was little difference between chromite ore and chromite products. Today most chromite ore is processed before it reaches the marketplace.

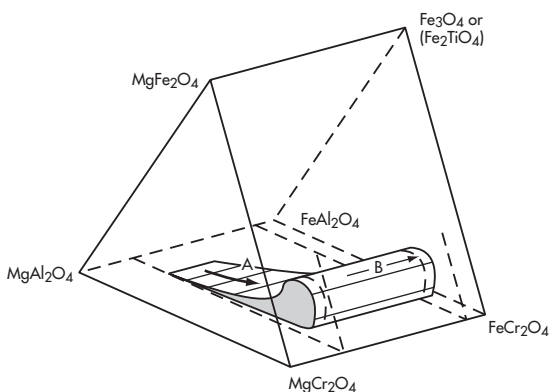


Figure 1. Representation of chromite compositions in stratiform and podiform chromite deposits: A, podiform trend with arrow showing change in composition with decreasing temperature of crystallization; B, stratiform trend with arrow showing direction of compositions with decreasing temperature

Table 1. Minerals of spinel structure

Series	Elemental Basis	Mineral Name	Chemical Composition
Chromite	Chromium	Chromite	FeCr_2O_4
		Magnesiochromite*	MgCr_2O_4
Spinel	Aluminum	Spinel	MgAl_2O_4
		Hercynite	FeAl_2O_4
		Gahnite	ZnAl_2O_4
		Galaxite	MnAl_2O_4
		Magnetite	FeFe_2O_4
Magnetite	Iron	Magnesioferrite	MgFe_2O_4
		Franklinite	ZnFe_2O_4
		Jacobsite	MnFe_2O_4
		Trevorite	NiFe_2O_4

* Also called picrochromite.

GEOLOGY

Mineralogy

Chromium is found in a wide variety of oxide and silicate minerals in the earth's crust. At standard temperature and pressure, chromium is a metal; it does not, however, occur in the native state. The most important chromium-bearing mineral is chromite, which is the only ore of chromium. It is in the spinel group with the general chemical formula XY_2O_4 , where X and Y represent divalent and trivalent metal ions, respectively. Figure 1 shows spinel minerals in a prism diagram with end member compositions at each corner. Because most spinel end members form at high temperatures, compositions of the mineral chromite form complete or extensive solid solutions within the prism.

The base of the prism consists of aluminum- and chromium-bearing spinels with no trivalent iron (or titanium). Compositions become richer in trivalent iron and poorer in divalent iron the higher they occur in the prism. Care is necessary using this nomenclature because the series based on aluminum and the MgAl_2O_4 end member is named *spinel*.

Compositions of the mineral chromite occupy the volume shown in Figure 1. Lode chromite ore deposits are of two types: stratiform and podiform. Compositions differ in the two types of

deposits. In podiform deposits the trend marked "A" is a ramp leading from high Al values to high Cr values with very low Fe^{3+} (or Ti^{3+}). This ramp leads to a cylinder in which compositions of stratiform and podiform deposits overlap, but podiform deposits generally have lower Fe^{3+} (or Ti^{3+}) than do stratiform deposits. Other minor constituents include nickel, zinc, and manganese (Table 1).

Ions in spinel-group minerals form a close-packed, cubic, face-centered lattice that imparts a relatively high density; the typical specific gravity of commercial chromite product is 4.5 to 4.8 g/cm³. The mineral chromite is black with a metallic to dull luster and yields a dark brown streak, distinguishing it from other black spinel-group minerals, which typically have a white streak (e.g., magnetite). The mineral chromite is opaque to slightly translucent in thin section, depending on the amount of trivalent iron present; it is opaque if it contains very little Fe^{3+} but slightly translucent if it contains more than a few percent Fe^{3+} . The mineral chromite with very low amounts of Fe^{3+} (less than a few percent) is nonmagnetic; higher amounts of Fe^{3+} make it weakly magnetic. Hardness is typically 5.5 to 6.5 on the Mohs scale. The mineral chromite typically does not show cleavage and exhibits conchoidal to uneven fracture.

Origin

Four types of chromite ore deposits occur as either lode deposits or secondary deposits. Lode chromite ore deposits comprise stratiform and podiform deposits, whereas secondary chromite ore deposits comprise laterite and placer deposits.

Stratiform deposits are found in layered igneous complexes and podiform deposits occur as irregularly shaped pods or folded lenses in lower portions of ophiolites. Economic stratiform chromite ore deposits have been found only in those layered igneous complexes older than 2.06 Ga. Ophiolites are pieces of mantle and oceanic crust that have been thrust over continental crust or island arcs by tectonic motion over time. For many years ophiolites were thought to be geologically young (<1 Ga), but Kusky, Li, and Tucker (2001) demonstrated that an ophiolite in China with chromite ore deposits is as old as 2.505 Ga. In addition, Stoen (1987) interpreted the approximately 3.5-Ga-old chromite ore deposits at Selukwe, Zimbabwe, to be of ophiolitic origin.

Secondary chromite-containing deposits exist as laterite deposits derived from weathering and leaching of peridotite host rock that contains 1% to 2% of the mineral chromite; they are not commonly ore grade. Large peridotite bodies in tropical climates with favorable topographic environments (not too mountainous) can undergo chemical weathering that results in residual soils. Subsequent leaching of silicate minerals helps accumulate chromite mineral. These lateritic soils make it easy and inexpensive to concentrate chromite mineral from its matrix. Such deposits are mined in Indonesia and Vietnam. Although production from these deposits is a tiny fraction of world production, their potential is enormous.

Placer chromite results from erosion of peridotite host rock. The relatively dense chromite mineral is concentrated as lag deposits on beaches or in streams. These have the least economic importance of the four types of chromite mineral deposits. None are currently being mined.

Some controversy exists about the origin of lode chromite ore deposits. In many layered igneous complexes it appears that repetitive layers were produced by multiple injections of magma into the rock chambers. A new magma injection commonly marks the beginning of a new cycle, with chromite mineral crystallizing typically with olivine or pyroxene in the ratio of approximately 98:1 silicate to chromite mineral. Then only chromite mineral crystallizes to form a layer of massive chromitite, or a mixture of silicate and chromite mineral in widely varying proportions. Temporary

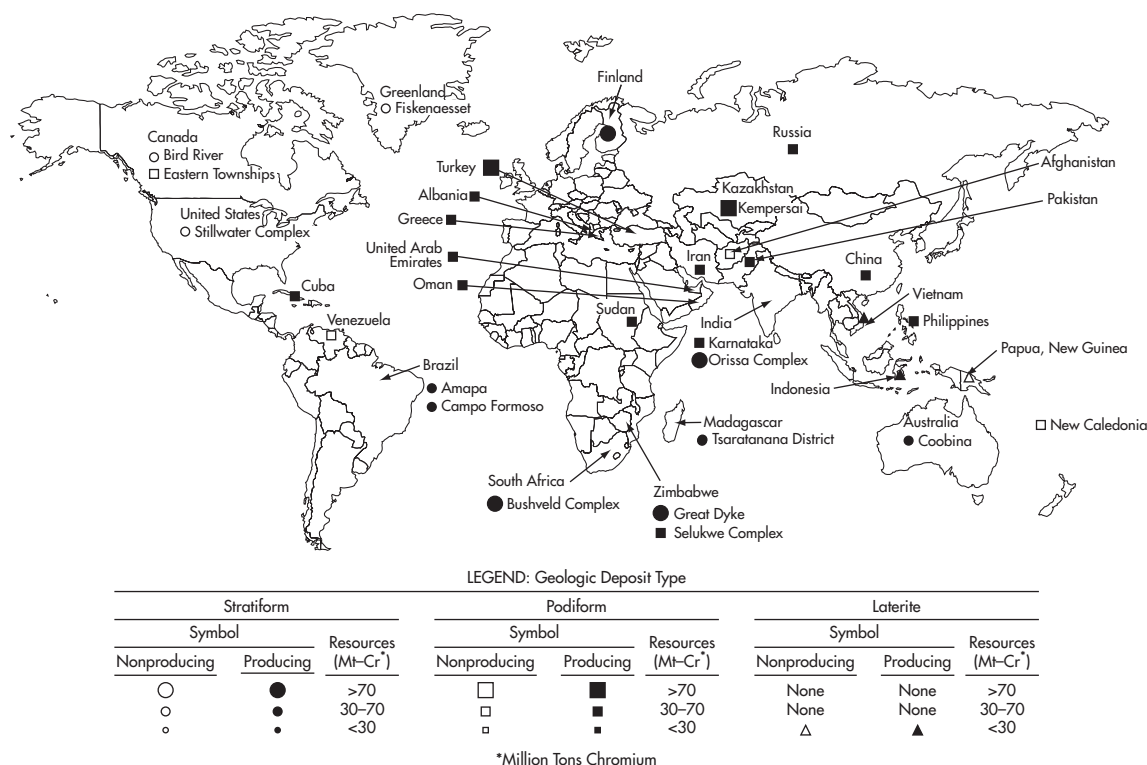


Figure 2. Location, geologic type, and size of major chromite ore deposits

cessation of silicate precipitation is not the normal sequence in fractional crystallization, suggesting that something disrupts the system. Two hypotheses have received special attention in explaining this phenomenon. Hess (1960) promoted the idea that new magma comes in contact with preexisting magma in the chamber (magma mixing). Irvine (1977) suggested that newly injected magma could mix with a granitic component, and later data from the Bushveld Igneous Complex (Schoenberg et al. 2001) supported the idea. The other hypothesis was first suggested by deVilliers (1970) and Cameron (1975), and later explored by Lipin (1993). Their idea was that temporary pressure increases within the magma chamber cause only chromite mineral to crystallize, an effect that Sen and Presnall (1984) verified experimentally.

Several ideas regarding the origin of podiform chromite ore deposits in ophiolites are based on the complicated structural setting and varied shapes of the deposits. These fall into the following categories: (1) residue from partial melting in the mantle; (2) crystallization from a mafic magma during deformation; (3) magma conduits in which pyroxene was dissolved out of peridotite through which it flowed, thus changing the magma composition, and where only chromite mineral crystallized; and (4) interaction of metamorphic fluids in the mantle with peridotite to form chromite mineral.

Abundance

Chromium is the 13th most common element in the earth's crust at about 185 ppm; it is the 26th most common element in seawater at about 0.2 ppb (Taylor and McLennan 1985). The highest concentration is in igneous rock at 0.06% (Parker 1967).

Chromite mineral commonly occurs in mafic and ultramafic rocks, which cover large portions of the Earth's surface. Peridotite, an ultramafic rock predominated by olivine, is the common host for economic chromite mineral deposits. Chromite mineral deposits

also occur in pyroxenite and rarely in anorthosite. Peridotite contains 1% to 2% chromite mineral as an accessory mineral. Most economic chromite mineral deposits contain concentrations of at least 25% chromite mineral. Exceptions are laterites in Indonesia and Vietnam derived from weathering of peridotite.

Mafic rocks, mainly basalt, also contain the mineral chromite; flood basalts, however, which represent the most voluminous of these rocks and cover thousands of square kilometers, rarely contain mineral chromite. For example, the average chromium content of Columbia River Basalt is less than 100 ppm; thus, chromium is dispersed in very low concentrations in common mafic minerals. Oceanic basalts have more chromium on average and mineral chromite occurs in trace amounts. For example, Hawaiian basalts contain about 400 ppm chromium, which is high enough to form the mineral chromite; its grain size, however, averages only 29 µm. The small grain size makes bulk separation difficult.

Although many rocks contain chromium or mineral chromite, they are not potential hosts for economic mineral chromite deposits. Lipin (1983) showed that only mineral chromite occurs with enough chromium to be an ore.

Distribution of Major Deposits

Figure 2 shows the distribution of major chromite ore deposits around the world. Ophiolite complexes are more abundant than stratiform igneous complexes older than 2.06 Ga. About 70% of all chromite ore mined in 2002 came from stratiform deposits (Papp 2005). About 95% of the world's chromite ore resources are in the Bushveld Igneous Complex of South Africa and the Great Dyke of Zimbabwe; the majority is in the Bushveld. The largest concentration of podiform chromite ore is in the Kempersai area of Kazakhstan (Papp 2001). Since the dislocation of traditional markets that resulted from the dissolution of the Soviet Union in 1991, chromite

ore production in the Bushveld from 2000 through 2004 has been two to three times greater than that of the Kempersai.

The Bushveld Complex is one of the largest layered intrusions in the world, occupying about 64,340 km². The great amount of magma intruded into the rocks of the Bushveld Complex cooled very slowly. As a result, different minerals crystallized from the liquid magma at different times, forming layers with different mineralogies. The cyclic layering indicates that the process of intrusion and cooling occurred often over a long period of time. Geologists call the differentiated mineral layers the *upper*, *middle*, and *lower groups*. (Each of these groups is further subdivided into layers; e.g., UG2 means layer 2 in the upper group and LG6 means layer 6 in the lower group.) All economic chromite layers originated at or about 2.06 Ga. The Bushveld contains more than 11 billion t of total resource (Vermaak 1986). One layer, informally called the Steelport Seam, contains 1.5 billion t of resource. The Steelport Seam can be traced over much of the Bushveld.

The Bushveld Complex also is the world's largest repository of platinum and palladium, some of which are found in chromite seams.

The Kempersai (also known as the Kimpersai or Kimpersaisky) area of the Southern Urals in Kazakhstan is home to the world's largest podiform chromite ore deposits, covering about 1,200 km². These deposits occur where parts of the ocean floor were obducted over continental rocks. This area has more than 75 times the reserves and about 4 times more production than the podiform deposits of Turkey, which rank second in podiform chromite production and reserves.

TECHNOLOGY

Exploration Techniques

The Bushveld Complex (South Africa), Great Dyke (Zimbabwe), and Kempersai (Kazakhstan) have been thoroughly investigated through geological mapping, geophysical methods, and exploration drilling, so these chromite ore deposits are well known. Resources in the Bushveld Complex can easily be upgraded from inferred to demonstrated, or from indicated to measured, by additional exploration. Because podiform chromite ore bodies are irregular in shape and unpredictable, gravity and electrical methods may offer some promise as exploration tools.

Laterites that develop over ophiolite deposits may indicate the presence of chromite ore. Such laterites are extensive in area and the chromite ore they contain is relatively easy to remove and concentrate.

Reserves and Resources

Resources presented here are based on public information. Sources include individual company reports, the International Chromium Development Association (ICDA) Web site (www.chromium-asoc.org), government documents, and domestic government reports such as DeYoung, Lee, and Lipin (1984); Thomas and Boyle (1984); and Boyle, Shields, and Wagner (1993).

The revised resource estimates based on company reports may be more accurate because they are more recent and are based on detailed geologic, mining, and economic information from company engineers and geologists responsible for mine planning; resource estimates may be based on different criteria, however, depending on the company and country. Unfortunately, for many locations resource information has not been recently published. Estimates were made when there were no reported data.

Reserves for Kazakhstan were based on resource categories used in the former Soviet Union (now the Commonwealth of Independent States [CIS]). That system emphasized certainty of physi-

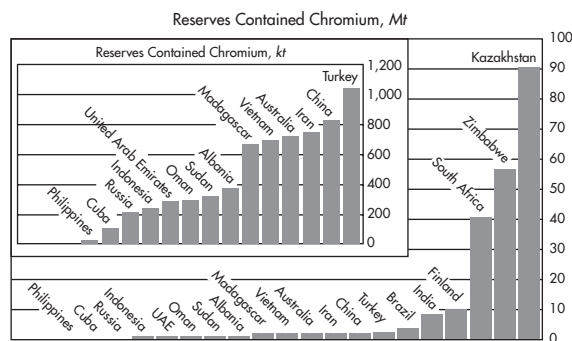


Figure 3. World chromite ore reserves by country. The bar chart shows countries with smaller reserves at a smaller scale so that their relative size is apparent.

cal resources and downplayed the economics of recovery. Kazakhstan reserves are likely to be discounted when recovery economics are factored in. South African reserves are based on the reports of major chromite producers in accordance with reporting standards for such business information. As a result, South African reserves are constrained by reporting standards and by the geographic area of mineral title. The reserves of Zimbabwe are based on resource analyses by Boyle, Shields, and Wagner (1993). These reserves are likely to be discounted when property boundaries and economic factors are taken into account. In addition, tax codes and the high cost of drilling may affect how a company chooses to prove reserves and how much to delineate.

The United States has no chromite ore reserves; it does, however, have resources that could be developed for mining. The U.S. reserve base is estimated to contain about 2 Mt of chromium. The largest U.S. chromite mineral deposit is the Stillwater Complex of Montana.

World reserves of chromium are about 213 Mt, and the world reserve base of chromium is about 444 Mt. The world wide distribution of 1.52 billion t of chromium in identified chromite ore resources is Africa, 52%; Asia, 38%; Europe, 5%; the Americas, 3%; the Middle East, 2%; and Oceania, 0.1%. The U.S. Geological Survey (USGS) reports reserves and reserve base information annually in *Mineral Commodity Summaries*. Figure 3 shows world chromite ore reserves.

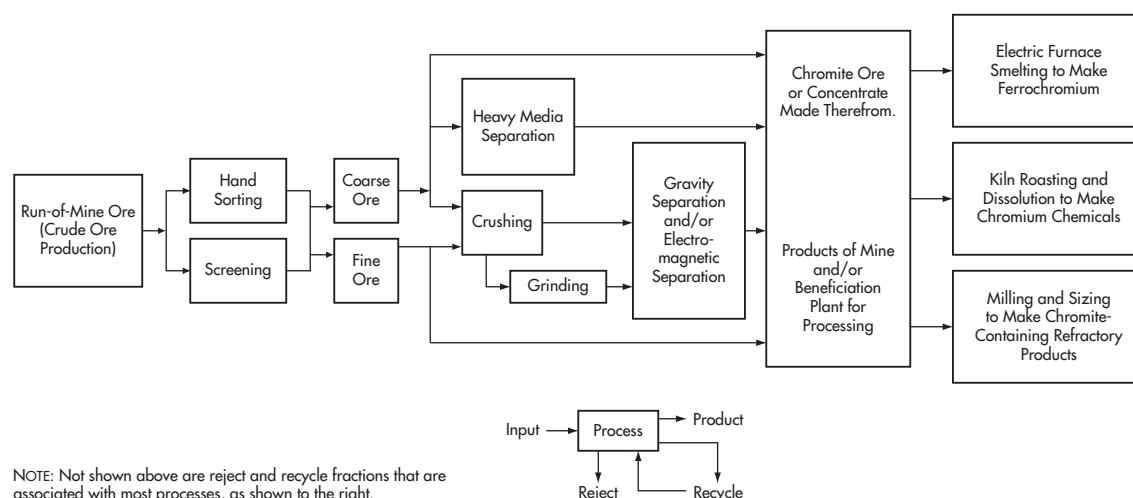
Mining, Beneficiation, and Processing

Recovery of chromite from chromite ore includes surface and underground mining methods. Beneficiation produces chromite, the marketable product containing chromite mineral, and ranges from hand sorting to gravimetric and electromagnetic separation methods. Processing of chromite ore to produce chromite for refractory, chemical, and metallurgical markets involves crushing and grinding, and size sorting by pneumatic and hydraulic methods. Chromite processing by the chemical and metallurgical industries includes kiln roasting and electric furnace smelting (Table 2 and Figure 4). The flow chart of Figure 4 shows beneficiation and processing, which may be carried out at the mine site, at a plant serving several satellite mines in one geographic area, or at a plant associated with an end user. Today, chromite ore is beneficiated to produce physically and chemically uniform products before reaching the marketplace.

The nature of the deposit dictates the mining method(s). The characteristics of a chromite ore deposit that must be considered are whether it is stratiform or podiform, high grade or low grade,

Table 2. Factors used to characterize chromite deposits and mining, beneficiation, and processing methods applied to those deposits

Mineral	Mineral Appearance in Ore	Deposit Types	Host Rock	Mining Method	Beneficiation Method	Processing Method
Chromite (a spinel structure oxide mineral)	Massive (spinel mineral of varying chemistry) Disseminated (spinel mineral intermixed with other minerals)	Stratiform (bedded) Podiform (lenticular)	Mafic Ultramafic	Surface Subsurface	Hand sorting Screening Gravity concentration Electromagnetic separation Heavy-media separation	Sizing Roasting and dissolution Smelting

**Figure 4. Chromite ore mining, beneficiation, and processing**

subsurface or near surface, or massive or disseminated. Because surface mining typically is less expensive than underground mining, it is preferred.

Beneficiation depends on the characteristics of the ore deposit and on the mining methods used. For example, an operation extracting only high-grade ore may require only hand sorting and screening. Beneficiation is necessary when chromite mineral is mixed with other minerals because of geologic conditions or when mechanized mining methods are nonselective.

Beneficiation methods depend on the end use and may include increasing chromic oxide content, the chromium-to-iron ratio, or alumina content. Reducing silica content or eliminating waste rock associated with chromite ore also may be desirable. Certain sizes may be selected for or rejected as well. Techniques used to accomplish these tasks further depend on the physical properties of the minerals present. Beneficiation cannot change the chemical characteristics of the chromite mineral; because chromite ore is a mixture of minerals, however, altering the mineral mixture can change its characteristics for its respective market. A deposit producing lumpy ore in which chromite mineral is easily distinguished visually may require only hand sorting and screening; otherwise, heavy media separation can be used. A deposit that yields chromite ore thoroughly mixed with gangue minerals may require milling and sizing followed by gravimetric or electromagnetic separation to produce marketable chromite products. Beneficiation methods are used to process tailings when sufficient quantities have been stockpiled (see the By-products and Coproducts section of this chapter).

Specifications

Chemical and physical specifications for chromite vary among producers and consumers. Chromite producers make chemical specifica-

tions of their products available. Table 3 shows chemical specifications of several chromite products by end use and by source.

In the United States, the American Society for Testing and Materials (ASTM) sets chemical and physical specifications for chromium materials. Other organizations also promulgate specifications for chromium materials. The Defense Logistics Agency (DLA), in cooperation with the U.S. Department of Commerce, maintains purchase specifications for chromium materials contained in the National Defense Stockpile (NDS). The U.S. Department of the Treasury, in cooperation with the U.S. Department of Commerce and signatories to the General Agreement on Tariffs and Trade, maintains definitions of chromium materials for recording trade and applying tariffs.

The import category "chromite ore and concentrates made therefrom" of the Harmonized Tariff Schedule of the United States is subdivided by chromic oxide content as follows: containing not more than 40% chromic oxide; containing more than 40% and less than 46% chromic oxide; and containing 46% or more chromic oxide. Chromite producers typically specify the following: chromic oxide content, chromium-to-iron ratio, and iron, silica, alumina, magnesia, and phosphorus contents. Size also is specified for some applications. The chromic oxide content of chromite ranges from 36% to 56%, with values in the 40% to 50% range most common. Chromium-to-iron ratios range from about 1.5:1.0 to about 4.0:1.0, with typical values of about 1.5:1.0 to 3.0:1.0.

The import category of chromium ferroalloys is divided into ferrochromium and ferrochromium-silicon. Ferrochromium-silicon, also called ferrosilicon-chromium and chromium silicide, is not classified further. Ferrochromium is classified by its carbon content as follows: containing not more than 0.5% carbon; containing more than 0.5% carbon but not more than 3% carbon; containing more than

Table 3. Chemical specifications for chemical, foundry sand, refractory, and metallurgical grade chromite (representative % content of specified chemicals and chromium-to-iron ratio [Cr:Fe])

End-Use Industry and Source		Grade*	Specified Chemicals and Cr:Fe Ratio														
			Cr ₂ O ₃	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	MgO	MnO	TiO ₂	V ₂ O ₅	CaO	Ni	P	S	Cr:Fe	
Chemical																	
Australia																	
Pilbara		44–56	10–15	na†	1–7	11–14	10–14	na	na	na	0.2–0.4	na	0.006	0.007		2.2–4	
Brazil																	
Magnesita		44.55	na	17	7	16.5	13.5	0.15	0.27	na	0.53	na	na	na		2.56	
India																	
Misrilall		44–56	10–15	na	2–7	11–14	10–14	na	na	na	0.2–0.4	na	0.006	0.007		2.2–3.5	
OMC	Concentrate	40–56	10–18	na	3–8	10–12	8–15	na	na	na	na	na	0.005	0.007		1.6–3.3	
OMC	Lump	40–56	10–16	na	3–8	10–16	na	na	na	na	na	na	na	na		1.6–3.4	
Indonesia																	
Palmabim		43	na	25	1.5	19	10.5	na	na	na	0.02	na	0.001	0.001		na	
South Africa																	
ASA		46.8	26.1	na	0.8	14.6	9.8	na	0.55	na	0.21	na	na	na		1.6	
Assmang		46.2	26.3	na	0.8	14.5	10	na	na	na	0.19	na	na	na		1.55	
Bayer		46.05	25.79	na	1.1	14.8	9.75	na	0.62	na	0.25	na	0.003	0.001		1.57	
Hernic		45–46	26.5	na	<1	15.5	10.5	na	0.64	0.44	0.26	na	0.003	0.004		1.52	
National Manganese		45.5	26.3	na	0.8	14.3	11	na	0.71	na	0.34	na	0.003	na		1.5	
Samancor		46.3	26.3	na	0.8	14.5	9.6	na	0.6	0.2	0.13	na	<0.001	<0.001		1.55	
Xstrata		>46	25.7	na	>1	15.4	10.3	na	na	na	0.8	na	0.002	0.004		1.55	
Foundry Sand																	
Indonesia																	
Palmabim		43	na	25	1.5	19	10.5	na	na	na	0.02	na	0.001	0.001		na	
South Africa																	
ASA		47.1	29	na	0.6	13	10.5	na	na	na	na	na	na	na		na	
Assmang		46.4	26.3	na	0.7	15.6	9.5	na	na	na	0.19	na	na	na		1.55	
Bayer		46.5	25.8	na	0.55	15.5	10.1	na	0.6	na	0.2	na	0.003	0.003		1.56	
Hernic		45–46	26.5	na	<1	15.5	10.5	na	0.64	0.44	0.26	na	0.003	0.004		1.52	
National Manganese		45.8	26.8	na	0.7	14.5	10.6	na	0.92	na	0.34	na	0.003	na		1.5	
Samancor		46.5	26	na	0.8	14.5	10.3	na	0.6	0.2	0.13	na	<0.001	<0.001		1.57	
Turkey																	
Bilfer		52–55	18	na	1	14	14	na	na	na	0.05	na	na	na		na	
Refractory																	
Brazil																	
Magnesita		49.09	na	17.89	2.71	16.58	13.15	0.16	0.29	na	0.13	na	0.0048	0.0023		2.68	
India																	
OMC	Lump	46–56	10–15	na	3–7	10–12	na	na	na	na	na	na	0.007	na		1.9–3.4	

(Table continued next page)

Table 3. Chemical specifications for chemical, foundry sand, refractory, and metallurgical grade chromite (representative % content of specified chemicals and chromium-to-iron ratio [Cr:Fe]) (continued)

End-Use Industry and Source	Grade*	Specified Chemicals and Cr:Fe Ratio													
		Cr ₂ O ₃	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	MgO	MnO	TiO ₂	V ₂ O ₅	CaO	Ni	P	S	Cr:Fe
India (continued)															
OMC	Concentrate	45–49	na	na	5–6	12–13	na	na	na	na	na	na	0.005–0.007	0.007–0.03	2.3–2.6
Tisco	Lump	45–55	8.5–12.5	na	3–9	na	na	na	na	na	na	na	na	na	2.8–3.9
Tisco	Concentrate	50–54	10–13	na	1.0–2.5	11–12	na	na	na	na	na	na	0.005–0.007	0.01 max†	2.4–3.5
Indonesia															
Palmabim		43	na	25	1.5	19	10.5	na	na	na	0.02	na	0.001	0.001	na
Oman															
Oman Chromite	Lump	43.12	16.1	na	2.96	18.2	14.82	na	na	na	0.23	na	na	na	na
Oman Chromite	Fines	41.96	15.7	na	3.46	19.11	14.79	na	na	na	0.44	na	na	na	na
South Africa															
Samancor		46.3	26.3	na	0.7	14.5	9.6	na	0.6	0.2	0.13	na	<0.001	<0.001	1.55
Turkey															
Bilfer	Concentrate	48	15	na	5	19	18	na	na	na	0.5	na	<0.007	na	>2.7
Bilfer	Fines	36–40	15	na	6–9	18	17	na	na	na	0.5	na	<0.007	na	>2.5
Bilfer	Lump	38–41	na	na	4–6	na	na	na	na	na	na	na	na	na	na
Dedeman	Lump	50–52	13–14	na	3	15–16	16	na	na	na	0.1–0.3	na	0.002	0.007	3.1–3.2
Dedeman	Concentrate	54–56	11–12	na	1–1.5	14–15	16	na	na	na	0.2–0.3	na	0.002	0.007	3.2
United Arab Emirates															
Derwent		43–48	14	na	3–5	18	15	na	na	na	0.4	na	na	na	na
Metallurgical															
Albania															
Albkrom	Grade 1	40–42	11.8	na	11.5	8	23.5	na	0.160	0.110	0.31	na	na	na	3
Albkrom	Grade 2	36–38	12.5	na	15	7	23	na	0.160	0.020	0.50	na	na	na	2.7
Albkrom	Grade 3	30–34	10.0	na	18	7	27	na	0.160	0.060	0.15	na	na	na	2.6
Albkrom	Concentrate 1	48–50	13.93	na	7	9.37	17.94	na	0.160	0.060	0.14	na	na	na	3
Albkrom	Concentrate 2	45–47	13.93	na	9	9.37	18.2	na	0.160	0.060	0.14	na	na	na	3
Australia															
Pilbara		44–56	10–15	na	1–7	11–14	10–14	na	na	na	0.2–0.4	na	0.006	0.007	2.2–4
Brazil															
Magnesita		41.32	na	14.92	9.01	16.8	16.05	0.12	0.31	na	1.46	na	0.0109	0.0016	2.71
Finland															
AvestaPolarit	Concentrate	44.3	24.4	na	3.6	13.6	10.8	na	0.53	0.21	0.4	na	0.0014	0.005	1.62
AvestaPolarit	Lump	35.5	18.3	na	11.3	12.4	15	na	0.45	0.18	1.4	na	0.003	0.003	1.76
India															
Facor	Boula	38–47	14–19	na	8–18	7–10	10–14	na	traces	traces	0.2–0.3	na	0.003–0.004	traces	1.8–2.9
Facor	Kathpal	40–46	11–13	na	5–10	7–8	10–13	na	traces	traces	0.2–0.3	na	0.001	traces	2.4–3.5

(Table continued next page)

Table 3. Chemical specifications for chemical, foundry sand, refractory, and metallurgical grade chromite (representative % content of specified chemicals and chromium-to-iron ratio [Cr:Fe]) (continued)

End-Use Industry and Source		Grade*	Specified Chemicals and Cr:Fe Ratio											Cr:Fe		
			Cr ₂ O ₃	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	MgO	MnO	TiO ₂	V ₂ O ₅	CaO	Ni		P	S
India (continued)																
Factor		Ostapal	42–45	23–24	na	8–11	6–10	10–13	na	traces	traces	0.6–1.0	na	0.01	traces	1.6–2.0
IMFA		Bangur	47.41	9.2	na	7.38	na	na	na	na	na	na	na	na	na	1.24
IMFA		Bangur	40.07	9.35	na	9.5	na	na	na	na	na	na	na	na	na	2.14
IMFA		Bangur	32.92	10.11	na	7.02	na	na	na	na	na	na	na	na	na	0.87
IMFA		Bangur	23.69	27.77	na	7.5	na	na	na	na	na	na	na	na	na	0.55
IMFA		Chingudipal	54.98	10.84	na	na	na	na	na	na	na	na	na	na	na	3.47
IMFA		Chingudipal	43.13	16.95	na	na	na	na	na	na	na	na	na	na	na	1.74
IMFA		Chingudipal	35.27	20.24	na	na	na	na	na	na	na	na	na	na	na	1.19
IMFA		Nuasahi	54	13	na	5	11	14.5	na	na	na	1.8	na	0.01	na	3
IMFA		Nuasahi	48	13.5	na	7	10	16	na	na	na	2.5	na	0.1	na	3
IMFA		Nuasahi	42	11	na	16	10	17	na	na	na	3	na	0.1	na	3
IMFA		Nuasahi	33	10	na	17	11	18	na	na	na	3	na	0.1	na	2.6
IMFA		Nuasahi	50	10	na	8	na	na	na	na	na	na	na	na	na	3.4
IMFA		Nuasahi	42	11	na	11	na	na	na	na	na	na	na	na	na	2.5
IMFA		Nuasahi	33	9.5	na	17	na	na	na	na	na	na	na	na	na	2.4
IMFA		Sukinda	51.52	12.53	na	5.08	na	na	na	na	na	na	na	na	na	3.60
IMFA		Sukinda	45.77	15.55	na	4.72	na	na	na	na	na	na	na	na	na	2.58
IMFA		Sukinda	39.8	18.86	na	7.08	na	na	na	na	na	na	na	na	na	1.85
Misrilall			44–56	10–15	na	2–7	11–14	10–14	na	na	na	0.2–0.4	na	0.006	0.007	2.2–3.5
OMC		Friable	40–56	10–18	na	3–8	10–12	8–15	na	na	na	na	na	0.005	0.007	1.6–3.3
OMC		Lumpy	40–56	10–16	na	3–8	10–16	na	na	na	na	na	na	na	na	1.6–3.4
Tisco		Concentrate	54 min [§]	na	na	1.5 max	12 max	14 max	na	na	na	na	na	0.007 max	0.01 max	3.3 min
Tisco		Concentrate	52 min	na	na	1.5 max	12 max	14 max	na	na	na	na	na	0.007 max	0.01 max	3.0 min
Tisco		Concentrate	50 min	na	na	2 max	14 max	14 max	na	na	na	na	na	0.007 max	0.03 max	2.8 min
Tisco		Concentrate	48 min	na	na	2.5 max	14 max	14 max	na	na	na	na	na	0.007 max	0.03 max	2.6 min
Tisco		Concentrate	48 min	na	na	3 max	14 max	14 max	na	na	na	na	na	0.007 max	0.03 max	2.4 min
Tisco		Friable	40 min	na	na	4–8	14 max	14 max	na	na	na	na	na	0.007 max	0.01 max	1.8 min
Tisco		Friable	42 min	na	na	4–7	14 max	14 max	na	na	na	na	na	0.007 max	0.01 max	2.0 min
Tisco		Friable	44 min	na	na	4–7	14 max	13 max	na	na	na	na	na	0.007 max	0.03 max	2.2 min
Tisco		Friable	48 min	na	na	4–7	12.5 max	12.5 max	na	na	na	na	na	0.007 max	0.03 max	2.6 min
Tisco		Friable	50 min	na	na	4–7	12 max	12 max	na	na	na	na	na	0.007 max	0.03 max	2.8 min
Tisco		Lumpy	38 min	na	na	17 max	11 max	23 max	na	na	na	na	na	0.007 max	0.03 max	2.6
Tisco		Lumpy	36 min	na	na	17 max	11 max	23 max	na	na	na	na	na	0.007 max	0.03 max	2.5
Indonesia																
Palmabim			43	na	25	1.5	19	10.5	na	na	na	0.02	na	0.001	0.001	na

(Table continued next page)

Table 3. Chemical specifications for chemical, foundry sand, refractory, and metallurgical grade chromite (representative % content of specified chemicals and chromium-to-iron ratio [Cr:Fe]) (continued)

End-Use Industry and Source	Grade*	Specified Chemicals and Cr:Fe Ratio													
		Cr ₂ O ₃	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	MgO	MnO	TiO ₂	V ₂ O ₅	CaO	Ni	P	S	Cr:Fe
Iran															
Faryab	Grade 1	40–52	na	na	6–10	6–10	16–26	na	na	na	0.5–1	na	0.003 max	0.004 max	2.8–3.5
Faryab	Grade 2	33–41	na	na	5–14	14–18	9–12	na	na	na	1.5–3	na	na	na	2.3–2.5
Faryab	Grade 3	34–38	na	na	2–8	22–33	16–18	na	na	na	0.5–1	na	na	na	2.3–2.5
Madagascar															
Kroamita	Concentrate	48	17–18	na	6	13–16	12–14	na	na	na	na	na	0.009	na	2.4
Kroamita	Lumpy	42	13–16	na	12–14	13–16	17–20	na	na	na	na	na	0.007	na	2.5
Kroamita	Friable	48	17	na	7	na	na	na	na	na	na	na	0.009	na	2.4
Kroamita	Fines	49	21	na	6	na	na	na	na	na	na	na	0.007	na	2
Oman															
Oman Chromite		41.33	14.6	na	6.47	15.93	18.05	na	0.22	0.07	0.42	na	0.01	0.01	2.52
Philippines															
Velore		30–45	10–12	na	9–17	11–15	na	na	na	na	0.8	na	0.004	0.01–0.03	2.4–2.8
South Africa															
ASA	Grade 1	45	29	na	3	13.5	11	na	na	na	na	na	na	na	1.55
ASA	Grade 2	45.3	25.4	na	2.2	14.1	10.9	na	0.42	na	0.21	na	na	na	1.55
Assmang		45	25.5	na	3.5	14.7	9.5	na	na	na	0.2	na	na	na	1.55
Bayer		44.5	23.4	na	3.5	15.84	10.7	na	na	na	0.57	na	0.004	0.005	1.52
Hernic		44–45	26.5	na	2.5	15.5	10.5	na	0.64	0.44	0.3	na	0.003	0.004	1.5
National Manganese		44.5	26.1	na	2.3	14.3	11	na	0.71	na	0.55	na	0.003	na	1.4
Samancor		45	25.5	na	3	15.6	10.5	na	0.5	na	0.25	na	<0.003	<0.002	1.54
Xstrata		44–45	24.9	na	2.5	15.6	10.6	na	na	na	1.4	na	0.002	0.005	1.55
Sudan															
Advanced Mining		50.1	10.26	na	7.35	6.24	17.96	na	na	na	na	na	0.003	0.001	3.341
Turkey															
Bilfer	Concentrate	48	15	na	5	19	18	na	na	na	0.5	na	<0.007	na	>2.7
Bilfer	High Al	38–40	15	na	8–9	18	18	na	na	na	0.5	na	<0.007	na	>2.5
Bilfer	Standard	34–42	14	na	12–15	8	21	na	na	na	0.6	na	<0.007	na	>2.8
Eti Management		42–48	12–15	na	5–9	12–14	14–19	na	0–0.01	na	0.3–1	na	0–0.01	0–0.04	2.9

* Blank cells indicate that producer does not provide specs for more than one grade.

† na = not available.

‡ max = maximum.

§ min = minimum.

3% but not more than 4% carbon; and containing more than 4% carbon. Producers classify their material as low- or high-carbon or charge-grade ferrochromium (also known as *charge chrome*). Sometimes the terms *medium-carbon* and *extra-low carbon ferrochromium* are used. Low-carbon ferrochromium contains less than 4% carbon; high-carbon contains more than 4% carbon. Producers of chromium ferroalloys specify chromium, carbon, silicon, phosphorus, and sulfur content, as well as material size. Ferrochromium-silicon typically contains 24% to 40% chromium; 38% to 50% silicon; and 0.05% to 0.1% carbon. Ferrochromium typically contains 50% to 75% chromium and 0.05% to 8% carbon. Low-carbon ferrochromium typically contains 55% to 75% chromium and 0.02% to 0.1% carbon. High-carbon ferrochromium typically contains 60% to 70% chromium and 6% to 8% carbon. Charge-grade ferrochromium typically contains 50% to 55% chromium and 6% to 8% carbon.

The Steel Founders' Society of America (1967) suggested specifications for chromite sand, used primarily as either molding sand or as core sand in the production of steel castings, and chromite flour, an additive to chromite sand. Among other requirements, they describe chemical composition as 44% Cr₂O₃ (minimum); 26% FeO (maximum); 3% SiO₂ (maximum); 1% CaO (maximum); and Al₂O₃, MgO, and trace elements as the balance.

By-products and Coproducts

By-product or coproduct here means a mineral product that is different from the primary product and not different grades of the primary mineral product. No by-products or coproducts are associated with chromite ore mining operations. A chromite ore mining operation is likely to produce more than one grade of chromite. These grades are distinguished by size and chemistry. In the Bushveld Complex, MINTEK (South Africa's mining research organization) demonstrated the feasibility of recovering platinum from the LG-6 chromitite layer mineralizings; there is, however, no commercial recovery.

Platinum has been mined from the Merensky Reef, a chromite-free seam of the Bushveld Complex. As platinum reserves are depleted, platinum mining is moving to the chromite-containing UG-2 seam. Chromite-containing tailings are produced when UG-2 ore is processed to recover platinum. Since MINTEK demonstrated ferrochromium production from UG-2 platinum mine chromite by-product, South African smelters have adapted their processes and furnaces to accommodate that material.

USES

The ICDA (2003) reports world production of chromite by end use sector, and categorizes them as chemical, foundry sand, metallurgical, and refractory. From 1998 through 2002, ICDA reported chromite use as 90% metallurgical, 6% chemical, 3% foundry sand, and 1% refractory. These account for an average demand of 15 Mtpy gross weight of chromite, which is equivalent to about 4.3 Mtpy chromium content.

U.S. chromium demand from 1998 to 2002 is estimated to have averaged about 463,000 tpy of chromium, based on chromium content in chromite; chromium chemicals, ferroalloys, and metal; and stainless steel scrap. For that time period, about 88% of U.S. average chromium consumption per year was in the metallurgical industry, 12% in the chemical industry, and <1% in the refractory industry. About 75% of metallurgical domestic apparent consumption went into stainless steel based on reported consumption of chromium ferroalloys and metal. Refractory chromite use was most likely greater than that estimated here, because it is based on reported consumption of chromite by the refractory industry and not consumption of refrac-

tory materials. Foundry sand has never been included in refractory chromite consumption. Material categories for the purpose of monitoring trade do not differentiate among chromite end uses nor do they differentiate chromium-containing refractories from other refractories. Consequently, domestic chromite use and chromium-containing refractory use cannot be accurately tracked using trade statistics. Figure 5 shows material flow associated with the use of chromite materials and illustrates the relationships between industrial and metallurgical uses of chromium materials. (Chromium consumption differs from chromite consumption because chromium consumption includes chromite and chromium chemicals, ferroalloys, and metal, whereas chromite consumption includes only chromite.)

Chromite Uses

The metallurgical industry processes chromite into ferrochromium or chromium metal, which are used as alloying materials to make a variety of ferrous and nonferrous alloys. The major end use is stainless steel, a ferrous alloy made resistant to oxidation and corrosion by the addition of chromium. The chemical industry uses chromite to make sodium dichromate, which is a chemical industry product and an intermediate product used for making other chromium chemicals. Chromium chemicals find a wide variety of end uses such as leather tanning, pigments, plating for both decorative and engineering applications, surface treatment of reactive metals, and manufacture of chromium metal, a key ingredient in alloys for aircraft engines and land-based turbines. Chromite is useful in the foundry and refractory industries because it retains its physical properties at high temperatures and is chemically inert. Chromite is used as facing sand in the foundry industry, and the refractory industry uses chromite to produce refractory materials, including shapes, plastics, and gunning mixes. Refractory materials are used in the production of ferrous and nonferrous alloys, glass, and cement.

Chromite Consumption in the United States

U.S. chromite consumption was reported from 1940 through 1994; after 1994, data could not be kept confidential because of the small number of consuming companies. Figure 6 shows reported consumption by industry (i.e., chemical, metallurgical, and refractory), total reported consumption, and net imports of chromite. Net imports of chromite exceeded total reported consumption before 1965, the time during which the U.S. federal government was building the NDS. At its peak in 1962, the NDS contained 7.92 Mt of chromite. Since 1994, chromite consumption by metallurgical and refractory industries ended and virtually all U.S. chromite consumption is now by the chemical industry.

Based on net chromite imports, U.S. chromite consumption averaged 145,000 tpy from 1998 through 2002, a decline from the 1940 through 1997 average of 927,000 tpy. The decline occurred when domestic chromite users shifted from domestic to foreign ferrochromium suppliers for the metallurgical industry.

Figure 6 shows an increase in U.S. chromite use from 1940 to the mid-1950s, a period coinciding with increased consumption in the metallurgical industry. Between 1939, when NDS legislation was passed, and 1961, when NDS chromite inventories were made public, accumulated domestic chromite production (measured as reported shipments) plus net trade in excess of reported consumption amounted to 7.1 Mt and the NDS inventory amounted to 6.7 Mt. Attributing all the difference to reported chromite use suggests unaccounted-for consumption was <3% (of accumulated reported consumption) from 1940 through 1961.

The largest changes in reported consumption were in the metallurgical and refractory industries. Chemical industry use

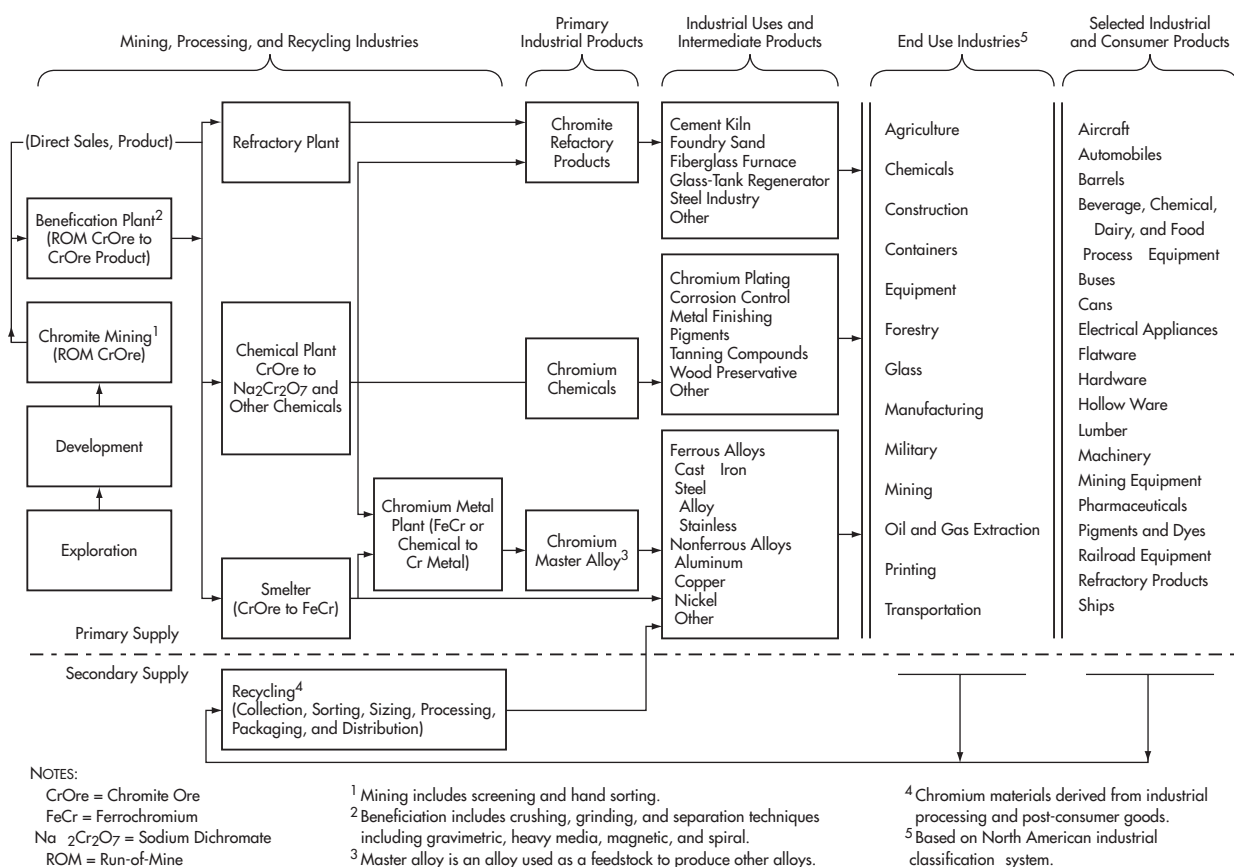


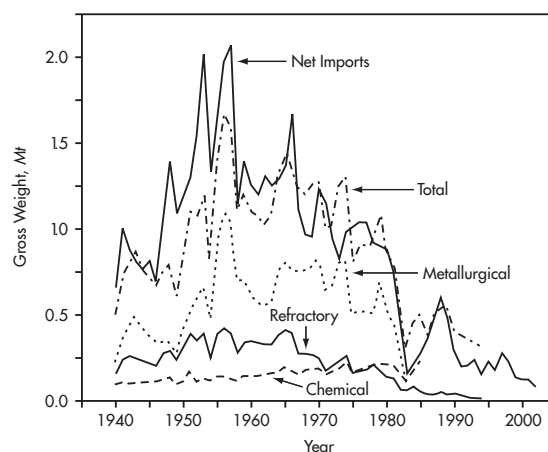
Figure 5. Chromium material flow from chromite ore mining to end use

increased slowly from 1940 to 2002. Refractory industry use reached a plateau from about 1950 to 1965, after which it slowly declined. Metallurgical industry chromite use increased from 1940 to the mid-1960s, after which it declined to nothing. Coinciding with the drop in metallurgical use, chemical use increased its share of the U.S. market. Declining metallurgical industry use resulted from declining domestic ferrochromium production. From 1940 through 1985, the metallurgical, chemical, and refractory industries data were reported separately: the metallurgical industry accounted for 56% of reported total chromite consumption; the refractory industry, 27%; and the chemical industry, 18%. After 1985 the amount of chromite consumed by various industries remains unknown because chromite end use cannot be inferred reliably from trade data.

Metallurgical Industry

Figure 6 shows metallurgical industry chromite consumption, and Figure 7 shows its chromite market share. The metallurgical industry dominated domestic chromite consumption from 1940 to 1980. The patterns of total chromite consumption and net imports match those for metallurgical consumption over that period. With the dramatic drop in metallurgical consumption of chromite from 1980 to 1983, chemical industry consumption surpassed metallurgical consumption for the first time since record keeping started in 1940.

In the metallurgical industry, chromite is used to make ferrochromium, which is used to make steel and nonferrous alloys. Ferrochromium is produced from chromite ore in an electric-arc furnace using reductants and fluxes to remove oxygen. Ferrochromium

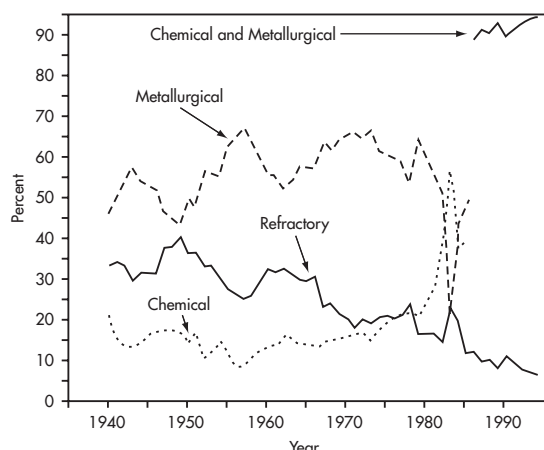


Courtesy of USGS and U.S. Census Bureau.

Figure 6. U.S. chromite reported consumption by consumer industry (i.e., chemical, metallurgical, and refractory), total reported consumption, and net imports

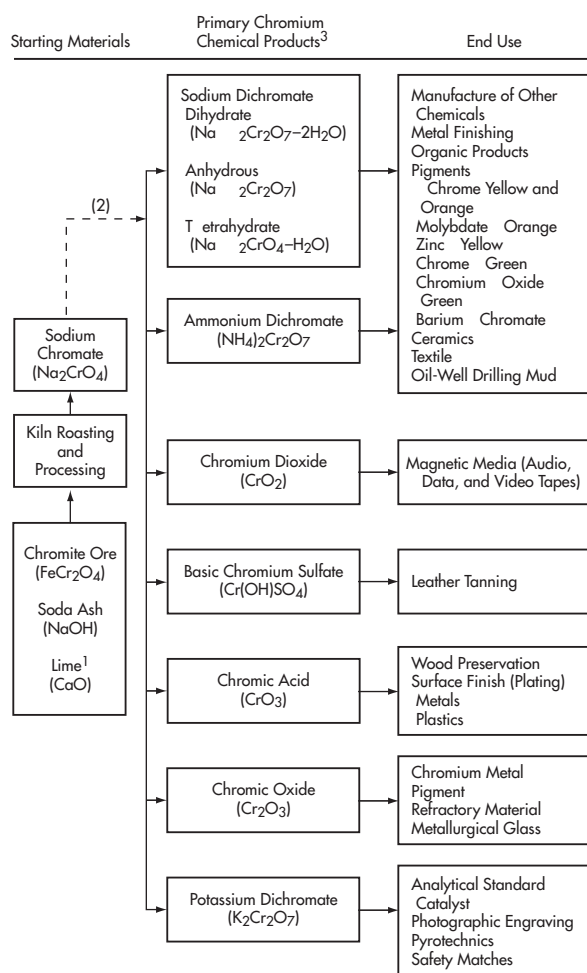
mium production is electrical energy intensive; the process was modified in various ways, however, making it more energy efficient and less polluting.

Macalloy Corp., the only producer of ferrochromium from chromite in North America, stopped electric furnace production of



Courtesy of USGS and U.S. Census Bureau.

Figure 7. U.S. chromite percent consumption by consuming industry (i.e., chemical, metallurgical, and refractory)



¹ In 2002, more than one half of chromium chemicals were produced using a lime-free process.

² The dashed line indicates that there is more than one processing route.

³ Chemical formulas are indicative of the material. Commercial products are often mixtures that include other compounds.

Figure 8. Major chromium chemicals and their end uses

high-carbon ferrochromium at its Charleston, South Carolina, plant in 1998. Since 1941 ferrochromium was produced at the Charleston plant site, which was built as part of the World War II mobilization effort. It was located to take advantage of access to ocean-going transportation. The Santee Cooper Project, a public power supply project there, provided electrical power. During the war Pittsburgh Metallurgical Corp. manufactured ferrochromium, a key ingredient in armor plating for tanks and ships.

The Charleston plant operated under a variety of names (in chronological order): Pittsburgh Metallurgical Corp., Airco Alloys Division, Air Reduction Co., Inc.; Airco Alloys and Carbide Division, Air Reduction Co., Inc.; Airco Alloys, Air Reduction Co., Inc.; and Airco Alloys, Airco Inc. Macalloy Corp. had operated the plant since 1980; 8 chromium ferroalloy producers in the United States were operating 12 plants in 1980.

Chemical Industry

Chromite has been the key raw material in the manufacture of chromium chemicals since the early 19th century, initially to make brightly colored pigments. Today, production includes biocides, catalysts, corrosion inhibitors, metal plating and finishing chemicals, oil field chemicals, pigments, printing chemicals, tanning compounds, and high-purity chromium metal. The largest single use of chromium chemicals today is the use of chromium salts in the manufacture of leather from animal skins, a process which began in the middle of the 19th century. Chromium plating is the electrodeposition of chromium from a solution of chromic acid; it was started in the early 1900s. A recent use for chromium is for wood preservation. Chromium-copper-arsenate (CCA) impregnates wood to protect it from weathering, insects, and decay for up to 30 years. Major chromium chemical plants are in Japan, Kazakhstan, Russia, South Africa, the United Kingdom, and the United States; only Kazakhstan and South Africa, however, are significant chromite producers. Sodium dichromate and chromic acid accounted for the largest amount of U.S. chromium chemical exports and imports, respectively.

The terms *chromium* and *chrome* are synonymous in the chemical industry for elemental chromium. Historically, the term *chrome* was used more commonly than *chromium*; thus, many chemical products (namely pigments) have “chrome” in their name. The terms *bichromate* and *dichromate* are interchangeable in the chemical industry. Dichromate is consistent with the convention for naming compounds; the term *bichromate*, however, also is used in trade and commerce.

Sodium dichromate, an intermediate chemical produced from chromite, is used to manufacture other chromium chemicals. The process involves pulverizing chromite and mixing it with soda ash (sodium carbonate; Na_2CO_3) and a diluent. Historically, the diluent was lime (calcium oxide; CaO), limestone (calcium carbonate; CaCO_3), or dolomite (calcium magnesium carbonate; $\text{CaMg}(\text{CO}_3)_2$); today, however, the “high-lime” process accounts for about one half the global chromium chemical production capacity, mainly in China, the CIS, and India. Around 1960, western producers had developed “zero lime” or “very low lime” processes in which the diluent was recycled material from production processes. The chromite- Na_2CO_3 -diluent mixture is roasted in a rotary kiln to produce a compound containing sodium chromate, which is leached and treated with acid to produce sodium dichromate prior to purification. This process is used in United States. Sodium dichromate dihydrate is the first commercial product made when converting chromite into chromium chemicals; it is the commercial product produced and traded most. Many other chromium chemicals are manufactured from sodium dichromate (Figure 8). In 2002, more than one-half of

chromium chemical production came from no-lime processes (54%); 0.5%, from low-lime processes; and the remainder from lime processes that used dolomite or limestone.

The use of chromium chemicals for pigments is a familiar use to many people. Medium yellow pigment, a lead-chromate compound, is used in yellow paint for traffic control on major streets and highways. Copper-chrome pigment is used in the black coating on outdoor grills and wood-burning stoves. Chromium pigments are important in anticorrosion coatings; the U.S. military and the federal government are major users of chromate metal primers. Chromium oxide is a green pigment used in camouflage because it is efficient in reflecting infrared wavelengths.

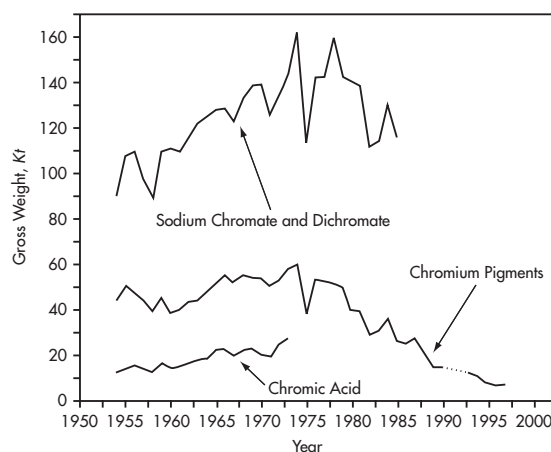
China has the largest overall chromium chemical production capacity; Chinese plants, however, have only small production capacities (<50,000 tpy of sodium dichromate). The largest chromium chemical plants (>100,000 tpy of sodium dichromate) are in Kazakhstan, Russia, the United States, and the United Kingdom. An intermediate size plant (between 50,000 and 100,000 tpy of sodium dichromate) in South Africa is the newest chromium chemical plant. The United States is a major consumer, producer, and supplier of chromium chemicals. Table 4 shows chromium chemical production capacity by country and year. Worldwide production capacity in 2002 was about 299,000 t contained chromium, or about 855,000 t sodium dichromate dihydrate equivalents. Many small chromium chemical plants are located in chromite-producing countries. Industry rationalization in developed countries has replaced small plants with larger, more efficient ones operated to higher occupational safety and environmental standards. For example, the number of chromium chemical plants in Europe and the United States decreased from 17 to 2 in the past 40 years. The opposite occurred in China, where chromium chemical production began in the 1950s, with more than 20 plants operating today. China's policy today is to modernize chromium chemical production and to reduce the number of small plants.

Figure 9 shows domestic production of major chromium chemicals: sodium dichromate, chromic acid, and chromium pigments. Sodium dichromate production was reported until 1985, when production was about 120,000 t. Chromium pigment production declined from >50,000 tpy in the mid-1970s to <10,000 tpy in 1996, the last year the U.S. Department of Commerce reported such production. Chromic acid production was about 27,000 tpy in 1973, the last year it was reported (Anon., various years). In Figure 9, chromium pigment production is shown as a composite of the production of several chromium pigments. Chromium pigment production in Figure 10 includes chrome yellow and orange, chrome molybdate orange, chrome oxide green, zinc yellow, and chrome green. The greatest production is for chrome yellow and orange followed by chrome molybdate orange. For both, production peaked in the mid-1970s. Chrome yellow and orange annual production declined from about 34,000 to <5,000 t when production was last reported in 1997. The chrome molybdate orange production series was discontinued in 1987. Zinc yellow annual production peaked between 1965 and 1967; the series was discontinued in 1987. Zinc yellow production data were withheld from 1976 to 1985. The decline in chromium pigment manufacture is associated with pigments that contain hexavalent chromium. Use of hexavalent chromium pigments declined because of increased awareness of health and environmental hazards associated with hexavalent chromium compounds, and the availability of less hazardous alternatives. The reporting of chrome oxide green production data was discontinued in 1985; chrome green production data were no longer reported after 1972. Chrome oxide green is trivalent; chrome green is a mixture of hexavalent chromium compounds.

Table 4. Chromium chemical production capacity (in kilotons of chromium per year)

Country	1992	1994	1996	1998	2000	2002
Argentina	6	6	6	6	6	13
Brazil	12	12	12	na*	na	na
China	16	16	21	21	21	70
Germany	20	20	24	na	na	na
India 5		5	8	8	8	4
Iran 2		2	2	2	2	2
Japan	21	21	20	17	17	17
Kazakhstan	42	42	42	42	42	37
Macedonia	5	5	5	5	5	na
Mexico	5	na	na	na	na	na
Pakistan	3	3	3	3	3	3
Poland	7	7	3	5	5	na
Romania	5	5	9	9	9	na
Russia	63	63	60	60	60	31
South Africa	na	na	24	24	24	23
Turkey	10	10	10	10	10	17
United Kingdom	52	68	52	52	52	44
United States	55	55	53	56	56	38
Total	329	340	336	320	320	299

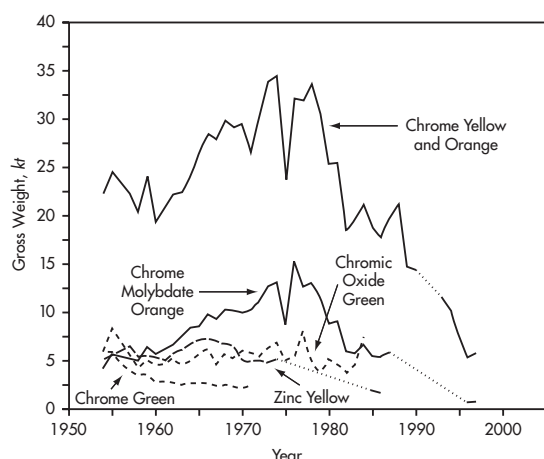
* na = not available.



Courtesy of USGS and U.S. Census Bureau.

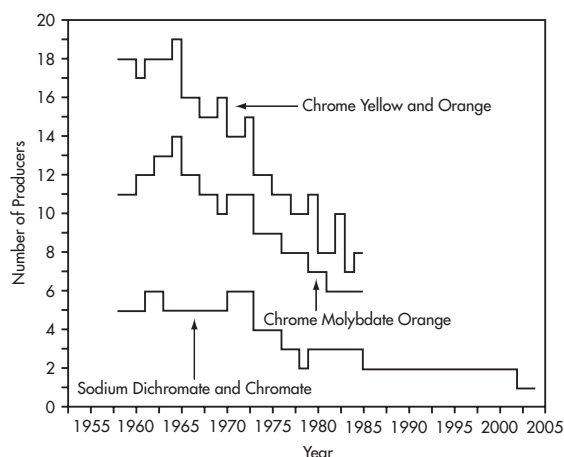
Figure 9. U.S. chromium chemical production by material (sodium chromate and sodium dichromate, chromic acid, and chromium-containing pigments). (The dotted line segment indicates linearly interpolated data.)

Figure 11 shows the number of producers of the following chromium chemicals: sodium dichromate and chromate, chrome yellow and orange, and chrome molybdate orange. Figures 10 and 11 show the decline in both production of chromium pigments and the number of producers. The number of sodium dichromate and chromate producers has also declined; production did not decline, however, suggesting that production was consolidated by the remaining two producers in 1990. The general trend of reported production (Figures 9 and 10) appears to be consistent with that of chromite consumption (Figures 6 and 7).



Courtesy of USGS and U.S. Census Bureau.

Figure 10. U.S. chromium pigment production by pigment (chrome green, chrome molybdate orange, chromic oxide green, chrome yellow and orange, and zinc yellow). (The dotted lines that connect the chrome yellow and orange, chrome molybdate orange, and zinc yellow data curves are linearly interpolated.)



Courtesy of USGS and U.S. Census Bureau.

Figure 11. Number of U.S. chromium chemical and pigment producers, by product

A review of the world chemical industry in 2001 (Darrie 2001; Tomkinson and Moore 2001) characterized the industry as mature and growing slowly. Access to modern technology, capital investment in new plants and equipment, and excess production capacity were barriers to market entry. Pressure from competition and environmental regulation forced producers to consolidate. These factors were expected to reduce the number of producers and limit production to large plants. Global demand in 2000 was estimated at 692,000 t (sodium dichromate equivalent) of which 32% went into chromic acid; 34%, chromium sulfate; 20%, chromic oxide; and 14%, other uses. Chromic acid was used for metal finishing (50%), timber treatment (35%), magnetic media (5%), and other uses (10%). Chromium sulfate was used for leather tanning. Chromic oxides were used for pigments (47%), the manufacture of

chromium metal for alloys (33%), ceramics (8%), and other uses (12%).

CCA was a popular wood treatment chemical in the United States. It was the second largest worldwide market for chromic acid, the major product from sodium dichromate, accounting for about 78,400 t of chromic acid in 2000. The United States accounted for about one half the global CCA market, of which about three quarters was used to treat wood for residential applications. In 2002 U.S. manufacturers of treated wood planned to phase out CCA use by voluntary agreement with the U.S. Environmental Protection Agency (EPA). EPA banned CCA use for residential applications under the Federal Insecticide, Fungicide, and Rodenticide Act (EPA 2002). As a result, U.S. chemical industry chromium consumption was expected to drop between 2002 and 2004 and cause the U.S. chromium chemical industry to reorganize.

In 2002 the chemical industry worldwide consumed about 1 Mtpy of chromite to produce 692,000 t of sodium dichromate. Sodium dichromate was converted to chromic acid at the rate of 224,000 tpy. Chromic acid accounted for 32% of sodium dichromate demand; chromium sulfate, 30%; chromic oxide, 20%; and other chemicals, 18%. Chromic acid was converted to CCA at the rate of 100,000 tpy. CCA accounted for 35% of chromic acid demand; metal finishing, 50%; magnetic media, 5%; and other uses, 10%.

Since 1967, when five chromium chemical plants owned by four companies consumed chromite to produce sodium dichromate in the United States, the number of U.S. chromium chemical plants has been declining, whereas chromium chemical production has been slowly increasing. Rationalization of the U.S. chromium chemical industry left one plant producing chromium chemicals from chromite in 2002.

Refractory Industry

Chromite is used directly in the refractory industry because it resists degradation when exposed to heat. Chromic oxide, a chemical industry product, also is used in refractory applications. Basic refractories are a type of nonclay refractory that behave chemically as bases. Basic refractories are made of chromite, dolomite, magnesite, or various combinations of magnesite and chromite. In the refractory industry, chromite-containing refractories are called *chrome refractories*. Chrome-magnesite refractories contain more chromite than magnesite; magnesite-chrome refractories contain more magnesite than chromite.

Refractories also are categorized as shaped or unshaped. Shaped refractories are manufactured to fit together, like building blocks, to form a desired geometric structure. Unshaped refractories include mortars (materials used to bind shaped refractories together), plastics (materials that are formed into a desired shape), and gunning (material that is sprayed onto a surface). In the refractory industry, the term *monolithics* describes refractories that are not shaped. Units for reporting shipments of shaped and unshaped refractories differ. Shaped refractories have been reported in thousand "9-in. brick" equivalents, and unshaped refractories have been reported in metric tons based on U.S. Department of Commerce reports (Anon., various years). A 9-in. brick equivalent (9be) is a solid volume of 0.165919 m³.

Major end users for chromite refractories are in the cement, copper, glass, nickel, and steel industries. Basic refractories are used in copper and nickel furnaces. The glass industry uses chromite refractories in glass tank regenerators; the cement industry uses chromite refractories primarily in transition zones of cement kilns. Basic refractories typically have been used in open hearth and electric arc steelmaking furnaces.

Contemporary steelmaking processes using the basic oxygen furnace or the electric arc furnace use much less chromite-containing refractories than open-hearth furnaces. Open-hearth furnaces used about 30 kg of refractories per ton of steel, the basic oxygen furnace uses about 1 kg/t, and the electric arc furnace uses from 1 to 2 kg/t. Steel industry demand for basic refractories has declined dramatically as open-hearth furnace steelmaking is phased out. Chromite use in cement kiln refractories has declined owing to hexavalent chromium mobilization. The introduction of technically acceptable substitutes has eliminated chromite refractories in cement kilns. Recycling chromite refractory brick in the cement industry was discontinued in the 1990s.

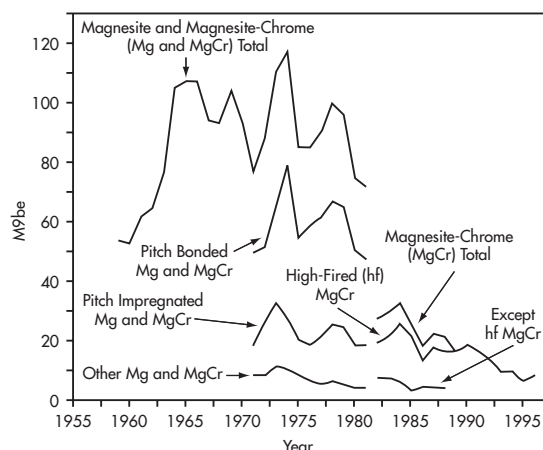
Figures 12 through 14 show historical trends of chromite refractory shipments. Chrome and chrome-magnesite refractories represent at least one-half the chromite consumed in refractories. The ASTM promulgates specifications for the identification of chrome, chrome-magnesite, and magnesite-chrome brick. Chrome brick is refractory brick manufactured substantially or entirely of chromite product. Chrome-magnesite and magnesite-chrome brick are classified by magnesia (MgO) content. Nominal MgO content is from 30% to 80%, therefore the chromite content is more than 20%. The amount of chromite in magnesite and magnesite-chrome refractories is unknown.

Because chromite represents only a part of the refractory industry, one can only infer the performance of chromite refractories from shipment data for basic unshaped refractories. This is because the data include other refractory materials such as dolomite, forsterite, magnesite, and zircon.

Figure 12 shows shipments of chromite-containing shaped refractories. Chrome and chrome-magnesite refractory shipments declined from 1960 through 1981 (Figure 14; the data series was discontinued in 1981). The number of chrome and chrome-magnesite refractory producers fell from nine to seven during that same time period. Since 1981, the number of chromite refractory producers has fallen from seven to zero because of declining demand. Magnesite and magnesite-chrome refractory shipments grew from 1960 through 1965 (Figures 12 and 14), after which large variations occurred. From 1982 through 1990 magnesite-chrome refractory shipments decreased from 28 to 18 M9be (Figure 12). The U.S. Department of Commerce reported chrome and chrome-magnesite shipments, whereas magnesite and magnesite-chrome, and magnesite-chrome shipments data are a composite of reported shipments.

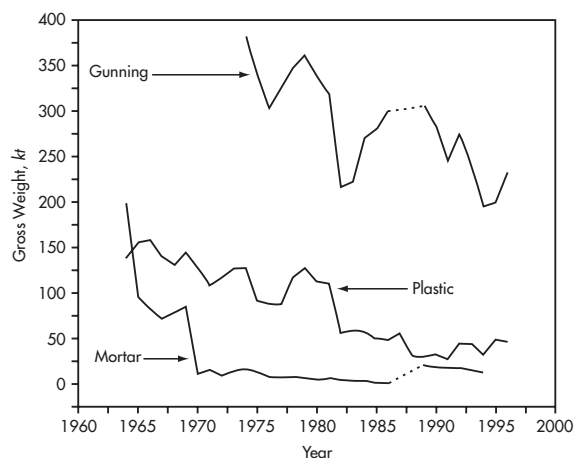
Figure 13 shows U.S. shipments of chromite-containing unshaped refractories. Mortar shipments declined rapidly from 1964 to 1970, and then very slowly decreased until 1986, when they were no longer reported. Plastic and gunning shipments show a slow decline.

Figure 14 shows refractory shipments for magnesite and magnesite-chrome (1960 to 1981) and magnesite-chrome (1982 to 1997). Magnesite and magnesite-chrome shaped refractory shipments were reported as such and represent the 1960 through 1970 time period in Figure 14. From 1971 through 1981, magnesite and magnesite-chrome shaped refractory shipments were reported as pitch bonded, pitch impregnated, or other (Figure 12). These three categories were combined to form the magnesite and magnesite-chrome shaped refractory shipments curve for the 1971 through 1981 time period in Figures 12 and 14. From 1982 through 1990, magnesite and magnesite-chrome refractory shipments were reported as high-fired magnesite-chrome, except high-fired magnesite-chrome, and magnesite and magnesite-carbon refractories (not shown). Starting in 1982, magnesite-chrome was reported separately from other magnesite refractory shipments. From 1982 through 1990, magnesite-chrome shaped refractory shipments were



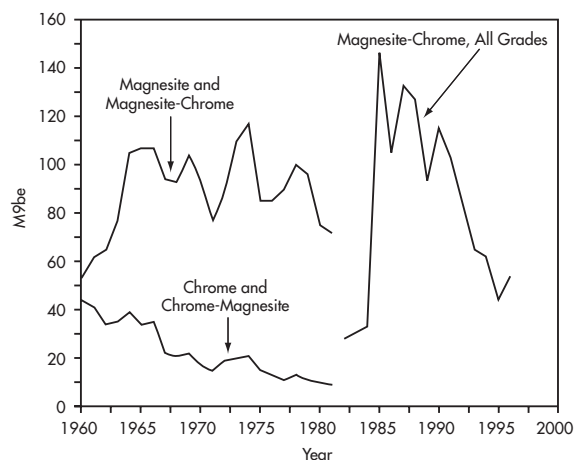
Courtesy of USGS and U.S. Census Bureau.

Figure 12. U.S. chromite-containing shaped refractory shipments



Courtesy of USGS and U.S. Census Bureau.

Figure 13. U.S. chromite-containing unshaped refractory shipments. (The dotted line that connects the gunning and mortar solid lines is linearly interpolated.)



Courtesy of USGS and U.S. Census Bureau.

Figure 14. U.S. chromite-containing shaped refractory shipments by type of refractory.

Table 5. U.S. foundry sand products, end uses, and producers

Products	End Uses	Producers
Chromite sand	Casting facing sand	American Colloid Company http://www.colloid.com/accis.htm
Chromite flour	Mold coating	American Minerals http://www.ceramics.com/american/
	Colorant	
	Architectural brick	
	Glass	
	Ceramic	
	Brake shoes	

reported as high-fired and except high-fired (Figure 12), forming the magnesite-chrome shaped refractory shipments curves for the 1982 through 1990 time period shown in Figures 12 and 14.

Because the chromite-containing magnesite refractories data were separate from the chromite-free magnesite refractories data beginning in 1982, the fraction of magnesite and magnesite-chrome refractory shipments that contain chromite can be calculated for the 1982 through 1990 time period. By volume, magnesite-chrome refractory shipments averaged 50% (ranging between 41 % and 57%) of magnesite and magnesite-chrome refractory shipments from 1982 through 1990.

Beginning in 1985, shapes were reported in tons also. From 1985 through 1990, the weight per volume of magnesite-chrome refractories averaged 4,700 t/M9be with a range of from 4,300 to 5,000 t/M9be.

Chromic oxide, a chemical industry product, also is used to make refractories for the glass industry. Chromic oxide refractories are used in contact areas of glass melting furnaces to achieve long furnace life.

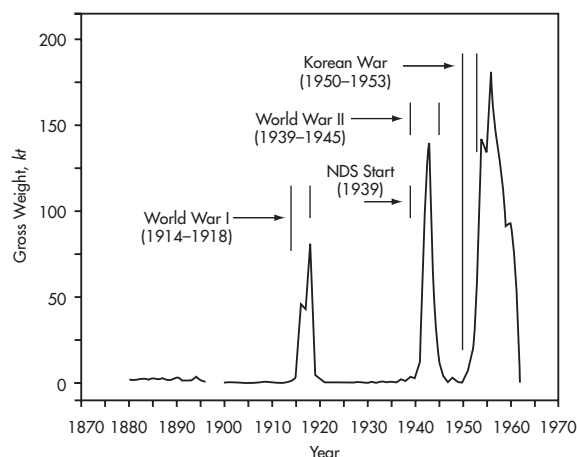
The general decline in refractory use resulted, in part, from more efficient use of refractories. Use of longer-lasting refractories decreases downtime associated with replacing spent materials, which consequently lowers labor costs and increases production (less time for relining equipment). The decline in chromite-containing refractory use is directly related to the cessation of open-hearth steelmaking in the United States.

EPA regulation of waste chromium significantly affected chromite refractory use (discussed under the Environmental Regulations section).

To protect company proprietary data, the USGS discontinued reporting chromite consumption by the refractory industry when the number of reporting producers fell to three in 1994. Chromite-containing refractory production in the United States was virtually zero in 2002; U.S. consumers today rely on imports. Because the amount of domestic chromite-containing refractory production is no longer reported, and because trade data are inadequate to track consumption, it is no longer possible to quantitatively characterize the industry using publicly available statistics.

Foundry Sand

Foundry sand forms the mold in which molten metal is contained until the metal solidifies in the desired shape. The sand is washed, graded, and dried beforehand. Because silica sand is refractory, common, and inexpensive, it is the most widely used mineral for foundry sand; other sands (e.g., zircon, olivine, or chromite) may be chosen, however, depending on physical or chemical conditions. The use of chromite foundry sand is a modern development. Chromite foundry sand is used in the ferrous and copper casting industries.



Courtesy of USGS.

Figure 15. U.S. chromite production

Chromite sand is compatible with steel castings. It is typically used as facing sand in heavy section (greater than 4 t) casting and enjoys a technical advantage over silica sand in casting austenitic manganese steel (chromite sand does not react with the manganese in steel). Because chromite and zirconia have higher melting temperatures than silica, they are chosen when casting temperatures exceed those acceptable for silica sand. Table 5 shows U.S. foundry sand producers, products, and end uses.

Chromite sand casting was developed in South Africa where chromite fines are readily available as an inexpensive grade of chromite. After successful results in South Africa in the late 1950s, use expanded into the 1960s in the United Kingdom and closely thereafter in the United States. Initial use of chromite sand coincided with a shortage of zircon sand; chromite sand had the additional advantage of being an inexpensive substitute. Foundry characteristics that make chromite sand desirable are good thermal stability, good chill properties, not easily wetted, resistant to metal penetration, highly refractory, and chemically nonreactive. Compared with zircon sand, the disadvantages of chromite are higher thermal expansion, occasional presence of hydrous mineral impurities, and different bonding characteristics with some binding agents.

As much as 90% of chemically bonded foundry sand (average of minerals used) can be reclaimed (Heine 1989) using mechanical, pneumatic, wet, or thermal processes, or combinations of them. These processes have been adapted to chromite sand. After casting, chromite sand, typically used as facing sand, is mixed with bulk sand (silica). Because the size distribution of chromite sand is similar to that of silica sand, mechanical methods cannot separate them sufficiently; hydraulic spiral separation and magnetic separation, however, effectively separate chromite sand from silica and zircon sands (silica and zircon sands are nonmagnetic). Some chromite sand degrades and then tends to adhere to castings, so it is not part of the reclaimed sand. Reclaimed chromite sand is indistinguishable from new chromite sand. Sontz (1972) estimated that about one-half the foundry industry chromite demand could be met with reclaimed chromite sand.

The USGS does not survey for chromite-containing foundry sand consumption, and the Harmonized Tariff Schedule of the United States does not clearly identify such material in trade; therefore, no statistics are publicly available with which to characterize the U.S. industry.

Table 6. Chromite world production by country, 1994–2004 (in metric tons, gross weight of chromite product)

Country	1994	1996	1998	2000	2002	2004
Afghanistan	na*	3,409	3,409	5,345	6,136	0†
Albania	118,000	143,763	102,189	120,400	91,000	158,392
Australia	na	6,000	80,000	90,000	132,665	265,987
Brazil	359,788	408,495	537,426	550,000	283,991	462,755
Burma	1,000	1,000	4,059	227	318	0†
China	62,000	130,000	220,000	208,000	180,000	200,000
Cuba	28,800	37,300	46,000	56,300	46,000	34,000
Finland	572,747	582,000	498,075	628,414	566,090	579,780
Greece	5,000	11,725	4,432	na	na	na
India	909,076	1,363,205	1,311,310	1,946,910	2,698,577	2,948,944
Indonesia	2,500	13,300	4,700	na	na	na
Iran	354,100	130,220	211,555	153,000	80,000	183,171
Kazakhstan	2,103,000	1,190,000	1,602,700	2,606,600	2,369,400	3,267,000
Macedonia	5,000	5,000	5,000	5,000	5,000	na
Madagascar	90,200	137,210	104,300	131,293	11,000	77,386
Oman	6,166	15,252	28,684	15,110	27,444	18,585
Pakistan	6,240	27,987	77,500	119,490	62,005	10,000
Philippines	76,003	107,068	53,871	26,361	23,703	25,000
Russia	143,000	96,700	150,000	92,000	74,300	320,200
South Africa	3,642,000	5,078,000	6,480,000	6,622,000	6,435,746	7,625,545
Sudan	25,000	12,000	30,500	28,500	14,000	26,000
Turkey	1,270,431	1,279,032	1,404,470	545,725	313,637	436,639
United Arab Emirates	55,000	56,000	76,886	30,000	na	7,089
Vietnam	63,000	37,000	59,000	76,300	80,000	150,000
Zimbabwe	516,801	697,311	605,405	668,043	749,339	668,391
Total	10,414,852	11,568,977	13,701,471	14,720,018	14,245,351	17,464,864

* na = not available.

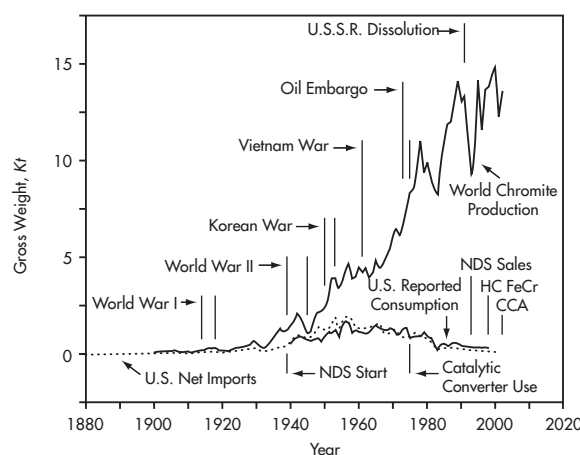
† Estimated.

ECONOMIC FACTORS

Production, Consumption, and Trade

Chromite currently is not produced in the United States. Russia was the original source of chromite in the 1700s and was the major world supplier into the nineteenth century. During the 1800s, chromite was discovered and mined in Maryland, Pennsylvania, and later, California. The United States then became a major producer of chromite ore. Chromite mined in Maryland and Pennsylvania fed the first U.S. chromium chemical plant at Baltimore, Maryland. Chromite was then discovered in Turkey, which soon dominated world production. U.S. production peaked during times of major conflict (e.g., World Wars I and II and then declined until commercial production ended, although some noncommercial production continued sporadically into the 1960s (Figure 15). The figure shows events significant to U.S. industry, including World War I (1914–1918); NDS acquisition enabling legislation (1939); World War II (1939–1945); and the Korean War (1950–1953).

Since 2000, India, South Africa, and Kazakhstan have been the leading producers of chromite. Table 6 shows chromite production by country. Figure 16 shows world chromite production and U.S. chromite consumption. The figure shows the same events as in Figure 15 significant to world industry or U.S. industry, adding the Vietnam War (1961–1975); oil embargo (1973); catalytic converter use adopted in the United States (1975); dissolution of the U.S.S.R. (1991); closure of the last U.S. high-carbon ferrochromium plant; and discontinued use of FCCA to treat wood for domestic use.



Courtesy of USGS.

Figure 16. World chromite production and U.S. chromite reported consumption and net imports. U.S. net chromite imports are shown as a dotted line; reported chromite consumption, as a solid line.

World chromite production declined significantly beginning in 1940 through 1945, from 1978 through 1983, and from 1990 through 1993. The United States dominated world chromite consumption from 1945 through 1948. World chromite production has grown since then, whereas U.S. chromite consumption declined

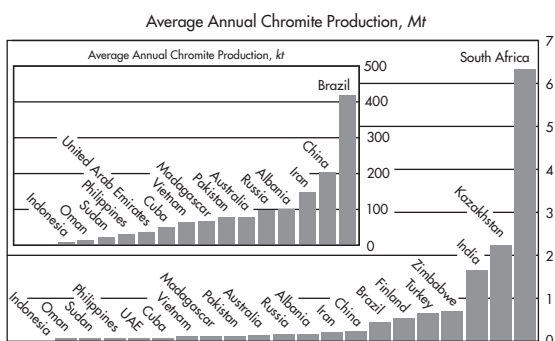


Figure 17. World chromite production by country (1998–2002 average). The bar chart shows the countries with smaller production on a smaller scale so that their relative production is apparent.

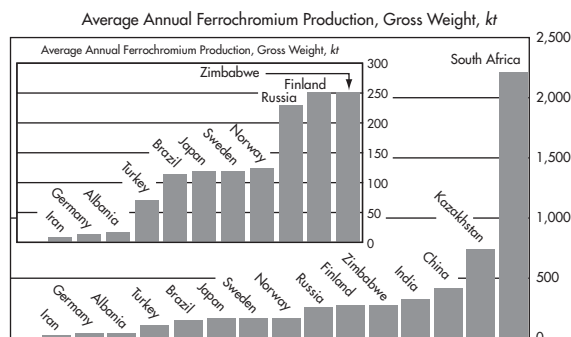


Figure 18. World ferrochromium production by country (1998–2002 average). The bar chart shows the countries with smaller production on a smaller scale so that their relative production is apparent.

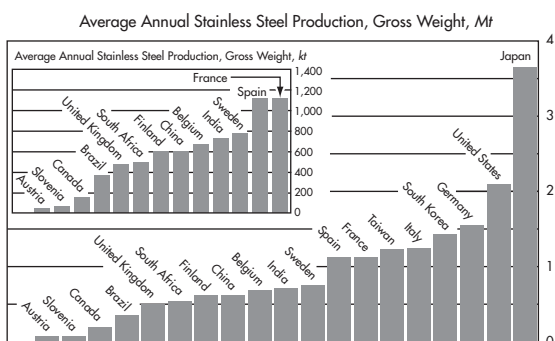


Figure 19. World stainless steel production by country (1998–2002 average). The bar chart shows the countries with smaller production on a smaller scale so that their relative production is apparent.

between the 1950 and 1970 average. Reduced U.S. chromite consumption beginning about 1970 resulted primarily from the replacement of chromite by ferrochromium as a source of chromium units for the domestic metallurgical industry and, secondarily, from declining use of chromite by the domestic refractory industry. Since 2002, reduced demand for chromite by the chemical industry also contributed to the decline.

The United States continues to be a major consumer of chromium; it now gets chromium units via downstream products such as ferrochromium, chromium chemicals and metal, and stainless steel scrap, however, rather than from chromite. U.S. annual chromium consumption is equivalent to about 12% of annual world chromite production.

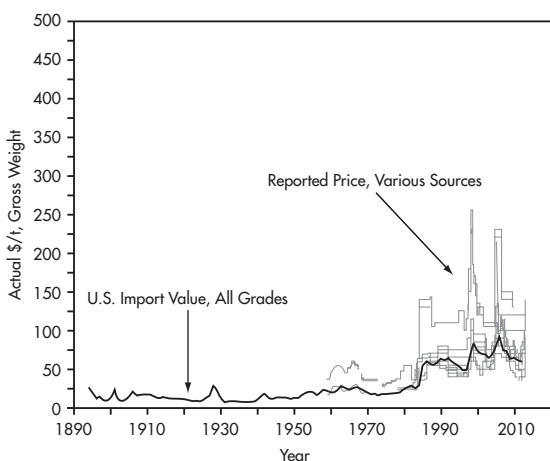
Since 2000, three major chromite producers (India, Kazakhstan, and South Africa) were producing consistently more than 1 Mtpy each. They accounted for about 80% of annual world production, and South Africa accounted for nearly one-half of world production. Seven other significant chromite producers have annual production ranging from 100,000 t to 1 Mt: Albania, Australia, Brazil, China, Finland, Turkey, and Zimbabwe. These seven accounted for more than 15% of annual world production (see Table 6 and Figure 17).

Chromite is consumed mostly by steel, chemical, and refractory industries located in developed countries. Historically, chromite ore was mined, exported, processed, and then consumed; chromite-producing countries, however, are developing the vertical integration of their chromium industries. For example, South Africa increased the number of ferrochromium plants, integrated chromite mining and ferrochromium operations, restarted chromium chemical production (in 1999), and significantly increased stainless steel production. Kazakhstan began chromium metal production with a process that requires chromic oxide, a chemical industry product, as feed material. Thus it sustains an existing industry (chromium chemicals) and enters a new product area (chromium metal). Kazakhstan rebuilt its ferrochromium industry and marketed its ferrochromium in Asia, Europe, and the United States after the dissolution of the Soviet Union in 1991 resulted in reduced demand for its product. Since about 1970, ferrochromium production has shifted from areas that historically had produced stainless steel (i.e., Japan, the United States, and Western Europe) to chromite-producing countries. Finland, India, Kazakhstan, and South Africa are the only chromium-consuming countries not dependent on imports of chromite or chromium. The development of ferrochromium production in chromite-producing countries has reduced international trade of chromite. South Africa continues to build ferrochromium production and capacity, and Japan and Western Europe retain marginal production capacity (see Figures 18 and 19).

Prices

Chromite, ferrochromium, and chromium metal are not traded in open market exchanges like gold, silver, nickel, and other metals. The price of chromite usually is negotiated between buyer and seller. Some trade publications survey chromite sellers and buyers and report a calculated composite price. Included among these are *Platts Metals Week* (<http://www.platts.com/Metals>), *Metal Bulletin* (<http://www.metalbulletin.com>), *Industrial Minerals* (<http://www.indmin.com/index.html>), and *Ryan's Notes* (<http://www.ryansnotes.com>). Unfortunately, the volume of trade is unknown.

When the United States imports materials, the invoice value is declared at the port of export. This is called the f.o.b. (free on board) value. Figure 20 shows the mass-weighted average declared f.o.b. actual value of U.S. chromium imports (averaged over all grades). The price of chromite from important chromite suppliers (South Africa and Turkey) as reported in trade journals is shown along with the import value. The upper price lines are typically for Turkish chromite; the lower price lines are typically for South African chromite. Import values closer to the lower prices reflect the fact that South African chromite was imported in greater quantities than was Turkish chromite. Figure 20 shows that the value of U.S. chromite imports and the reported prices have similar trends over time. Figure 21 shows the same values and prices in Figure 20



Source: USGS; U.S. Census Bureau; *Engineering and Mining Journal*; *Platts Metals Week*; *Ryan's Notes*; *Industrial Minerals*.

Figure 20. U.S. chromite actual value (based on import statistics) and price (as reported in trade journals). Price histories from various sources are shown as narrow gray lines; value history based on all grades of chromite imports is shown as a broad dark line. Value history is mass-weighted average value over all grades.

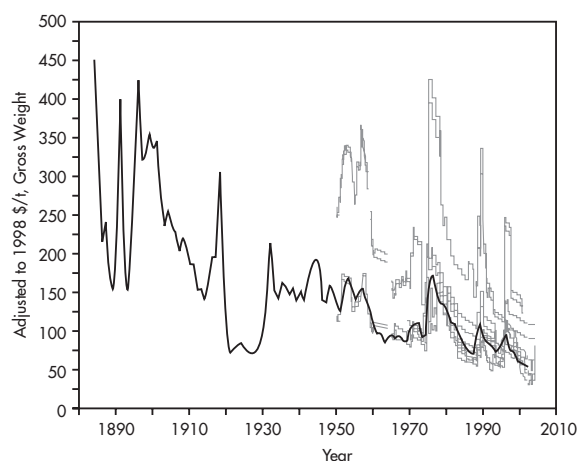
adjusted for inflation and normalized to 1998 dollars. Chromite declined in real value but increased in actual dollars.

Figure 22 shows the actual value of chromite by grade. Unit values are given in dollars per metric ton, gross weight of chromite based on declared f.o.b. values. Figure 22 also shows the unit value of each import grade and the mass-weighted average over all grades, which is called the *import value*. In the latter part of the time period (20th century), unit values by grade differ from import value significantly more than they did earlier. Although not obvious in Figure 22, when unit values deviate significantly from the import value, the import value very closely approximates imports of 40% to 46% Cr_2O_3 grade chromite (the dominant imported grade after 1991). Significantly deviant values are thought to result from specialty items that have high unit value but are relatively low in volume (measured in tons of material imported). When these are averaged with bulk materials, the bulk materials value tends to dominate. High values of less than 40% Cr_2O_3 and 40% to 46% Cr_2O_3 grades after 1990 result from declining bulk imports of those grades, so that these categories are represented by small volume-high price, specialty materials. The figure illustrates that high-unit-value chromite at the end of the time period shown was small in quantity.

The value of chromite was relatively stable through 1970, when it started to rise. Chromite value declined from 1982 to 1988, when steel production in general and stainless steel production in particular was weak. Stainless steel recovery from 1988 through 1990 resulted in a short supply of ferrochromium that nearly doubled the price of ferrochromium and stimulated an expansion of capacity in the industry, primarily in South Africa. The price of chromite also rose as a result. Chromite production capacity was added to meet an anticipated demand from increased ferrochromium production capacity, primarily in South Africa and India.

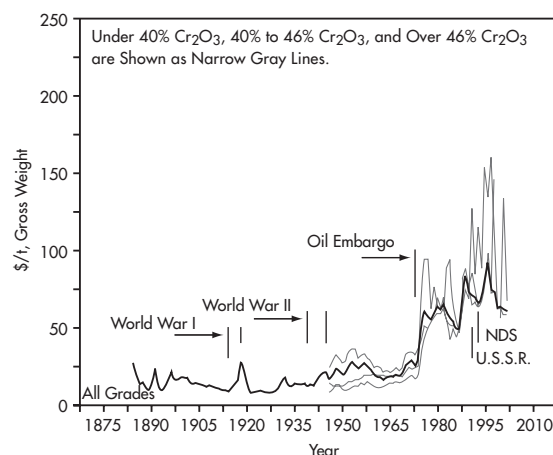
Availability

The U.S. Bureau of Mines studied the availability of chromium in 10 market economy countries (MECs) (Boyle, Shields, and Wagner 1993). The analyzed for the simultaneous availability of chromium contained in chromium ferroalloy products and in exportable



Source: USGS; U.S. Census Bureau; *Engineering and Mining Journal*; *Platts Metals Week*; *Ryan's Notes*; *Industrial Minerals*.

Figure 21. U.S. chromite value and price adjusted for inflation and normalized to 1998 dollars



Courtesy of USGS and U.S. Census Bureau.

Figure 22. U.S. value of chromite by grade (<40% Cr_2O_3 , 40% to 46% Cr_2O_3 , >46% Cr_2O_3 , and mass-weighted average over all grades) and by year. The narrow gray lines represent linearly interpolated values for <40% Cr_2O_3 and 40% to 46% Cr_2O_3 grades that replace values >\$200 per ton for 1999–2001. Although not graphed, these values were included in the average over all grades.

chromite products (metallurgical, chemical, refractory, and foundry sand).

In the same work, the author assessed about 874 Mt gross weight of in situ material containing about 203 Mt of chromium. Extraction and beneficiation of this material was estimated to result in about 475 Mt of chromite products, of which 289 Mt would be available for export and the remaining 186 Mt would be smelted in the countries in which it was mined to produce about 80 Mt of chromium ferroalloys. The chromium ferroalloys would then be available for use in the countries of production or for export. The 80 Mt of chromium ferroalloy included about 74 Mt of high-carbon ferrochromium, 4 Mt of low-carbon ferrochromium, and 2 Mt of ferrochromium-silicon.

Table 7. Availability of chromite and chromium ferroalloys from 10 market economy countries

Chromium Materials	Quantity Available, Mt gross wt	Cost,* \$/t		
		Weighted Range		
		Average	Low	High
Chromite				
Chemical grade	64.3	53	35	174
Foundry sand grade	16.4	49	39	83
Metallurgical grade				
Primary product	145.4	101	42	705
Secondary product	35.6	54	33	117
Subtotal	181.0	92	33	705
Refractory grade	26.8	87	54	180
Total	288.5			
Chromium ferroalloys				
Ferrochromium				
High-carbon ferrochromium	74.3	473	417	1,286
Low-carbon ferrochromium	3.9	937	635	1,309
Ferrochromium-silicon	2.0	737	578	814
Total	80.2			

* Price required for 0% discounted cash flow rate of return in January 1989 dollars per metric ton, gross weight, of product.

South Africa and Zimbabwe hosted about 80% of the contained chromium in situ. India and Finland accounted for an additional 11% of the contained chromium; another 8% of the contained chromium was divided evenly among Brazil, the Philippines, Turkey, and the United States; the remainder was in Greece and Madagascar.

Based on Cr₂O₃ content of in situ chromite ore, the 10 MECs fit into 2 groups. The high-grade group (ore grades ranging from 33.96% to 43.01% Cr₂O₃) included India, Madagascar, South Africa, Turkey, and Zimbabwe. The low-grade group (ore grades ranging from 9.16% to 26.65% Cr₂O₃) included Brazil, Finland, Greece, the Philippines, and the United States. The high-grade group averaged 38.76% Cr₂O₃ and the low-grade group averaged only 15.90% Cr₂O₃.

Table 7 shows the results of the Boyle, Shields, and Wagner (1993) analysis. Chromium material costs were calculated on a weighted average basis, f.o.b. ship at port of export. The chromite cost shown covers mining and beneficiation of the ore (including capital costs at the mine, operating costs, and taxes) and transportation of ore and products to port facilities. Chromium ferroalloy cost includes chromite, but excludes smelter capital cost. On a weight basis, the analysis shows that South Africa and Zimbabwe could produce the following at their respective estimated breakeven costs: about 78% of metallurgical chromite, 93% of chemical chromite, 85% of refractory chromite, and 93% of foundry chromite. South Africa and Zimbabwe also could produce the following at their respective estimated breakeven costs: about 69% of the high-carbon ferrochromium; 89% of the low-carbon ferrochromium; and 100% of ferrochromium-silicon. The product breakdown between chromium ferroalloy and chromite, and among the grades within those product categories, was based on mine and smelter production capacities and known operating relationships for 1987 through 1988.

GOVERNMENT CONSIDERATIONS

Strategic Factors, Stockpile

The U.S. government has maintained the NDS in the event of a national defense emergency since 1939. The DLA is currently

responsible for the NDS. The Strategic and Critical Materials Stock Piling Act (50 U.S.C., section 98 *et seq.*) mandates that a stockpile of strategic and critical materials be maintained to decrease and preclude, where possible, dependence on foreign sources of supply in times of national emergency. The NDS was intended to provide raw materials to industry while mine production capacity was being increased, thereby reducing the amount of time needed to mobilize the domestic economy. Chromium materials that were included in the NDS are chromite (metallurgical, chemical, and refractory grades), chromium ferroalloys (high- and low-carbon ferrochromium and ferrochromium-silicon), and chromium metal. The use of chromite foundry sand post-dated NDS legislation. Since the dissolution of the Soviet Union in 1991, the perceived threat has diminished. As a result, the DLA, by act of Congress, eliminated chromium materials in the NDS and the inventory has been for sale. Figure 23 shows historical NDS chromium material inventories. The last of the ferrochromium-silicon stocks were shipped in 2002 and the last of the metallurgical grade chromite stocks in 2003. The graphs show the National Defense Stockpile conversion program (1984 to 1994; during which chromite was converted to high-carbon ferrochromium and low-carbon ferrochromium was converted to chromium metal), dissolution of the Soviet Union (1991), and the NDS disposal enabling legislation (1993).

Inventories of ferrochromium-silicon were exhausted in 2002; metallurgical grade chromite, in 2003. Continued sales at current rates suggest that NDS inventories will be depleted as follows: chemical-grade chromite by 2006, refractory-grade chromite by 2006, high-carbon ferrochromium by 2011, low-carbon ferrochromium by 2015, and chromium metal by 2020.

Health Factors

Chromium is both an essential nutrient and a toxic substance depending on molecular form (called *speciation*) and exposure (mode, concentration, and duration). Chromium is chemically characterized by its valence state. Common valence states of chromium are chromium 0, chromium 3 (also denoted III, +3, or trivalent), and chromium 6 (also denoted VI, +6, or hexavalent). Chromium 0 is found in metals; chromium (III), in naturally occurring organic and inorganic compounds; and chromium (VI), in industrial chromium chemicals.

Chromium is an essential human nutrient in trace amounts. The National Research Council (NRC 1989) recommended a daily nutritional intake of 50 to 200 µg Cr. Chromium is a cofactor for insulin, a hormone involved in carbohydrate and fat metabolism. A cofactor is a molecule with which certain enzymes must combine in order to be functionally active.

Anderson (1997, 1999) studied the safety of chromium as a nutrient supplement by feeding chromium chloride and chromium picolinate to rats. Data demonstrated a lack of trivalent chromium toxicity at levels several thousand times above that which is estimated to be safe and adequate for daily dietary intake for humans. Animals consuming the picolinate-supplemented diets were found to contain concentrations of chromium several-fold higher in their livers and kidneys than those fed the chromium chloride.

Chromium is a micronutrient that improves the efficiency of insulin in individuals with impaired glucose tolerance. The Institute of Medicine (IOM) reported on the dietary reference intake (DRI) values for chromium based on the diets of healthy Americans and Canadians (IOM 2001). DRI values comprise recommended daily allowance (RDA), a adequate intake (AI), tolerable upper intake level (UL), and estimated average requirement. Life stage and gender affect DRI. IOM found that there were inadequate data to set an RDA; they set an AI, however, based on the

average unit chromium content of balanced diets and balanced diet intakes as reported by the Third National Health and Nutrition Examination Survey, 1988–1994. Data for chromium are not sufficient to develop a UL, suggesting the need for caution in consuming amounts greater than recommended in intakes. Chromium chemical speciation and the route of exposure are important factors in chromium toxicity. Inhaled, hexavalent chromium is carcinogenic. Chromium in food appears universally as trivalent chromium and is nontoxic (Institute of Medicine 2001).

The dietary chemical form of chromium is trivalent. Hexavalent chromium compounds generally are recognized as toxic and carcinogenic. Chronic occupational exposure to hexavalent chromium has been associated with an increased incidence of bronchial cancer. The toxic status of trivalent chromium compounds is not clear; trivalent chromium compounds are less toxic, however, than hexavalent chromium compounds. Chemical compounds containing chromium in lower valence states (i.e., divalent or less) generally are recognized as benign.

The U.S. Department of Health and Human Services (HHS) prepares toxicological profiles for health professionals. HHS reported toxicological and health effect information for chromium (Syracuse Research Corp. 2000).

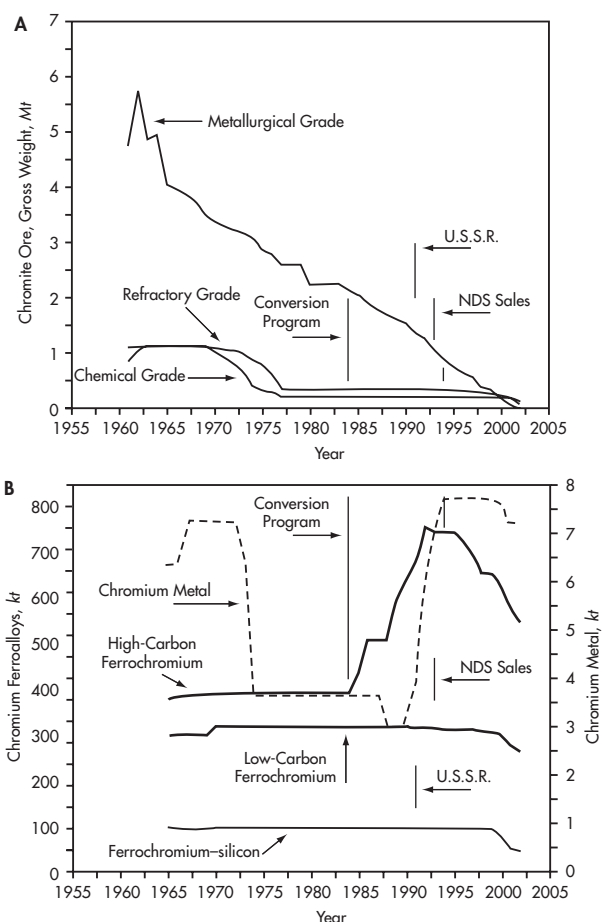
Cross and colleagues (1997) critically reviewed hexavalent chromium exposure limit data in preparation for European Union regulation of hexavalent chromium. They found that hexavalent chromium compounds were potent skin sensitizers in humans and that they caused respiratory sensitization. They reported that speciation is important and relate health effect with solubility in water. Some hexavalent chromium compounds were reported as carcinogenic based on workplace exposure. They found human health effects of hexavalent chromium compounds included carcinogenicity (lung cancer), sensitization, renal toxicity, and irritancy and corrosivity of the skin, respiratory tract, and gastrointestinal tract. They recommended consideration of a time-weighted-average exposure limit in the range of 25 to 10 $\mu\text{g}/\text{m}^3$ to protect the health of workers exposed to hexavalent chromium compounds. Guertin, Jacobs, and Avakian (2005) evaluated the chromium (VI) factors (including persistence in groundwater, taste-and-odor thresholds, health risks, transport and fate, current laboratory analytical methods and detection limits, and regulatory issues) related to water remediation and public policy.

The ICDA (2004a) published industry guidelines on health, safety, and the environment. Guidelines take account of extensive international changes and developments in legislation and regulation of chromium materials that are intended to help companies implement appropriate workplace practices and procedures for environmental protection (Gericke 1998).

Fairhurst and Minty (1998) reviewed the toxicity of chromium and inorganic chromium compounds; included were chromium compounds in valence states 0, +2, +3, +4, and +6. With the exception of chromyl chloride, a volatile liquid, they reported that these compounds were solid at room temperature and that they had a wide range of solubility in water. Solubility and valence state were found to play a role in the behavior of chromium in biological tissue.

Aw (2002) found that the effects of chromium compounds on human health depend on its chemical species. He reported that the health risk posed by hexavalent chromium compounds is established, whereas that of other classes of chromium compounds is uncertain.

Huvinen (2002) described occupational exposure to chromium and its long-term health effects in stainless steel production. Workers in chromite ore mining and ferrochromium and stainless steel production environments were studied. Observed health



Courtesy of Defense National Stockpile Center and USGS.

Figure 23. NDS year-end inventory of chromium-containing materials: (A) various grades of chromite and (B) chromium ferroalloys and metal

effects were minimal for production workers exposed to chromium. Huvinen concluded that it is technically and economically possible to achieve low exposure levels in the stainless steel production chain with no adverse health effects.

Aitio (2001) described the carcinogenic risk of chromic acid mist in electroplating, an area where information has recently been improved. He found insufficient information to quantify the risk; the available information, however, indicates a significant increase of lung cancer risk resulting from inhalation of chromic acid mist. He recommended a range of modifications in chromium plating processing to mitigate the risk to health.

Environmental Regulations

NIOSH (National Institute for Occupational Safety and Health, a part of the U.S. Department of Health and Human Services, Centers for Disease Control and Prevention) is responsible for recommending occupational health and safety standards. OSHA (Occupational Safety and Health Administration, a part of the U.S. Department of Labor) is responsible for promulgation and enforcement of health and safety standards in the workplace.

Environmental concerns have resulted in a wide variety of studies to determine the following about chromium: natural background levels, sources of environmental emissions, movement in the

environment, interaction with plants and animals, effects on plants and animals, measurement methods, and recovery technology. Merian (1991) gave a broad review of many environmental factors and the role of chromium, among other metals, in the environment.

The EPA extended Toxic Release Inventory reporting requirements to seven industry groups that included metal mining, coal mining, electric utilities, and commercial hazardous waste treatment facilities under authority of the Emergency Planning and Community Right-to-Know Act of 1986. These industries started reporting in calendar year 1998 (EPA 1997).

Effluents

Chromium in water effluents must be managed. Solubility of trivalent chromium compounds in neutral pH water usually results in a chromium concentration of <0.1 ppm as required for drinking water. Thus, when water is pH neutralized, filtration can remove chromium. If hexavalent chromium compounds are present, chromium must first be reduced to its trivalent state.

The EPA announced proposed national effluent limitation guidelines and pretreatment standards for wastewater discharges from stand-alone landfills. The EPA maximum recommended concentration of trivalent chromium compounds in freshwater is 570 mg/L, and a continuous concentration of 74 mg/L. The EPA maximum recommended concentration of hexavalent chromium compounds in freshwater is 16 µg/L, and a continuous concentration of 11 mg/L (EPA 1998a, 1998c). The EPA also required community water systems to prepare annual water-quality reports and to provide them to their customers. Reports must contain information about chromium, a regulated contaminant (EPA 1998b).

Emissions

The U.S. Congress enacted the Clean Air Act Amendments of 1990 (Public Law 101-549), completely revising the Air Toxics Program. Congress identified 189 hazardous air pollutants to regulate. Chromium compounds—defined as any chemical substances that contain chromium as part of their structure—were included among those hazardous air pollutants. Under the revised Air Toxics Program, Congress instructed the EPA to regulate hazardous air pollutants by regulating the source of those pollutants. Congress required the EPA to identify pollution sources by November 1991, then to set emission standards for those sources. The EPA eliminated the use of chromium chemicals in comfort cooling towers, one source of chromium emissions. The agency also banned the use of chromium chemicals for corrosion inhibition in industrial process water cooling towers in 1994. It was reported that 90% of industrial cooling tower operators had eliminated the use of chromium chemicals in anticipation of such an EPA ban; the remaining 800 operations were given 18 months within which to comply with the new ruling (EPA 1994).

The EPA, as required under Section 112(c) of the Clean Air Act identified major sources and areas of sources of hazardous air pollutants. The EPA identified chromium electroplaters and anodizers as an area source of hazardous air pollutants that warrant regulation under Section 112 of the Clean Air Act and described the adverse impact of that source. The chromium electroplating industry includes hard chromium platers (usually a thick chromium coating on steel for wear resistance in hydraulic cylinders, zinc diecastings, plastic molds, and marine hardware); decorative chromium platers (usually over a nickel layer on aluminum, brass, plastic, or steel for wear and tarnish resistance for auto trim, tools, bicycles, and plumbing fixtures); and surface-treatment electroplaters or anodizers (usually a chromic acid process to produce a corrosion-resistant oxide surface on aluminum used for aircraft parts and

architectural structures subject to high stress and corrosive conditions). The EPA estimated that 1,540 hard chromium electroplaters, 2,800 decorative electroplaters, and 680 chromic acid anodizers nationwide were affected. They further estimated that electroplaters collectively emit 175 t of chromium per year, most of which is hexavalent and thus carcinogenic in humans. According to the EPA, the resulting U.S. nationwide population risk was an additional 110 cases of cancer per year from chromium electroplating emissions. The resulting individual risk in the proximity of particular facilities ranged from less than 2 chances per 100,000 for small chromic acid anodizing operations to 5 chances per 1,000 for large hard plating operations. OSHA currently promulgates regulations affecting worker exposure at chromium electroplater and chromic acid anodizer operations (EPA 1992).

Solid Waste

The EPA regulates solid waste generated by the chemical industry in the production of sodium chromate and dichromate. Chromium-containing treated residues from roasting or leaching of chrome ore are regulated under Subtitle D of the Resource Conservation and Recovery Act (RCRA). The EPA found no significant danger associated with treated residue from roasting or leaching of chrome ore based on waste characteristics, management practices, and damage case investigations.

The EPA determined that chromium-containing wastes are toxic and established that if a representative waste sample contains chromium concentrations of 5.0 mg/L (total chromium), the waste is hazardous. They also promulgated treatment standards for chromium-containing refractory brick wastes based on chemical stabilization, a process that keeps a compound, mixture, or solution from changing its form or chemical nature. In addition, the EPA determined that some chromium-containing refractory brick wastes can be recycled as feedstock in the manufacture of refractory bricks or metal alloys, and recognized that there is insufficient capacity to process inorganic solid debris (i.e., treatable material >9.5 mm in size that requires cutting or mechanical crushing and grinding) prior to chemical stabilization. As a result, chromite-containing refractory bricks were granted a 2-year capacity variance (i.e., a variance until May 1992) (EPA 1990).

The EPA regulated solid waste disposal of wood treatment waste by setting treatment standards and excluded printed circuit boards and scrap metal from RCRA regulation (EPA 1997).

The EPA proposed to exempt chromite ore mined in the Transvaal Region of South Africa and the unreacted ore component of the chromite-processing residue from this region from reporting requirements under Section 313 of the Emergency Planning and Community Right-to-Know Act of 1986 (EPCRA) (EPA 1999). EPA criteria to add or delete are in Section 313(d) of EPCRA. To be added, a chemical must meet one of the criteria; to be deleted, a chemical must be shown to meet none of the criteria. Petition to delete a chromium chemical was denied on two previous occasions—a 1990 petition to delist chromium antimony titanium buff rutilite and a 1991 petition to delist chromium (III) oxide. In 2001, the EPA granted the request to delete both chromite ore mined in the Transvaal Region of South Africa and the unreacted ore component of chromite processing residue from reporting requirements under Section 313 of EPCRA (EPA 2001).

Safety Regulations

The U.S. Department of Labor regulates chromium in the workplace under OSHA, which reviewed health, risk, and feasibility evidence for chromium metal, chromic acid and chromates, and chromyl chloride. Table 8 summarizes OSHA permissible exposure limits

(PELs). OSHA announced plans to go forward with proposed rule-making on occupational exposure to hexavalent chromium based on a request in 1993 by the Oil, Chemical and Atomic Workers Union and Public Citizen Health Research Group petition to lower the exposure limit (U.S. Department of Labor 2002). The current OSHA PEL for chromic acid and chromates is reported in Table 8 (29 CFR 1910.1000). This table specifies a ceiling limit of $100 \mu\text{g}/\text{m}^3$ of air for all forms of hexavalent chromium, measured as chromium (VI) and reported as CrO_3 . The entry has been unchanged since published in 1971. The OSHA interpretation is that the PEL for chromium (VI) in industry is a ceiling value of $100 \mu\text{g}/\text{m}^3$ of air, measured as chromium (VI) and reported as CrO_3 , as promulgated; in the construction industry, however, the PEL is measured in micrograms per cubic meter as an 8-hr, time-weighted average.

The Health Council of the Netherlands recommended changes to the Netherlands' exposure limits to chromium compounds (see Table 8) based on the health effects of occupational exposure to inhalable toxic substances in the air. For water insoluble chromium (III) compounds, chromium (II) compounds, and chromium metal dusts, they made no recommendation. For water-soluble chromium (III) compounds, they recommended changing the exposure limit from 0.5 to $0.06 \text{ mg}/\text{m}^3$, 8-hr time-weighted average. For chromium (VI) compounds, they recommended an exposure limit of $0.05 \text{ mg}/\text{m}^3$, 8-hr time-weighted average. As part of their review, the council reported occupational exposure limits from Germany, Sweden, and the United Kingdom.

The California Office of Environmental Health Assessment (1994) reported noncancer chronic reference exposure levels to hexavalent chromium. It reported an inhalation reference exposure level of $0.002 \mu\text{g}/\text{m}^3$ for chromic acid and $0.2 \mu\text{g}/\text{m}^3$ for other soluble hexavalent chromium compounds. The same assessment found an oral reference exposure level of $0.02 \text{ mg}/\text{kg}/\text{day}$ for other soluble hexavalent chromium compounds.

FUTURE TRENDS

World chromite production has been rising since 1900, when chemical and refractory use dominated world chromite use. Although the chemical and refractory industries continue to account for a portion of chromite consumption, the metallurgical industry is the dominant user today. The major use for chromite is the manufacture of ferrochromium, which is used as the source of chromium in steel-making. Stainless steel manufacture accounts for most ferrochromium use. Since the discovery and development of stainless steel in the early 1900s, world stainless-steel production has grown both in magnitude and in its share of world steel production. The processes applied to chromite (electric-arc furnace smelting in the metallurgical industry and kiln roasting in the chemical industry) are basically unchanged; many improvements have been made, however, to these processes, increasing productivity, production efficiency, and chromium recovery while reducing costs and emissions. The dissolution of the Soviet Union in 1991 brought previously isolated chromium industries into the global economic system. The effects of that change are still occurring.

Chromite, chromium chemical and metal, ferrochromium, stainless steel, and chromite refractory producers make up the world chromium industry. As ferrochromium production capacity was rationalized in historically producing countries (which traditionally have been stainless steel-producing countries), new furnaces or plants were constructed in chromite ore-producing areas.

Chromite ore production is moving from independent producers to vertically integrated producers; chromite ore mines now tend to be owned and operated by ferrochromium or chromium chemical producers. Associated with this trend is the movement of ferrochromium production capacity from stainless steel-producing countries to chromite-ore-producing countries.

Table 8. PELs for chromium compounds

Material	PEL
United States	
Chromic acid and chromates	$0.1 \text{ mg CrO}_3/\text{m}^3$, ceiling
Chromium metal and insoluble salts	$1.0 \text{ mg Cr}/\text{m}^3$, 8-hr time-weighted average
Soluble chromic and chromous salts	$0.5 \text{ mg Cr}/\text{m}^3$, 8-hr time-weighted average
The Netherlands	
Chromium metal dust	$0.5 \text{ mg}/\text{m}^3$, 8-hr time-weighted average
Soluble chromium (VI) compounds	$0.5 \text{ mg}/\text{m}^3$, 8-hr time-weighted average
	$0.1 \text{ mg}/\text{m}^3$, 15-min time-weighted average
Calcium-, strontium-, and zinc chromate	$0.01 \text{ mg}/\text{m}^3$, 15-min time-weighted average
Lead and barium chromate	$0.025 \text{ mg}/\text{m}^3$, 15-min time-weighted average
Combined chromium exposure	$0.01 \text{ mg}/\text{m}^3$, 15-min time-weighted average

Courtesy of U.S. Occupational Safety and Health Administration; Health Council of the Netherlands.

mium production capacity from stainless steel-producing countries to chromite-ore-producing countries.

Both electrical power capacity and production capacity of submerged-arc electric furnaces used in the production of ferrochromium have been increasing, whereas the unit consumption of electrical power and emissions has been declining. Retrofitting at major producer plants has improved production processes such as agglomeration of chromite ore to prevent it from blowing out of the furnace during smelting; preheating of furnace feedstock to reduce electrical energy consumption; and closed furnace technology to reduce emissions. These improvements also are being incorporated into newly constructed plants. The first industrial ferrochromium furnaces were rated in low kilovolt-amperes, whereas furnaces built recently have electrical capacities in the tens of megavolt-amperes. The capacities of ferrochromium plants, as well as the chromite mines that supply them, has been increasing. In effect, chromite is becoming more like a bulk commodity. As chromite and ferrochromium production has grown, so too have investments and sales, while production has been concentrated in only a few companies. Although the amount of production has increased, the number of producers has decreased. As the industry grows, mines and plants get larger and the capital cost barrier to market entry rises. As a result, new entrants into the market tend to be absorbed by established producers.

The introduction of post-melting refining in the steel industry after 1960 shifted ferrochromium production from low-carbon to high-carbon grades. Years of ferrochromium production have resulted in large slag stockpiles. Processes that recover ferrochromium from slag have recently improved in recovery efficiency. These processes have been or are being installed now at plant sites. In South Africa, the leading chromite- and ferrochromium-producing country, two trends are emerging: ferrochromium plants are being developed in the western belt of the Bushveld Complex and ferrochromium production processes have begun to use chromite by-product from platinum operations.

In the United States, chromite use has declined dramatically; the demand for chromium, however, is well established and is increasing, especially for chromium ferroalloys and metal imported for metallurgical use, mostly to make stainless steel. Chromite use

in producing chromium ferroalloys and for refractories has ended and chemical industry demand has decreased substantially. U.S. industry has replaced domestic chromium ferroalloys and refractory materials with imports, and demand for chromium chemicals has declined.

In the United States, several trends are developing simultaneously in chromium industries. Ferrochromium production from chromite declined to zero in the United States in 1998. Chromite use for chemical production grew slowly, with industry eliminating excess, uneconomic capacity, and concentrating production and growth in surviving plants until 2002, when production dropped dramatically. This left one chromite-consuming chemical plant in the United States. Chromite use for shaped and unshaped refractory materials declined to zero in 2003; foundry use, however, has been growing slowly.

Environmental regulations are affecting chromite consumption, primarily in the chemical and refractory industries. Regulations limiting worker exposure and limiting chromium in emissions, effluents, and solid wastes continue to increase operating costs and, for new operations, capital costs.

Chromium-related businesses are international in nature. Chromium-containing materials are mined and processed in various countries, but chromium-containing industrial and consumer products also are distributed and used throughout the world. Diverse regulations on product manufacturing, labeling, and shipping are concerns for the chromium industry. It will be affected most by the regulatory requirements of its most important markets. Similarly, health and safety regulations adopted by countries where chromium-containing materials are processed and used will continue to affect the industry.

Economic growth in China resulted in chromium industry growth. Industrial growth in China required the construction of infrastructure and industrial plants and equipment, processes that are steel intensive. China mines little chromite ore; however, it manufactures ferrochromium from imported chromite. Since 2003, China expanded its stainless steel industry by constructing modern, large-capacity stainless steel production plants, turning itself into a major chromite ore and ferrochromium consumer. Continued growth in China and a similar economic transition in India were anticipated; however, the duration of growth in China and the economic path that India will follow remain unclear.

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An Overview

Colin C. Harvey and Haydn H. Murray

INTRODUCTION

The term *clay* is somewhat ambiguous unless specifically defined, because it is used in three ways:

- As a diverse group of fine-grained minerals
- As a rock term
- As a particle size term

As a rock term, clay is difficult to define because of the wide variety of materials that comprise it; therefore, the definition must be general. Grim (1962) defined clay as a fine-grained, natural, earthy, argillaceous material. The particle size of clays is very fine and is generally considered to be about 2 μm or less by most clay scientists. These minerals are hydrous silicates composed mainly of silica, alumina, and water. Several of these minerals also contain appreciable quantities of magnesium, iron, alkalis, and alkaline earths. Many definitions state that a clay is plastic when wet. Most clay materials do have this property, but some clays are not plastic, such as halloysite and flint clay.

As a particle size term, clay is used for the category that includes the smallest particles. The maximum size particles in the clay size grade are defined differently on various grade scales. Soil investigators and mineralogists generally use 2 μm as the maximum size, whereas the widely used scale by engineers (Wentworth 1922) defines clay as material finer than approximately 4 μm .

Some authorities find it convenient to use the term clay for any fine-grained, natural, earthy, argillaceous material (Grim 1968). When used in this way, the term includes clay, shale, argillite, and some fine soils.

Even though no standard definition of the term clay is accepted by geologists, agronomists, engineers, and others, the term is generally well understood by those who use it. Clay is an abundant natural raw material, and it has an amazing variety of uses and properties, which are discussed in the following chapters.

Clay Types and the Clay Chapters

The following seven chapters, written by experts on clay mineralogy, categorize the clay minerals on the basis of their composition:

- Ball clays
- Bentonite
- Common clays and shale
- Fuller's earth
- Kaolin

- Palygorskite and sepiolite (hormites)
- Refractory clays

There is some overlap between fuller's earth, bentonite, and hormites because they all have similar properties for some applications. Therefore, both the bentonite and palygorskite-sepiolite chapters discuss fuller's earth. *Fuller's earth* is a term based on use, and both bentonites and hormites may be sold as fuller's earth. The overlap is particularly evident where both bentonite and nonbentonite fuller's earth are used for the same purposes or products, such as in drilling mud, for bleaching or clarifying fats and oils, and as carriers for insecticides and fertilizers. Kaolin, ball clay, halloysite, and refractory clays are sometimes grouped together because they consist mainly of minerals of the kaolin group. Common clays have no unique mineral composition and may be composed of any mixture of the clay types and other fine-grained materials, including shale, sometimes referred to as miscellaneous clay.

WORLD PRODUCTION STATISTICS

Unfortunately no comprehensive world production statistics are available for the clay minerals. The U.S. Geological Survey (USGS; Virta 2003) publishes an annual review of statistical data but, unfortunately, numerous countries, including India and China, are not always included. Virta (personal communication) estimates that the recorded world production figure for kaolin reported by individual countries may also include the actual mined tonnage figures and does not take into account the losses incurred during processing. Although Virta (2003) quotes a world tonnage of 43 Mtpy of kaolin, he believes that the tonnage actually sold (raw plus processed) is closer to 26 Mtpy. His statistics, however, do not include China, India, and many former eastern bloc countries. Besides this estimate of world production of about 26 Mtpy of kaolin, other clay types include 10.3 Mtpy bentonite, 3.9 Mtpy of fuller's earth, and 13 Mtpy of ball clay, whereas hormite (palygorskite-sepiolite) production is estimated to be about 3 Mtpy.

The amount of common clays used worldwide is difficult to estimate since there are no comprehensive statistics. It is likely, however, to exceed many hundreds of million metric tons/year. Statistics for refractory clays also are not well documented. Their world production, however, exceeds 10 Mtpy and may indeed exceed 20 Mtpy. There are also a few unique deposits of high-purity clays such as halloysite (used in high-quality porcelain and catalysis) and hectorite (used in cosmetics and pharmaceuticals).

Table 1. World production estimates

Clay Type	2002 World Production, Mt	Reference
Common	Hundreds	Estimate only
Refractory	Possibly more than 20	Estimate only
Kaolin	43 mined 26 sold	Virta 2003
Bentonite	10.3 V	irta 2003
Fuller's earth	Uncertain—possibly 10	
Ball	15.5	Chapter on Ball Clays in this volume
Hormites	2.1	Chapter on Palygorskite and Sepiolite in this volume

Table 2. Uses of clay minerals as inert components

Clay Family	Industry	Use
Kaolin	Paper, plastics, rubber	Filler
	Pesticides	Carrier, diluent
Vermiculite	Building	Heat insulation, sound dissipation
	Packaging	Shock-proof materials, thermal protection, liquid absorption
Mica	Foundries	Thermal protection
	Electrical	Insulation
	Paints	UV-, heat-stable and underwater paints
	Cosmetics	Nacreous pigments
	Coatings	Corrosion proofing, polymer coatings, underseal
Talcum, pyrophyllite	Plastics, rubber, paper	Filler
	Cosmetics, pharmaceuticals	Powders, pastes, ointments, lotions
	Refractories	Refractories
Palygorskite, sepiolite	Pesticides	Carrier for insecticides and herbicides
	Chemicals	Catalyst carrier, filter material, anticaking agent
	Cosmetics, plastics	Filler

that have unique properties leading to their classification as high-quality additives rather than bulk industrial minerals.

In addition, some nonclay minerals—finely ground to have similar properties to some industrial clays—are also frequently included in industrial clay surveys. These minerals include vermiculite, mica, talc, and pyrophyllite. The individual chapters present production statistics of the individual clays. Table 1 summarizes the estimated overall world production of clay minerals by both USGS sources and others.

CLAY USAGE

Clays and clay minerals are very important industrial minerals. They are used in many process industries, in agricultural applications, in engineering and construction, in environmental remediation, and in many other diverse applications (Grim 1962; Grim 1968; van Olphen 1977; Patterson and Murray 1983; Jepson 1984; Odom 1984; Murray 1986, 1999, 2000, 2003; Darley and Gray, 1991; Bundy 1993; Galan 1996; Harvey and Murray 1997; Ravichandran and Sivasankar 1997; and Philippakopoulou, Simonetis, and Economides 2003).

Table 3. Uses of clay minerals based on their rheological properties

Clay Family	Industry	Uses
Common clays	Ceramics	Tiles, bricks, earthenware, stoneware, sewer pipes, sanitary ware, refractory bricks
Kaolins	Paper	Coating
	Ceramics	Porcelain, bone china, vitreous sanitary ware, earthenware
Bentonites	See Table 4	
Palygorskite, sepiolite	Paints, chemicals, and mineral oils	Thickening and thixotropic additive, dispersing and antisetling agent, drilling fluids

Clay usage falls into two broad classes:

- Clays are used because their inertness and stability provide specific properties (such as unique rheology) to an industrial use. This leads to large variety of industrial applications.
- Clays are used because of their reactivity, which promotes or catalyzes specific reactions.

Tables 2, 3, 4, and 5 give a brief summary of uses; the individual chapters give a more detailed breakdown.

CLAY MINERAL STRUCTURES

All the clay minerals are basically hydrated aluminum silicates. There are, however, significant structural and chemical differences, which may include substitution of many cations that affect the neutrality or stability of the clay mineral. For example, iron or magnesium may substitute for aluminum; aluminum may substitute for silicon; and in some clay minerals, alkalis and alkaline earth elements are present as essential constituents. The structure of all the clay minerals consists of sheets of silicon tetrahedra and aluminum octahedra arranged in differing patterns for each individual clay mineral.

The physical properties of a particular clay mineral depend on the structure and composition (Murray 2000). Because of their extremely fine particle size, clay minerals were very difficult to identify until the advent of x-ray diffraction in the 1920s. Today, sophisticated analytical equipment is available to fully identify and characterize the clay minerals. The more important analytical methods that are used include x-ray diffraction, x-ray fluorescence, electron microscopy, infrared spectroscopy, and differential thermal analysis.

PHYSICAL AND CHEMICAL PROPERTIES

The important physical and chemical characteristics that relate to the applications of clay minerals are particle size, shape, and distribution; surface chemistry, area, and charge; pH; high and low shear viscosity; filter cake permeability; color and brightness; opacity; plasticity; green, dry, and fired strength; absorption and adsorption; fired color; electrical and heat conductivity; abrasion; cation and anion exchange capacity; refractoriness; dispersability; and thixotropy. The clay chapters each delineate and discuss these and other special properties. In most industrial applications, the clay materials are functional rather than just inert components in the system in which they are used. The common clays are the largest to manage usage in numerous engineering applications, including road construction, fill, and dam construction, and in waste containment. The mineralogy and particle size distribution in the common clays determine their engineering properties. They contain mixtures of different clay minerals such as illite/smectite minerals, kaolinites,

Table 4. Uses of bentonites based on their rheological properties

Industry	Uses	Activation*
Agriculture, horticulture	Soil improvement	r, s
Building	Supporting dispersions for cut-off diaphragm wall construction, shield tunneling, subsoil sealing, antifriction agents for pipejacking and shaft sinking	r, s
	Additions to concrete and mortar	r, s
Ceramics	Plasticizing of organic masses, improvement of strength, fluxing agents	r, a
Foundries	Binding agents for molding and core sands	r, s
	Binding agents for anhydrous casting sands	o
	Thickening of blackwashes	o
Mineral oil	Drilling fluids	r, a, o
	Thickening of greases	o
Paints, varnishes	Thickening, thixotrope, stabilizing, antisetling agents	s, o
	Coating materials, sealing cement, additives for waxes and adhesives	s, o
Cosmetics, pharmaceuticals	Bases of creams, ointments, and cosmetics	r, a, s
	Stabilization of emulsions	r, o
Tar exploitation	Emulsification and thixotrope of tar-water emulsions	a, o
	Tar and asphalt coatings, additives for bitumen	

* Bentonites are used as raw materials or in activated form: r = raw bentonite, a = acid-activated bentonite, s = soda-activated bentonite, o = organo-bentonite.

smectites, micas, and accessory minerals. A second class is termed *industrial kaolins*, which are recognized by their relatively high contents of kaolinite (kaolins) or sometimes a small proportion of high-quality kaolin minerals. Ball clays have very fine particle size and are composed predominantly of kaolin. A fourth class is clay that has a high montmorillonite (smectite) content (bentonites). A fifth class is the palygorskite and sepiolite clays (hormites), which have many similarities to bentonites and are used specifically for their surface properties and reactivity.

CLAY MINERAL SOCIETIES AND PUBLICATIONS

Several scientific societies and groups are devoted to the science and applications of clays. The major societies and groups that are currently active in clay science are as follows:

- The Clay Minerals Society in the United States
- The European Clay Group, which includes most of the European countries
- The Clay Science Society of Japan
- The Association Internationale pour l'Etude des Argiles (AIPEA)

Many of the individual clay groups in European countries hold meetings periodically. The Clay Minerals Society hosts an annual conference in the United States and publishes the journal *Clays and Clay Minerals*, plus special publications and workshop proceedings. The European Clay Group holds a Euroclay Conference every 2 years and publishes the journal *Clay Minerals*. The Clay Science Society of Japan sponsors an annual conference and publishes the journal *Clay Science*. AIPEA sponsors the International Clay Conference every 4 years and publishes the proceedings. The journal *Applied Clay Science* is published by Elsevier. Other organizations

Table 5. Uses of clay minerals based on their adsorption properties and reactivity

Clay Family	Industry	Uses
Kaolin	Fiberglass	Source of alumina
	Petrochemicals	Catalyst support
	Chemicals	Zeolite synthesis
Bentonite	Building	Additive in cement
	Agriculture, horticulture	Soil improvement, composting
		Adsorption of mycotoxins
	Chemicals	Sulfur production: refining, decoloration, bitumen extraction
		Catalysts
		Carriers for pesticides
		Dehydrating agents
		Adsorbents for radioactive materials
	Cleaning	Regeneration of organic fluids for dry cleaning
		Polishes and dressings
Palygorskite, sepiolite	Environmental technology	Additives for washing and cleaning agents and soap production
		Forest and water conservation: fire extinguishing powders, binding agents for oil on water
		Animal husbandry, manure treatment, cat litter
		Water and wastewater purification
		Sewage sludge pelletizing
	Food	Barriers
		Refining, decoloration, and stabilization of vegetable and animal oils and fats
		Fining of wine, must, and juices, beer stabilization, purification of saccharine juice and syrup
		Refining, decoloration, purification, and stabilization of mineral oils, fats, waxes, and paraffins
		Pigment and color developer for carbonless copying paper
Palygorskite, sepiolite	Cosmetics, pharmaceuticals	Adsorption of impurities in circulation water
		De-inking in wastepaper recycling
		Powders, tablets, drug carrier, odor control, liquid absorption
		Adsorbent, carrier, bleaching, decoloration, anticaking agent
		Cigarette filters (sepiolite), cat litter

and publications that feature articles on clays are the American Ceramic Society (annual meetings and monthly bulletin); SME (annual meetings, preprints, *Mining Engineering* magazine, books, and transactions); and *Industrial Minerals* magazine.

The scientific and technological publications pertaining to clays are too numerous to cover in this chapter. Therefore, the rest of this chapter summarizes the subject matter and, where possible, indicates by bibliographic reference where more detailed information is available. For example, Bicker (1970) is a bulletin containing only summary information on the economic geology of bentonite in Mississippi, but it contains references to virtually all published reports on bentonite in that state.

Major textbooks and reference volumes on various aspects of clay mineralogy and the industrial uses for clay published in the last 5 decades include Mackenzie (1957), Grim (1962, 1968), Zvyagin (1967), Beutelspacher and Van Der Mar el (1968), Gillott (1968), Clews (1969), Malkovský and Vachti (1969a, 1969b, 1969c), Carroll (1970), Gard (1971), Weaver and Beck (1971), Grimshaw (1972), Weaver and Pollard (1973), van Olphen (1977), Theng (1979), Brindley and Brown (1980), Velde (1985), Robertson (1986), Newman (1987), Bailey (1988), Chamley (1989), Murray, Bundy, and Harvey (1993), Moore and Reynolds (1997), Pinnavaia and Beall (2000), Worden and Morad (2003), and Kloppe (2005). Many other excellent books on clays could be mentioned. Various provincial, state, and federal geological surveys, mining bureaus, and other international agencies have also published much information on the geology, technology, and uses of clay.

Within the United States several industrial groups with similar industrial processes and markets have formed institutes or associations to share information, standardize specifications and test procedures, and lobby government or trade organizations for support. They include the following:

- The Sorptive Minerals Institute, formed mainly to represent the producers of absorbent granules and other fuller's earth products
- The Bentonite Producers Association, organized to represent the interests of the producers of bentonite
- The U.S. Clay Producers Traffic Association, incorporated in 1953 in New Jersey
- The China Clay Producers Association

In addition to these organizations dealing specifically with clays, the clay industry and other mining industries formed mining associations in many states, including Georgia and Texas in 1972, to protect their interests against restrictive state and federal legislation.

OCCURRENCE OF CLAY MINERALS

Clay resources may be formed from weathering processes, diagenesis, metamorphism, or hydrothermal processes. The nature of the formation process significantly affects the crystallinity and purity of the clay and its associated minerals. Resources that are still in situ after the formation processes are termed *primary clay resources* whereas, if subsequent erosion, sorting, and sedimentation occur, thereby concentrating the finer clay minerals, the resources are termed *secondary clay resources*. The origin of all clay types is discussed under the individual clay chapters. Pure clays do not usually occur in nature.

TECHNOLOGIES FOR CLAY PROCESSING

The processing technologies for clays are diverse. Many clays are used as mined, some are dry processed using air classification, whereas others are wet processed, chemically modified, or processed using a variety of complex processing steps. The individual clay chapters discuss these processes.

CATEGORIZATION OF CLAY RESOURCES

With the continued world population growth and movement toward urbanization and industrialization, there is an ongoing and growing need throughout the world to develop resources of industrial clays. During the early to middle part of the 20th century, developments in the industrialized world typically began on a small scale from a low technology base. The initial market focus was on construction materials or relatively low-quality ceramic products. With increas-

ing levels of industrialization, the level of technology and product sophistication increased, with the ultimate objective of achieving high product quality.

Over the past 20 years, the developed world has experienced the following:

- The exhaustion of many natural resources
- Mature low-growth markets
- Increasing environmental constraints
- Higher labor costs
- A general movement against mining in many countries

This has encouraged interest and investment in resources in developing nations. In addition, growth in the gross domestic product (GDP) of many developing nations has provided investment capital for the development of their indigenous clay mineral resources.

On the basis of many industrial clay mineral studies in both developed and developing countries, it has been found that categorizing industrial clays into one of four categories is a useful precursor to undertaking technical and economic evaluations of potential resources. Such categorization also benefits the explorer or developer because it:

- Assists in identifying the most suitable development strategy
- Provides a general estimate of the time required to move from greenfield development to production
- Enables a work program to be broadly defined
- Permits provisional project cost estimates to be made

Categories of Industrial Clays

Clay resources fall in to four categories (Harvey and Murray 1997):

- Category 1 clays are high-quality, high-technology clays requiring major investment for large tonnage production to supply both local and international markets.
- Category 2 clays are unique specialty clays requiring advanced technologies for small tonnage niche markets, locally and internationally.
- Category 3 clays include low-technology, moderate-quality clays that mainly supply local markets.
- Category 4 clays are of variable quality.

Category 4 low-quality clays may justify little or no processing but be suitable for large tonnage local markets. Some Category 4 clays may be of moderate to high quality but for one or more reasons are considered noneconomic. These reasons may include:

- Isolation from markets
- Politically or economically unstable locations
- Unfavorable legislative environment

Examples of Different Categories

Category 1

Three regions (kaolin provinces) currently produce Category 1 kaolin clays:

- The sedimentary kaolins of southeastern Georgia in the United States
- The hydrothermal kaolins of Cornwall in the United Kingdom
- The sedimentary kaolins of the Amazon Basin in Brazil

The limited number of kaolin resources identified in this category confirms the rarity of Category 1 clays currently known worldwide. They are discussed in detail in the Kaolin chapter.

Category 2

There are also very few resources that might be classified as Category 2. These are relatively rare, unique resources of somewhat unusual, but valuable industrial clay minerals. Such deposits are typically of high purity and are found in somewhat unique geological settings. Examples include the halloysite deposits of New Zealand, which are unusually pure deposits of halloysite formed by low-temperature hydrothermal alteration of volcanic ash (Harvey and Murray 1993, Harvey 1996). Halloysite is wet processed and supplied to a unique niche market in high-quality ceramics.

A second example is hectorite, a lithium smectite that also is the product of hydrothermal alteration. In this case, basaltic ash with elevated concentrations of magnesium and lithium was subjected to hydrothermal alteration, forming this lithium smectite (bentonite). It is wet or dry processed and used in a wide variety of industries (coatings, greases, adhesives, and paints) because of its high viscosity, high gel strength, and good temperature stability.

A third example is white bentonite, which is very rare in nature and commands high prices in colloidal applications, detergents, pharmaceuticals, and ceramics. For some specialty markets, these bentonites are wet processed or surface modified to achieve the high quality required for such applications.

Category 3

Category 3 resources are numerous and widespread. Their specifications are typically not rigid, which means that the level of processing is typically only moderate because the market quality requirements and pricing cannot justify high processing costs. All of the known Category 1 resources around the world also contain large tonnages of these clays, which are too impure to meet Category 1 requirements. Examples of large exploited resources of Category 3 clays associated with Category 1 clays are the filler kaolins of Georgia (United States) and of Cornwall (United Kingdom). Other Category 3 resources contain few if any Category 1 component. These include the kaolin resources of Central Europe in the Czech Republic, Ukraine, and Germany; the filler grade kaolins of Indonesia; and the bentonite resources of Wyoming and the southeastern United States.

An example of a Category 3 clay is the Belitung kaolins of Indonesia. During the 1960s and early 1970s these primary kaolins were mined as an adjunct to the associated, highly profitable, tin mining operations. With the radical drop in tin prices during the 1970s and 1980s, more emphasis was placed on the kaolin operations. These clays are currently exploited to supply large ceramic and filler clay markets within Indonesia and they are also exported to Asian countries, including Taiwan, Japan, and South Korea.

Category 4

Category 4 clays exist in all countries of the world and are typically used as mined.

Role of Categorization in Assessing Industrial Clay Resources

In any assessment of an industrial clay resource the explorer or developer has to go through the various stages of resource assessment, raw material testing, and assessment of product quality, market size, and market demand. All these data must then be integrated into a feasibility study that will recommend whether the project should proceed or be abandoned. An early classification of materials into one or more of the four categories can be a useful precursor to establishing development strategies and likely project costs. Such categorization can provide a useful insight into the complexities of such studies because these different categories have different requirements for the work program needed and the time frame to reach the feasibility study.

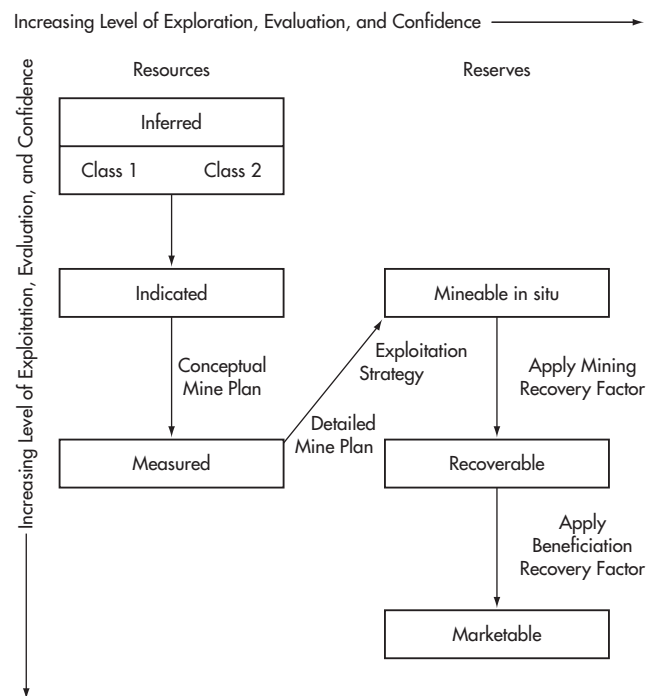


Figure 1. Flow chart showing levels of confidence and assessment of mineral resources and reserves

Relationship between Category and Annual Tonnage

In any mineral processing operation, the term *benefits of scale* is used to indicate that significant economic advantages can be obtained by having larger production volumes and by shipping in larger vessels. Larger tonnage operations operate with fewer labor hours per ton whereas capital costs for larger machines are less than the multiples of their relative production capacities. To compete on world markets, Category 1 producers must consider the benefits of scale. In the kaolin industry in the 1970s, for example, a 100,000 tpy operation was considered a reasonable commercial operation. For the current developments in Brazil, a minimum plant size of 300,000 tpy is being quoted. Category 2 clays have annual tonnage requirements that are governed by market size rather than benefits of scale. Annual production from such processing operations typically falls between 10,000 and 100,000 tpy. The sizes of Category 3 operations are typically governed by factors such as market size or accessible market share.

Relationship between Category and Resource Confidence

Based on the category criteria, the development of a Category 1 resource requires a very high level of confidence in the quality and quantity of the raw material. If a minimum resource life of 20 years is required at 300,000 tpy, then the resource must be of sufficient size to produce 6 Mt of product. For Category 2 and Category 3 industrial clays, the tonnage requirements may be significantly less and resource confidence may also be less.

Figure 1 shows the various levels of resource certainty that are internationally recognized in the classification of industrial mineral resources.

The lowest level of confidence (*Inferred*, in the upper left corner), exists when no drilling or detailed testing has been carried out. The level of confidence moves from *Inferred* to *Indicated* when an initial exploration and testing program has been carried



Figure 2. Flowsheet of project development

out and the boundaries of the resource in three dimensions may be reasonably estimated. Once a systematic exploration, drilling, and testing program has been completed, the level of confidence moves to *Measured*.

This may result in a prefeasibility study when a decision is made to proceed or withdraw from the project. If the project proceeds, then further drilling and testing leads to a mine plan, exploitation strategy, and calculations of *Mineable in situ* tonnages. A recovery figure for mining and processing may then be applied to calculate the *Recoverable* and *Marketable* reserves.

For resources in Categories 1 and 2 it is essential that the knowledge be at the Marketable reserves stage. For Category 3 minerals, the resource certainty may be much less, possibly at the *Inferred* resource level or less.

Relationship between Category and Value

Category 1 kaolin products command the largest tonnage and highest added-value positions in the industry. Frequently, however, it is the Category 2 products that command the highest unit value position, although their tonnages may be relatively small. Category 3 kaolins command an intermediate value between Category 1 and Category 4 kaolins.

Relationship between Category and Preinvestment Capital

Category 1 projects require significant preinvestment or “risk” capital. The level of confidence in the resource and markets has to be very high, requiring a significant level of investment that may well exceed US\$1 million. The payback time for such investments can be at least 5 years because of the time required to move from

reconnaissance to commissioning. The pre-investment capital requirements for Categories 2, 3, and 4 become progressively lower as the category of clay moves lower.

Relationship between Category and Investment Capital

The investment capital requirements for large tonnage, high-complexity Category 1 kaolin projects are quoted to be as high as US\$300 per processed ton (Harvey 1995; Pleeth 1997). For Category 2 kaolins, investment capital costs would depend on the complexity of the process but might range between US\$100 and US\$500 per processed ton. For Category 3 kaolins, the investment level may be less than US\$50 per finished ton.

THE RESOURCE EVALUATION PROCESS

The evaluation moves through a series of progressively more detailed stages as shown in Figure 2.

Translating from Laboratory-Scale Testing to Major Plant Scale

The clay industry has many examples of insufficient scale-up factors being applied to basic laboratory data. This ranges from basic recovery figures to assessments of product quality based on too few laboratory test data. For example, losses during commercial plant operations may be much higher than in small-scale laboratory test equipment. A conservative approach to both laboratory- and pilot-scale test data is essential.

The Level of Applied Technology

Almost anything can be done with a low-grade clay resource if a sufficient number of applied technologies are thrown at it. For example, with commercial kaolin resources, a wide-ranging selection of technologies can be applied. By applying a number of such technologies to a low-grade raw material, it may be possible to upgrade it significantly. When all the various processes are costed into the operation, however, the total expenditures (and process losses) may become prohibitive, effectively constraining development of the resource.

Losses Associated with Applied Processing Steps

For each technology introduced into a process there will be process losses. These may range from 2% to much higher values. If, however, it is generalized that each process step loses 4% of product, then the effects of multistage processing on recoveries may be very significant. Also, such losses will be cumulative.

Time to Move from Commissioning to Full Production

Industries that use industrial minerals are often conservative by nature and do not readily accept new products. For example, the paper industry uses a complex technology, and an industrial clay such as kaolin may be just one component in a complex formulation. Purchasing agents may have to be convinced that the product is compatible with their formulations, and further, that the product quality and supply will be consistent. To reach this stage, it is necessary to convince the company of the quality, consistency, and value of a new product over and above the quality of its existing supplier. In such cases it may be necessary to compete on the basis of higher quality, lower price, better continuity, or better technical support. Even with such strengths, however, the new player in the marketplace still has to deal with buyer conservatism. Therefore, the rate at which a product is accepted may be a combination of advantageous positioning and sheer luck. For some products, it may take years to gain full market acceptance. For example, recent developments of Category 1 kaolin resources in Brazil (Pleeth

Table 6. Timetable of activities and investments

Activity	Category			
	1	2	3	4
Stage I: Reconnaissance				
Geological reconnaissance, property surveys, testing, broad categorization of materials, market surveys and evaluation				
Decision to proceed (months)	12	9	6	3
Stage II: Exploration (prefeasibility)				
Property negotiation, drilling, testing, market surveys, precise material characterizations, process flowsheet development, resource calculations, economic studies and evaluation				
Prefeasibility study and decision to proceed (months)	18–24	9	9	6
Stage III: Delineation and feasibility				
Drilling, testing, market surveys, bulk samples, engineering studies, assessment of products in the marketplace, economic studies and evaluation				
Feasibility study (months)	24	12	9	3
Stage IV: Decision to invest				
Total elapsed time since project initiation (years)	4–5	2.0–2.5	2	1
Design, construction, and commissioning (years)	1–2	1	1	1
Typical overall project time (years)	5–7	3–4	2–3	1

1997) quote time intervals of at least 5 years to move from initial exploration through to commissioning. Table 6 illustrates typical times required.

Reducing Risk during Development

There are several procedures for minimizing risk and reducing the time necessary to develop Category 1 or Category 2 ventures:

- Associate or form a joint venture with established producers in the industry.
- Associate or form a joint venture with major market users of the product.
- Engage specialized consultants for resource evaluation, market surveys, and so forth.
- Develop resources adjacent to proven established resources.

SUMMARY

This overview illustrates the diverse nature of clay minerals and the breadth of their technologies and markets, and demonstrates why they are such important industrial minerals. The seven chapters that follow expand on the individual clay types.

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Ball Clays

Jason McCuiston and Ian Wilson

INTRODUCTION

Ball clays are kaolinitic sedimentary clays that are an important component in most ceramic bodies because they confer strength and plasticity. Most ball clays impart a light cream to white fired color in an oxidizing atmosphere. Ball clays have varying proportions of kaolinite, illitic mica, or sericite and fine quartz, with small amounts of organic matter and other minerals such as smectite. They are commercially valued because they increase the workability and strength of ceramic bodies. Contaminant minerals frequently include pyrite, siderite, iron and titanium oxides, gypsum, and dolomite. The quantity, form, and type of contaminant can influence the usefulness, processing route, and ceramic application of the clay. The major differences between the kaolinite in ball clay and in china clay (kaolin) are particle size and the degree of ordering within the crystal structure. Whereas the kaolinite in china clay is moderately

coarse and generally well ordered, kaolinite in ball clay normally has a very fine particle size and is predominantly b-axis disordered.

The term *ball clay* is thought to be derived from the old method of working the clay. The clay was cut into cubes about 9 in. (230 mm) square, each weighing 30–40 lb (13–18 kg); because of the plastic nature of the clay, these rapidly assumed a spherical shape during handling. Clay was sold in this form by the “ball.” Alternatively the name may have derived from a digging implement called a “tubal,” which is still used to mine ball clay in some parts of the world.

Figure 1 shows the locations of some of the major deposits worldwide. In 2003, the production of ball clay was estimated at 15.5 Mt (Table 1), and this should be considered only an estimate because many countries do not distinguish between ball clays and other types of clays. Nine countries—China, Germany, Indonesia,

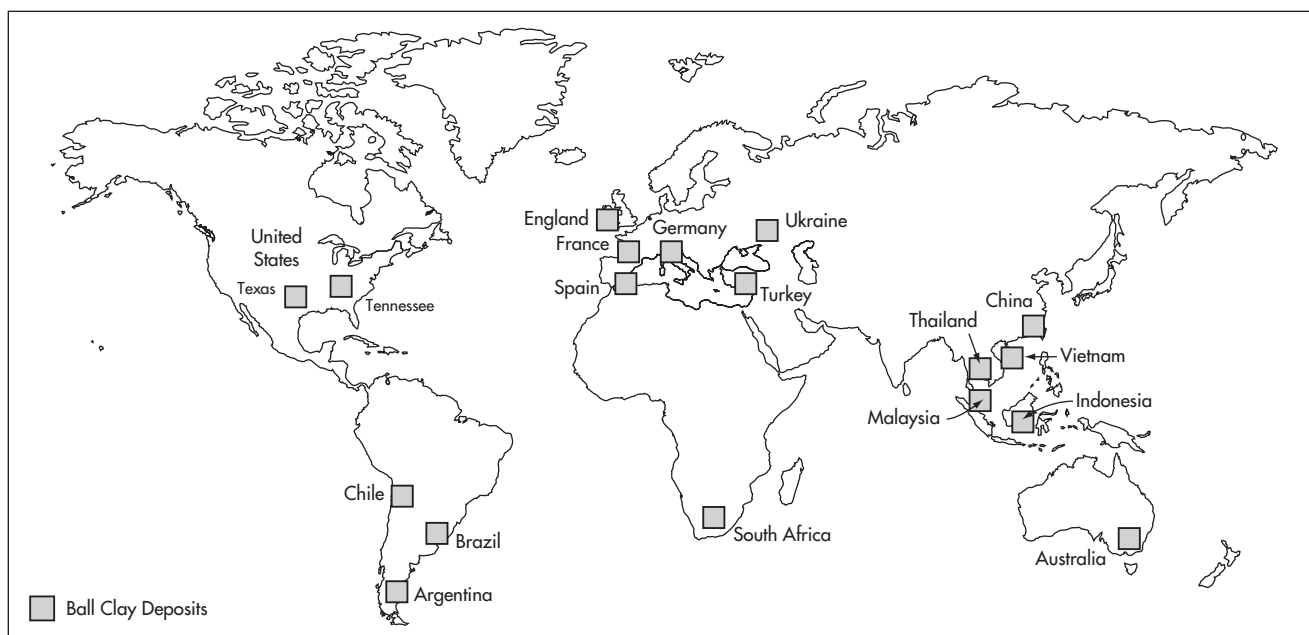


Figure 1. Map of some major ball clay deposits of the world

Table 1. Estimated ball clay production by region/country, 2002–2003

Region/Country	Production, t
North America	
United States	1,120,000
Europe	
Czech Republic	400,000
France	400,000
Germany	3,000,000
Italy	100,000
Poland	50,000
Spain	1,200,000
Turkey	550,000
Ukraine	3,500,000
United Kingdom	1,000,000
Asia and Oceania	
Australia	80,000
China	2,000,000
India	150,000
Indonesia	500,000
Malaysia	600,000
Thailand	300,000
Vietnam	200,000
Others	
Argentina	50,000
Brazil	250,000
Chile	5,000
South Africa	10,000
Total	15,500,000

Malaysia, Spain, Turkey, Ukraine, the United Kingdom, and the United States—account for 83% of the world's production with the largest, Ukraine, at 23% (Figure 2). The most significant development has been the dramatic increase in production from Ukraine mainly for the manufacture of Gres Porcellanato tiles. The clay is characterized by high strength, fine particle size, and particularly low water absorption, which is especially suitable for single firing.

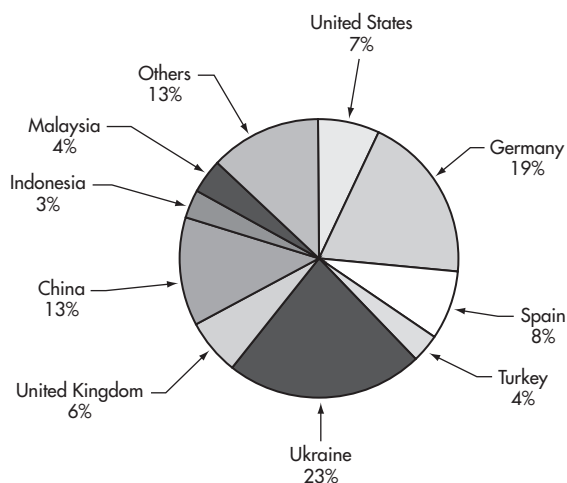
This chapter describes the ball clays of the United States in detail followed by a brief review of some other deposits of the world.

BALL CLAYS OF THE UNITED STATES

Local potters near Paris, Tennessee, in the 1800s were the earliest ball clay miners in the United States after European settlement. In 1894, Isador Mandle began selling clays out of state from Whitlock, in Henry County, Tennessee (Whitlatch 1940). Ball clay mining subsequently spread across Henry, Weakley, and Carroll counties in Tennessee and north into western Kentucky. With the migrations and population growth farther west, ball clay resources were discovered and exploited in California, Maryland, Mississippi, and Texas.

The four major suppliers of ball clay in the United States are H.C. Spinks Clay Company (Franklin Industries); Kentucky–Tennessee Clay Company (Imerys); Old Hickory Clay Company; and Unimin Corporation.

The major markets for ball clay are in the manufacture of sanitary ware, wall tile, and floor tile. Ball clay is also used in the manufacture of acoustic ceiling tile, dinnerware, electrical porcelain,

**Figure 2. Major ball clay producing countries, 2002–2003**

refractories, hobby ceramics, coal tar/asphalt, fiberglass, rubber, and a variety of coating and sealant applications.

Production and Trade

According to U.S. Geological Survey (USGS) statistics, in 2002, approximately 1,120,000 t of ball clay valued at US\$47 million was produced in the United States (Table 2). Tennessee was the largest producer at 59%, followed by Texas, Kentucky, and then Mississippi. Most of this tonnage was produced for ceramic applications (floor and wall tile, 35%; sanitary ware, 22%; pottery and miscellaneous ceramics, 15%). Figure 3 illustrates the distribution to each market.

Processing

Raw ball clay is processed into four different forms: shredded, mechanically dried, air-floated (powdered), and slurry. Shredded ball clay undergoes the least amount of processing. In this process, raw clay is run through a shredder, and the resulting product is no more than 2 in. (5 cm) in diameter with a moisture content of about 17%. Mechanically dried clay also has a diameter of no more than 2 in. (5 cm), but it has a moisture value of about 10%. In 2002, shredded and mechanically dried forms represented about 31% of the market and had an average value of \$34/t. Air-floated clay is powdered and has a moisture percentage of no more than 3%. In 2002, air-floated clay represented about 40% of the market and had an average value of \$54/t. Slurried clay is shipped in liquid form and consists of about 60% clay and 40% water. Slurried clay represented about 29% of the market and had an average value of about \$43/t in 2002 (Virta 2004). Reserves of ball clay in the United States at current consumption rates will last far more than 150 years.

Geology

Overview

The sedimentary environments into which ball clays were deposited appear to vary greatly. As a result, the physical characteristics of ball clays vary greatly. In Tennessee, many deposits are narrow and curved; in cross section, they appear to be river-channel shaped (Figure 4). These deposits are typically surrounded on the sides and undersides by cross-bedded sands and occasionally fine gravels. Clay deposits of this type generally are dark brown and have tan clay on both the top and the bottom of the deposits (Figure 5).

Table 2. Ball clay sold or used in 2002 by producers in the United States, by state*

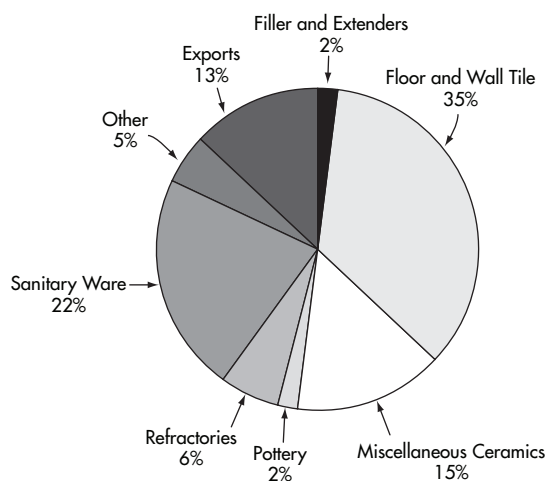
State	Airfloated		Water-Slurried		Mechanically Dried and Shredded		Grand Totals	
	Quantity, t	Value, \$US million	Quantity, t	Value, \$US million	Quantity, t	Value, \$US million	Quantity, t	Value, \$US million
Tennessee	248,000	12.4	194,000	8.4	217,000	7.3	660,000	28.1
Other†	196,000	11.5	W‡	W	W	W	459,000	11.5
Total	444,000	24.0	194,000	8.4	217,000	7.3	1,120,000	47.0

Source: Virta 2004.

* Data are rounded to no more than 3 significant digits; may not add to totals shown.

† Includes Indiana, Kentucky, Mississippi, and Texas.

‡ W = withheld to avoid disclosing company-proprietary data; included in Totals.



Adapted from Virta 2004.

Figure 3. Percentage usage of ball clay produced in the United States

Thicknesses of the deposits vary from 10 to 50 ft (3 to 15 m). Channels are typically about 300 ft (91 m) across and from 500 ft (152 m) to almost 1 mile (1.6 km) long. Deposit sizes range from 2 to 50 acres (1 to 20 ha) (McCuistion 1995).

Other Tennessee and Kentucky deposits are much larger and not confined to channels. These deposits can cover 100 or more acres (40 ha or more), but they do not have a typical lensoid shape. The clays in these deposits are mostly gray but grade into brown clay that is crisscrossed with root structures at the tops of the deposits. These deposits are commonly capped by 2–8 ft (0.5–2.5 m) of lignite with a contact that undulates a few inches with the underlying brown clay. These deposits also range from 10 to 50 ft (3 to 15 m) in thickness (McCuistion 1995). Most other types of deposits fall somewhere near or between the two extremes.

Occurrence and Origins

By far, most of the ball clay produced in the United States is shipped from the Kentucky–Tennessee region (Henry, Weakley, and Carroll counties in Tennessee; Graves County in Kentucky). Significant amounts of clay are also shipped from Panola County in Mississippi and from Cherokee County in Texas. The Tennessee, Kentucky, and Mississippi deposits are all located in the Middle Eocene Claiborne Group (Ackerman 1996), which is near the edges of the Mississippi Embayment (Figure 6). The economic clay

deposits in Texas are in the Lower Eocene Wilcox Formation (Fisher et al. 1965).

The environment in which these clays were deposited is generally considered to be on a fairly flat plain traversed by low-gradient, aggrading streams that occupied broad, flat valleys. Seasonal flooding caused major channels to shift paths, leaving behind abandoned, low-energy environments known as “ox bows.” These abandoned channels or oxbows became ideal low-energy environments for the deposition of fine-grained clays. It is conceivable that the larger deposits not confined to a channel are large-scale overbank deposits.

Two theories exist for the origins of U.S. ball clay sediments. The first is that Porters Creek Clay in the Middle Paleocene weathered to kaolinite and was transported a relatively short distance to its current locations (Hughes, Moore, and Reynolds 1993). The second is that the deposition of these sediments was the result of the Appalachian River system entering the Mississippi Embayment in Kentucky and meandering back and forth across this wide plain (Potter and Dilcher 1980). Both theories are worthy of more thought and further study.

Mineralogy and Properties

The two major components of ball clay are kaolinite and quartz. Many of the properties important to end users are tied to the relative percentages of these two minerals. The variations in composition can be quite large. In five profiles sampled from working clay pits by McCuistion (1995), the quartz contents ranged from 21% to 64% and the kaolinite contents ranged from 33% to 80%. Hughes, Moore, and Reynolds (1993) confirmed that much of the kaolinite present in these clays is mixed-layered kaolinite–smectite. Well-ordered kaolinite represents 37%–67% of the kaolinite within these clays. The kaolinite–smectite component has approximately 88%–99% kaolinite layers (McCuistion 1995). Hughes, Moore, and Reynolds (1993) examined many different deposits and stated that the kaolinite–smectite in ball clay had >80% kaolinitic layers. The presence of this poorly crystallized kaolinite contributes to the plasticity for which ball clay is so well known. Trace clay minerals present in ball clays include illite, smectite (discrete), chlorite, and other mixed-layer clay species. Other trace minerals are mica, pyrite, ilmenite, magnetite, tourmaline, and zircon (McCuistion 1995).

The physical properties of ball clay are as varied as their mineralogies, and the variations significantly affect the end uses of the ball clay. Ball clays have the following properties:

- Moisture content between 18% and 22%
- White, various shades of gray and brown, black, tan, pink, and all shades in between

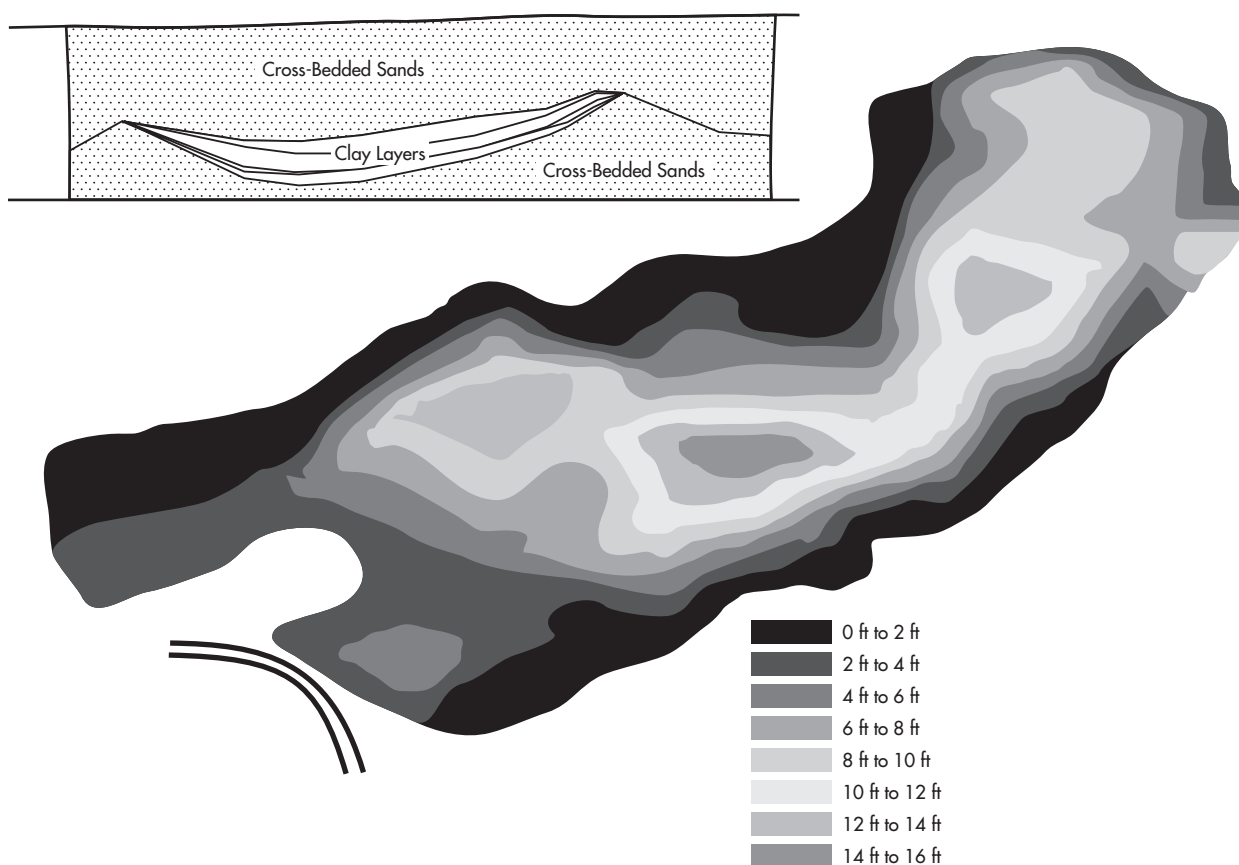


Figure 4. Cross section and isopach map of a ball clay deposit. Deposit is a clay lens within the Claiborne Formation sands and appears river-channel shaped.



Figure 5. Photo of a mine with tan clay overlying dark brown clay

- Particle sizes between 15% <0.5 μm and 65% <0.5 μm
- Specific surface area (SSA) between 8 m^2/g and 40 m^2/g
- Carbon content from 0.1% to >3%
- Sulfur content from <10 ppm to as much as 7,000 ppm
- With aging, sulfate content from between 200 ppm and 5,000 ppm

- Residues on +200-mesh screens from a trace to 30%
- Deflocculation demands from very low to very high
- Fired color can be white, peach, or pink
- SiO_2 from 50% to 70%
- Al_2O_3 from 18% to 35%
- Average Fe_2O_3 close to 1%

Technology

Exploration

Exploration involves planning, drilling, laboratory testing, and geologic interpretation. Ball clay deposits were originally located by finding outcrops that were visible in topographic lows such as ditches and stream bottoms. Although that method is still useful today, most deposits are generally found well below the elevations of even the most deeply incising streams. Drilling has been conducted in the Tennessee, Kentucky, Texas, and Mississippi regions for more than 75 years. Numerous ball clay deposits have been identified and located but not yet developed. In most of these deposits, the locations, depths, and thicknesses are known, but the only quality information recorded was what the drillers logged in the field (color, sandiness, etc.). Because of the extensive drilling done over the past 75 years, modern planning for exploration involves extensive review of historical records to find tracts of drilled land. Tracts of land that have never been drilled are chosen by proximity to known ball clay deposits and location within the

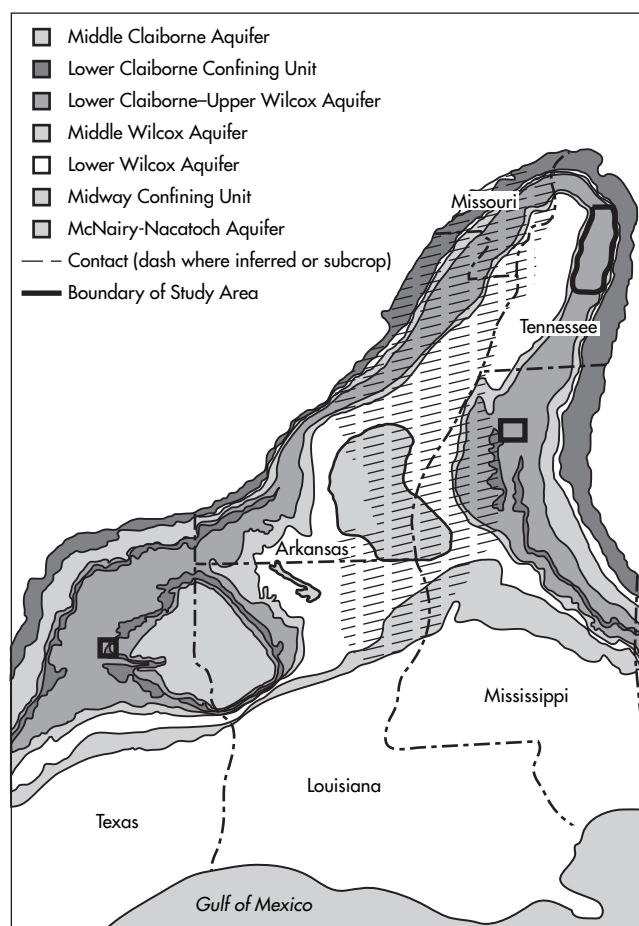


Figure 6. Approximate locations of Mississippi Embayment commercial deposits

general area in which the Claiborne or Wilcox formations outcrop or subcrop.

Ball clay deposits in the United States are now located using truck-mounted core or split-tube sample drills. These drills can recover nearly 100% of the clay encountered. Sampling is typically at 2.5-ft (0.8-m) intervals. Cores are generally 2 in. (5 cm) in diameter. Figure 7 shows a typical rig. Laboratory testing is performed at 2.5-ft (0.8-m) intervals. If an obvious change such as a variation in the color or sandiness of the clay is apparent within that interval, then the sampling interval may be further reduced.

Exploration drilling is done with 150-ft (46-m) spacing between holes. It is necessary to drill this close because some of the deposits may not be much wider across, and drilling at wider spacings could miss some smaller deposits. In most deposits, this distance between holes is sufficient to assess the quality and quantity of the ball clay before removing the overburden. In some smaller deposits and close to the edge of deposits, holes are spaced closer together to ensure quality and to minimize the amount of overburden removal. These holes are then surveyed using either laser-ranging transits or global positioning system (GPS) receivers. Aerial photography is widely used to assist in both exploration and mine planning. This enables sufficiently accurate contouring to be generated to assess both the overburden and reserves in each deposit. Exploration holes are typically drilled to between 75 ft and 100 ft (23 m and 30 m).



Figure 7. Typical truck-mounted drilling rig used in the United States

Each sample representing 2.5 ft (0.8 m) or less is tested for the following properties:

- Particle size (mainly % <20 µm; % <10 µm; % <5 µm; % <2 µm; % <1 µm; and % <0.5 µm)
- SSA (single and multipoint)
- +200 and +325 mesh residue
- Chemistry (mainly SiO₂, Al₂O₃, Fe₂O₃, K₂O, and loss on ignition [LOI])
- Total sulfur or carbon
- Fired color

Composites of samples are given the following ceramic tests:

- Casting rate
- Dry modulus of rupture (MOR)
- Moisture retention

Other application-specific tests may be run on certain individual or composite samples as appropriate.

Most mapping and modeling is now done with computer-aided design (CAD)-based computer programs. If a deposit has sufficient quality, quantity, and overburden ratio to justify development as a mine, then a three-dimensional property map is produced that displays the surface topography and drill-hole locations. After laboratory testing on the exploration samples, a geologist correlates each layer within a deposit between drill holes. Once the property map is produced, then the drill-hole information is entered into the computer to generate a three-dimensional model of the deposit. This model generates geologic tools such as cross sections and isopach maps (Figure 4) to aid in the mine-planning process. Just as important, volumes of individual layers can be calculated for both long- and short-term planning. Volumes of ball clay are transformed into weights by the following relationship:

$$1 \text{ ft}^3 = 100 \text{ lb} \quad (1 \text{ m}^3 = 128 \text{ kg})$$

Mining

Mining involves planning, permitting, overburden stripping, production drilling, actual mining, regular mine sampling, clay aging, and blending.

Mine planning requires the joint involvement of various disciplines. Quality, environmental concerns, and costs are all equally



Figure 8. Overburden is stripped using tractors with self-loading pans



Figure 9. Trackhoes selectively mining individual layers from a Tennessee clay pit

weighted in designing a mine plan to balance all three factors. Mine plans are constructed using the same maps generated by the CAD-based computer programs.

State environmental organizations issue permits. The main federal regulating authority for mine safety is the Mine Safety and Health Administration (MSHA).

Open-pit mining, the method used in all U.S. ball clay mines, requires overburden stripping. The dominant equipment used to remove overburden material is self-loading scrapers or tractors pulling self-loading pans (Figure 8). In particularly wet or soft material, it is sometimes necessary to top-load these pans or scrapers with a trackhoe.

Production drilling is done after the overburden has been removed and before mining takes place. Production holes are spaced 50 ft (15 m) apart to refine mine plans and reserve estimates. The test procedures used in exploration are again used on these production samples. After laboratory testing, the three-dimensional models are updated to make mine plans, cross sections, isopach maps, and estimates of reserves more accurate.

In the United States, the most common equipment used to mine ball clays is the trackhoe (Figure 9). The horizontal and vertical variability inherent in ball clay deposits demands precise mining. Some deposits contain six or more different strata. Each must be mined precisely and stored separately for later blending. The clay is loaded directly onto trucks where it is then transported directly to sheds or intermediate storage areas. Once in the sheds, bulldozers push each load of clay onto its appropriate pile.

Mine samples are taken on a regular basis at the stockpile in the shed. Testing is done to confirm that all steps up through transport of the clay have been performed correctly. If the samples show clay to be out of specification, the clay is either isolated and used appropriately or moved to its proper stockpile. Mine sample data are also used to make precise blends of different clays to achieve a required combination of properties.

Proper aging is important to the deflocculation characteristics of ball clay. Newly mined clays are almost always very difficult to deflocculate. Oxidation and bacterial attack on the mined clay change and degrade the organic matter over time. Sulfate growth is also a result of the aging process and has a profound effect on ceramic bodies. Another benefit of aging is drying; natural drying, in particular, significantly decreases costs.

Blending is a major step in the quality control process. Blending clay reduces variations in products by dampening the natural variation inherent in each strata. Blending also allows adjustment of relative percentages to account for changes in the mine. Blending enables adjustments to be made to control trends or sudden changes in a product that are caused by variations in the clay composition or physical properties. Blending also can create “engineered” products not found in the natural environment as individual strata.

The ball clays are blended in several different ways. Initial blending is done on the floor before loading into the hopper. With this method, the loader operator is given a recipe for the number of buckets of each clay to mix together. With the second method, the recipe is for the number of pounds of each clay to load directly into the hopper. Scales on the hopper guide the operator in this process.

Preprocessing quality control can be summarized in three major steps: drill sampling (premining), mine sampling (postmining), and blending. Figure 10 is a flow chart of this process.

Processing

Ball clay in the United States is processed in dry forms and wet forms (slurry). The flow chart in Figure 10 ends by branching to one of these two processes.

Dry Processing

Figure 11 illustrates the dry-processing technology pathway. Once a blend is batched and mixed together, a front-end loader deposits the blended clay into a hopper leading to a J.C. Steele feeder. The clay exiting this feeder is no larger than a softball. The clay is then carried up a belt to a crusher that further reduces the size of the clay pieces to 1 in. (2.5 cm) or less in diameter.

From the crusher, the clay runs through a dryer that reduces the moisture content of the clay from approximately 20% to about 12%. For mechanically dried product, the clay can be run into a stockpile or loaded directly into a railcar or truck. For air-floated product, the clay is diverted into a mill hopper that feeds clay into a mill that grinds the clay into a powder and dries it further to 3% or less moisture. From the mill, the powdered clay is pneumatically pumped into a hopper. From the hopper, the clay can either be bagged in 50-lb (22.5 kg) bags or pumped into a silo. Trucks and railcars can be loaded directly from the silos or clay can be loaded into 1-t supersacks.

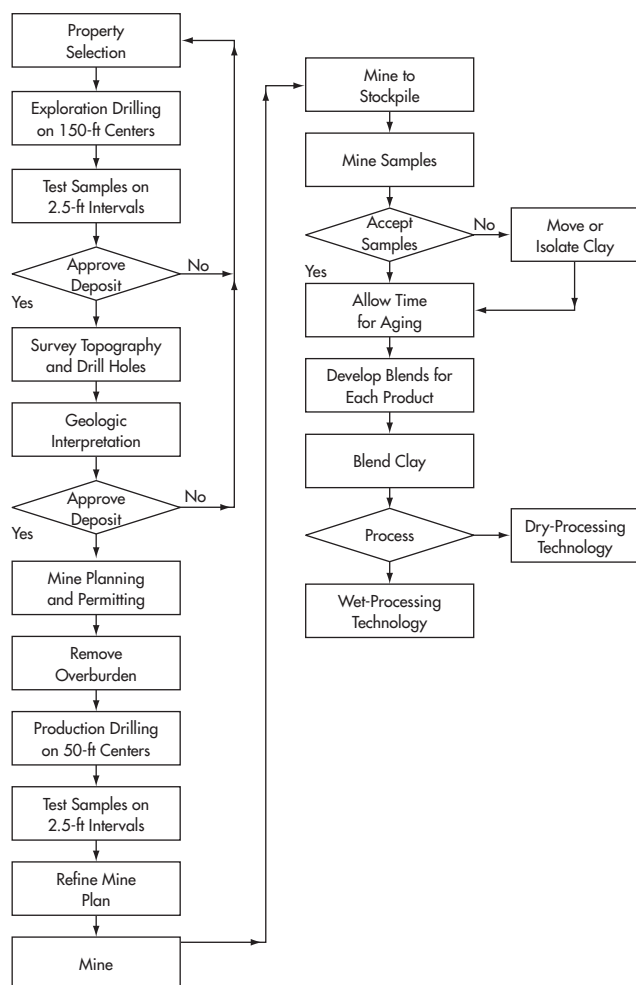


Figure 10. A generalized flow chart for exploration and preprocessing quality control of ball clay

Wet Processing

The other branch of the flow chart in Figure 10 leads to wet processing, which is further illustrated in Figure 12. Instead of blending clay on the floor as is done with dry processing, individual clays are loaded into the hopper by weight. A digital readout on the hopper shows the loader operator how many tons of each clay have been loaded. When the batch is completed, the J.C. Steele feeder feeds the clay onto a belt in softball-size or smaller lumps and into a crusher that crushes the clay into lumps 1-in. (2.5 cm) or less in diameter. The clay is then fed into a blunger and mixed with water and chemicals. Large blades blend the clay–water–chemical mixture until all the clay has broken down. When blunging is complete, the slurry is then pumped over coarse screens that scalp off the coarser material such as lignite and coarse sand. The slurry is pumped over fine screens that take out even more undesired material. After screening, the slurry is pumped into blend tanks. These blend tanks are checked for quality and consistency and, if necessary, are mixed with other tanks to improve the quality. From the blend tanks, the slurry is pumped in to ship-out tanks where the slurry is checked for consistency a final time before the tanks are loaded into either trucks or railcars.

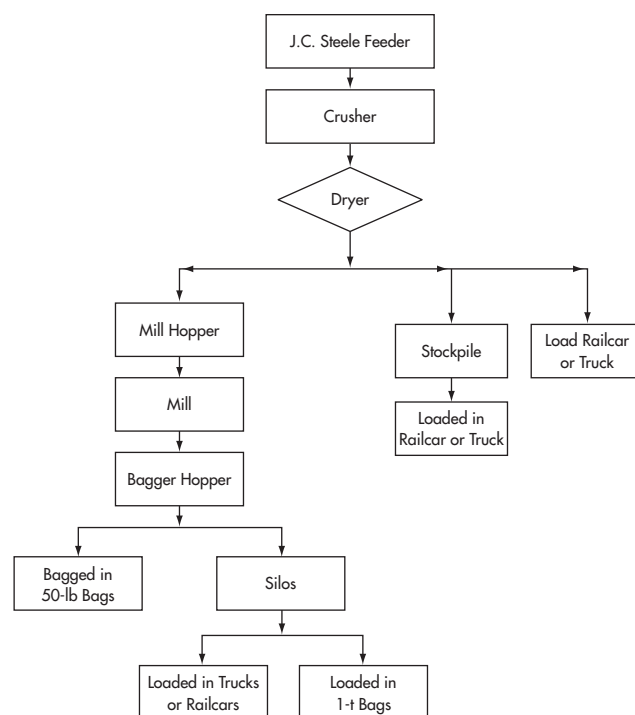


Figure 11. A generalized flow chart for ball clay dry processing

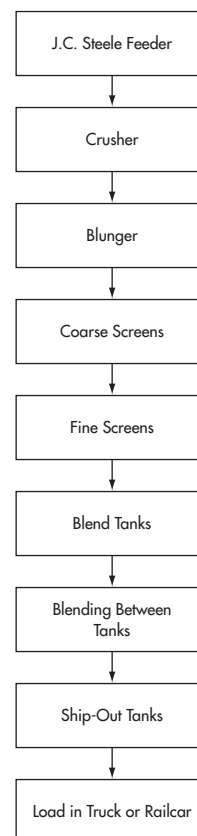


Figure 12. Generalized flow chart for wet-processing technology

Marketing

Ceramic Usage

Ceramic usages of ball clays include wall and floor tile, sanitary ware, and miscellaneous uses.

A typical tile body contains 20%–60% ball clay, and the rest is varying amounts of pyrophyllite, feldspar, silica sand, and talc. The ball clay in a tile body enables forming and imparts green strength so that the pressed tile retains its shape throughout the green or forming phase of the manufacturing process. The ball clay also helps the body continue to retain its shape throughout the firing process until a vitreous bond is established through melting and mineral transformations (Worrall 1986). Ball clays used for tile products are typically quite fine and fire white to off-white. For some of the darker styles, dark firing clays are more desirable.

A typical sanitary-ware body consists of 35% ball clay, 15% kaolin, and 50% nonplastics such as feldspar and silica sand. Because sanitary ware is cast instead of pressed, the rheological and viscosity characteristics that ball clay adds to a slip are very important. The ball clay acts as a suspending agent for the rest of the nonplastic materials in a slip so that the coarse, nonplastic materials do not settle out. During casting, the green forming characteristics that ball clay adds to the body become important. Green strength and plasticity are critical to the handling of unfired ceramic ware. Sanitary-ware blends are typically fairly coarse to maintain fast casting rates. The ideal blend, however, includes both fine and coarse clays to better balance the need for both casting rate and strength.

Electrical porcelain, hobbyware, and dinnerware all use ball clay for its plasticity and forming characteristics.

Nonceramic Usage

Ball clays are formulated in a wide variety of nonceramic applications such as coatings (interior and exterior), rubber, adhesives, sealants, fiberglass, and fire-retardant systems. Depending on the application, the fine particle size of certain ball clays offers the following processing characteristics or advantages: rheological modification and stabilization; bonding strength; desirable oil absorptions; extrudability; reduced sag and increased stiffness; pigment reduction; improved surface appearance; tack reduction; and controlled drying. Ball clay blends can be engineered to address specific processing needs, resulting in process and quality improvements for the end user.

Economic Factors of the Ball Clay Industry

Exploration and Mine Development Costs

No surface features signal that ball clay may be present on a particular tract of land. Therefore, it is necessary to drill hundreds of holes to find a potential deposit of economic ball clay. Once a deposit is found, it is necessary to drill 100 or more holes to properly characterize a deposit. Additional cost is involved in testing and recording data, interpreting the data, and creating three-dimensional models and mining plans. Permitting also incurs significant costs. A permit for a new mine can take 3–6 months to complete and be approved. Ball clay companies typically have 7–12 mines in some stage of development, mining, or reclamation at any given time.

Stripping, Mining, and Crude Clay Transport Costs

Both contracting and fleets owned by individual companies remove overburden. Costs of overburden removal vary greatly depending on the type of overburden, ratio of clay to overburden, length of haul to a dump site, and amount of water present in the sands.

Ball clay is mined from ground owned by the mining companies and from leases. Minimum payments are made to the landhold-

ers each year until mining begins. When mining begins, the landholders are paid a royalty for every ton removed from the property for purpose of sale. Another cost involves water: it is necessary to pump water continuously from most ball clay mines to keep both rain and groundwater away from the mining areas.

Both contractors and company-owned fleets truck crude clay to processing plants, usually traveling distances of 5–50 miles (8–80 km).

Processing and Drying Costs

Shredded material costs the least to process because it is run only through a shredder before it is ready for shipment. Mechanically dried material is run through a shredder, but it also runs through a dryer that uses significant quantities of gas or other energy source. Air-floated or powdered materials go through an additional costly step of being almost completely dried in a furnace and powdered in a ball or roller mill. Slurry products are also shredded, but they are introduced into a blunger with heated water and significant amounts of chemicals to break the clay down into a pumpable form.

Product Transport Costs

Ball clay product is transported by truck, railcar, barge, or container ship in North and South America. Transportation costs are significant and often exceed the cost of the product itself.

Customer Support Costs

Ball clay producers offer total support to customers and have teams of ceramic engineers that work directly with customers at their plants to help a customer with both production problems and efficiency issues. These teams of engineers discuss the problems and issues with the production facilities so that products can be adjusted to better suit a customer's needs.

BALL CLAY DEPOSITS OUTSIDE THE UNITED STATES

Europe

Ball clay is found in many countries in Europe; major production is in the Czech Republic, France, Germany, Spain, Turkey, Ukraine, and the United Kingdom. Figure 13 is a map of the ball clay deposits in Europe (for this chapter, Europe refers to western and eastern Europe, Ukraine, and Turkey).

Czech Republic

The main ball clay producing regions in the Czech Republic are in Cheb, Pilsen, Most, South Bohemia, and Western Moravia. Production of ball clay was 400,000 t in 2003, with the best-quality ball clay in the Cheb Basin where it is mined in the Nova Ves, Karel, and Vackov areas. These clays are characterized by fine particle size, very good plasticity, white firing, good MOR, and relatively low iron and titania.

France

The two principal clay-producing areas of France are the Charente Basin, worked by AGS, and the Provins Basin. Pornon et Cie SARL is part of WBB Minerals (Sibelco Group) with operations in the Allier region. Here Pornon manufactures selected plastic clay blends for sanitary ware (SanMix PT-28) and for refractory applications (Carat PT-13).

Germany

Clays are mined throughout Germany, but by far the most important region for the production of plastic clays is the Westerwald region. The Westerwald region is situated between Frankfurt and Bonn,



Figure 13. Map of the ball clay deposits of Europe

and the main basin is divided into a number of topographic and generic basins that are controlled by earlier fault patterns. Clay-bearing sequences were laid down in subsidence hollows in the Tertiary period, some 25–40 Ma.

The largest company in Germany is WBB Fuchs, which extracts and processes a wide range of plastic clays and kaolins from deposits in the Westerwald region and other areas of the country. Fuchs'sche Tongruben (Fuchs-Ton) was established as a family company in 1838 and grew into one of the country's leading clay suppliers, becoming part of the WBB Group in 1974. WBB Fuchs-Keramische Massen is a market leader in prepared ceramic bodies, with two dedicated plants at Ransbach and Kannenbäckerland in Höhr-Grenzhausen. WBB Fuchs produces approximately 2 Mtpy. A large range of ball clay products come from the Westerwald; these consist mainly of disordered kaolinite, illite, and quartz with good forming properties and range from red-firing to white-firing clays. The Italian floor-tile market accounts for more than 30% of the Fuchs Westerwald ball clay sales. This market, however, has been attacked by increasing imports of ball clay from Ukraine. Clays having good plasticity and high strength are also sourced from the Eifel region.

Spain

Ball clays used in Spain are mainly domestic (67%) with the rest imported from the United Kingdom, Germany, France, and Ukraine (Regueiro 2004). Total ball clay consumption in Spain

reached 1.2 Mtpy in 2003 and was worth about €36 million (2003 currency; Sanchez and Regueiro 2004).

Formed in 1999, WBB España SA is the market leader in the supply of red-firing clays to the Spanish ceramic tile industry. WBB extracts more than 4.5 Mt of clay, kaolin, and silica sand annually from four main quarries: Sant Joan de Moró near Castellón, Galve near Teruel, and from Madroño and La Yesa near Valencia. WBB also has two other smaller operations in the Castellón Area—Morella and El Campillo—and a kaolin and silica sand plant in Higuera de las Torres near Valencia. WBB España's clays are relatively low in calcium carbonate content and are ideally suited for the manufacture of single-fired floor tiles. The Spanish ceramic tile industry uses almost all of the output from WBB's quarries and produces about 650 million m² of tiles each year; the industry is in the Castellón region.

Euroacre, a subsidiary of the Samca Group, is the major ball clay body producer operating in Spain. The company developed a wet-purification system to produce 115,000 tpy for use in sanitary ware, glazes, and engobes, and has its own spray drying plant with a capacity of 475,000 tpy of ceramic bodies for floor and wall tiles. Euroacre has a quarry in Teruel that produces about 600,000 tpy of ball clays using a very selective extraction technology. These are ground and blended in a 350,000-tpy homogenization facility to produce illitic-kaolinitic clays for the ceramic industry. Minera Sabater is the second Spanish producer from three quarries in Teruel, reaching 250,000 tpy. Potome produces 90,000 tpy of ball clays consumed

exclusively in their factories. Smaller producers are Acrimuso, Minesa, and Minera Capilla, all with operations in Teruel.

Turkey

Ball clay producers in Turkey include Esan Eczacibasi Endustriyel Hammaddeler AS, Toprak Mining Company, and Matel Raw Material Industry & Trade Company. Matel produces 250,000 tpy of ball and ceramic clays in the northwest of Turkey in the Sile region. Matel also has a refined product plant in Bileci. Toprak also has operations in the Sile region and produces 300,000 tpy, mainly for floor and wall tiles. Esan produces about 150,000 tpy of ball clays and also imports clays from Ukraine.

Ukraine

Ukraine has become an important supplier of ball clay over the last two decades with production now reported at about 3.5 Mtpy. One of the companies, Donbas Clays JSC, was established in 1995 and is a joint venture between WBB Minerals and Ukrainian clay producers, YUG. Production increased dramatically from 70,000 t in 1996 to 660,000 t in 2001. Today Donbas exports premium quality white-firing plastic clays to customers in 20 countries around the world. In 2002 Donbas became the first Ukrainian ceramic raw material supplier to achieve the globally recognized ISO 9001 quality assurance standard. The production site in Mertsalo vo has Ukraine's first purpose-built covered storage area; it can hold up to 100,000 t of clay. A rail link straight into this storage unit enables fast and direct supply. Ukrainian clay deposits are characterized by very thick overburden (up to 148 ft [45 m]) and relatively thin clay seams (6.5 ft [2.0 m]), making extraction much heavier work than in other parts of the world. In creating a new quarry area at the South October deposit, an innovative technique for stripping overburden was developed using tractors with scraper pans; it has proved to be about 2.5 times faster than conventional methods.

WBB currently quarries four clay deposits: Yuzhno-Oktiabrskoye, Kucherov-Yarskoye, Novostepanovskoye, and Novoshveytskoye. This represents almost 11 Mt of reserves, and each year WBB prospects to identify new deposits.

Another company is Keramet Private JSC, which mines ceramic clays throughout the Druzhkovka Donetaka region of east Ukraine. The company produced approximately 500,000 tpy of ball clay in 2003, of which 80% was exported to Italy. Exports from Ukraine have grown rapidly because of their suitability for the manufacture of Gres Porcellanato tiles. The clay is characterized by high strength, fine particle size, and particularly low water absorption. When blended with Turkish feldspar, it makes an excellent blend for tiles and is particularly suitable for fast firing.

United Kingdom

The U.K. production of ball clay in 2002 was approximately 1.0 Mt from which sales were 0.92 Mt. U.K. ball clay sales had been on a rising trend for many years and reached a record 1.1 Mt in 2000. Of the 0.92 Mt sales in 2002, 20% was for U.K. customers and 80% was exported. Domestic sales were down from 337,000 t in 1980 to 158,000 t in 2002, partly reflecting the increasing overseas competition that the U.K. whiteware industry has been facing, notably in the tiles and tableware sector (British Geological Survey 2004).

Only two companies produce ball clay in the United Kingdom, WBB Devon Clays Ltd. (now WBB Minerals Ltd., part of the Belgium group Sibelco) and Imerys Minerals Ltd. (a French group formerly operated by ECC International Ltd.). For WBB Minerals, nearly 98% of ball clay products are sold into ceramics, with sanitary ware, tiles, and brick being the three most important sectors. Economic deposits of high-quality ball clay deposits in the United

Kingdom are confined to three areas in southwest England, the Petrockstow Basin in North Devon, the Bovey Basin in South Devon, and the Wareham Area in Dorset.

Ball clays have a limited distribution in the United Kingdom and globally. After the establishment in Devon and Dorset of ball clays consultation areas in the 1940s and 1950s, and the granting of widespread permissions, there are extensive reserves. The consultation areas are designed to ensure that other forms of development do not sterilize clay-bearing land. Table 3 shows estimates of permitted reserves of ball clay for the three basins.

Overall there are large reserves of ball clay, particularly in Devon. The Bovey Basin has by far the largest permitted reserves and unpermitted resources of the three basins, together with the greatest diversity of clays. It will continue to be the major source of ball clay in the United Kingdom for the foreseeable future.

The 921,000 t sold in 2002 was from the following basins:

- Wareham Basin, Dorset: 167,000 t (Imerys sole producer)
- Bovey Basin, South Devon: 661,000 t (WBB and Imerys producers)
- Petrockstow Basin, North Devon: 108,000 t (WBB and Imerys producers)

In Devon, palynological dating indicates that the clays were deposited in the Oligocene epoch (28–35 Ma). They are linked with fault-bounded, tectonic basins associated with the Sticklepath-Lustleigh fault zone, which has resulted in the accumulation and preservation of several hundred meters of ball clay-bearing sediments. The paleoenvironment of the Bovey Basin area during the Paleogene period was a broad floodplain containing seasonal shallow lakes, swamps, and fluvial outwash fans. Thick lignites are associated with the ball clays and formed from floating rafts or mats of vegetation. The Petrockstow Basin shows evidence of cyclothems, and the commercial ball clays are restricted to shelf areas in the northwest and southeast parts. In Dorset, the ball clays of the Wareham Area are dated to the Early to Mid-Eocene (40–50 Ma). They occur in distinct seams up to 5 m thick in host clay sequences that were deposited over a wide area in the lower reaches of a large, eastward-flowing, meandering river system in the western part of the Hampshire Basin.

Dorset ball clays are renowned for their high plasticity and green strength. Because of the relatively low amounts of coloring oxides, they are white to ivory when fired. Clay seams exhibit extensive lateral and vertical variation in chemical and physical properties, representing the variation through time of the source materials and the local depositional conditions. Generally clays become more illitic eastward, as would be expected with the greater marine influence. In Dorset, some 26 clay types are worked from the various seams in the host clays. All the kaolinite in these clays can be characterized as highly disordered with very fine particle size, frequently 90% <1 µm. In the Bovey Basin, significant differences exist in the mineralogy and ceramic characteristics of the ball clays from the various geological members. The Abbrook Member clays have more disordered kaolinite and micaceous mineral than the clays higher in the sequence, which gives a higher green strength and plasticity and a cream fired color. This might represent the exposure and weathering of the nearby Dartmoor granite, giving more kaolinite in the upper levels. The overlying Southacre Member clays are carbonaceous and have a higher percentage of well-ordered kaolinite. The laterally equivalent Chudleigh Knighton Member clays also contain well-ordered kaolinite and exhibit the weak, nonplastic, but white-firing characteristic of sedimentary kaolin. The ball clays in the Petrockstow Basin are basically two types: Type 1 contains appreciable quantities of montmorillonite,

Table 3. Estimated reserves and resources of U.K. ball clay in 2001

Basin	Permitted Reserves, Mt	Years	Resources Unpermitted, Mt	Years
Bovey	63.1	114	16.7*	34
Petrockstow	8.8	37	32†	136
Wareham	2.5	11	9.6	40
Total	74.4		58.2	

Adapted from British Geological Survey 2004.

* Only resources in the east of the basin. There is also potential in the central and western parts of the basin.

† Permitted but not fully explored.

resulting in high defloculant demand values and relatively high slip viscosities; Type 2 contains relatively little monmorillonite and consequently has lower deflocculant demand values and lower slip viscosities.

Table 4 summarizes the mineralogical composition of ball clays from the three U.K. deposits.

In the United Kingdom, some higher-value-added products are often based on wet refining and screening. Some dry grades may be a blend of five to six different components, often from different areas.

Table 5 gives the main types of ball clay, their properties, and utilization for Imerys Minerals in the United Kingdom. Table 6 lists the commercial properties of some of the products from the three areas.

The biggest constraints on future U.K. ball clay development are environmental concerns. It is very difficult to get permission for new ball clay extraction sites. This is especially so in Dorset where there are outstanding international and national habitats covering much of the ball clay consultation area. Also, the greatest constraint on ball clay extraction, particularly in Dorset, is the extent of European nature conservation designations (Special Areas of Conservation and Special Protection Areas), which restrict and potentially sterilize large parts of the Wareham Basin. There is also a multiplicity of both international and national nature conservation designations. Of the total resources in Dorset, some 65% are constrained by nature conservation and other designations. The habitats created after ball clay extraction, in many cases, provide alternative biodiversity benefits.

South America

Argentina

The San Julian Area of Patagonia contains sedimentary clays of Quaternary age that are exploited as ceramic kaolins and used as a ball clay substitute. There are 70 prospects in the area, of which several are being mined. The Tehuelche mine in San Julian has three distinct layers of clay that are mined selectively. The qualities of the layers differ little apart from the amount of carbonaceous (lignite) material present. The clay exhibits a gray to white matrix, the color depending on the carbonaceous content, and consists of kaolinite and fine-grained silica.

Brazil

Several small producers are mining so-called ball clay in Brazil, especially in the Sao Paulo region. All the clays, with a few exceptions, can be classified as ceramic kaolins rather than the true ball clays, and it is often necessary to blend one or two of the different clays to arrive at a suitable ceramic body. The Sao Simao is the best known and exhibits a wide range of fired brightness values. The

Table 4. Mineralogical composition of UK ball clays from three deposits, wt %

Mineral	Petrockstow Basin	Bovey Basin	Dorset
Kaolinite	33–68	20–90	20–83
Quartz	15–48	0–60	5–60
Mica	0–22	0–40	0–30
Organic matter	0–3	0–16	0–8

Table 5. Imerys U.K. ball clay types, main properties, and utilization

Type of Ball Clay	Main Properties	Utilization
Hycast	Good fluid properties	Sanitary ware
Hywhite	High fired properties	Tableware
Hymod	High strength	Tiles, electrical porcelain
Hyplas	Strong and plastic—siliceous	Tiles, electrical porcelain

principal clay mineral present is kaolinite. Free quartz varies from 3% to 24%, accounting for more than 90% of the remaining minerals. Mica content is low: the kaolinite–mica ratio is close to 20:1. Traces of montmorillonite are present and 1% is gibbsite. The clay shows a reasonable MOR, good casting concentration, and casting rates with low deflocculant demand and thixotropy.

Other ball clays are found in the Santo Amaro and Suzano areas. These clays are finer grained than Sao Simao and have higher strength and plasticity but also have the disadvantage of containing considerable amounts of free quartz. They are fairly open burning with low alkalis and good fired colors. Gibbsite is a common constituent in these clays but appears to have little effect on their good rheological behavior.

Africa

G&W Base & Industrial Minerals (Pty) Ltd. is the main ball clay producer in South Africa with 10,000 tpy from the Albertinia mine in West Cape Province. The ball clay consists of a dark, carbonaceous material and a light-colored clay. The two clays are blended 50:50 at the mine, stockpiled, and dried in the sun. Milling is carried out in Johannesburg where the powder clay is bagged. The majority of the clay is sold as a milled product. Further processing is limited because the clay contains very fine quartz, making it difficult to cyclone. The clay has a good green strength and is used in tiles and sanitary ware. The ceramic and tile market is growing in South Africa.

Asia and Oceania

Asia and Oceania is the fastest growing market in the world, mainly as a result of the tremendous growth in the Chinese economy. Also there has been a tendency for European ceramics producers to close some of their production facilities in Europe and move them to this region. Ball clay deposits are operated and being developed in China, Thailand, Vietnam, Indonesia, and Malaysia, among other countries (Figure 14).

Australia

The three main deposits in Australia are in Victoria State, and production is as follows:

- Axedale—about 50,000 tpy, mainly for floor tiles, roof tiles, and pavers. The quality of the Axedale ball clay allows road freight to New South Wales customers, and some is also exported to New Zealand.

Table 6. Properties of typical ball clays in production in 2003 in the United Kingdom

	Ball Clay Deposits						
	Bovey	Bovey	Bovey	Petrockstow	Petrockstow	Wareham	Wareham
Application	Sanitary ware	Sanitary ware	Tableware	Tableware	General	Refractory	Tableware
Producing company	Imerys	WBB	WBB	WBB	Imerys	Imerys	Imerys
Product	Hycast Rapide	Sanblend 75 Slurry	Prestige BLU	Prestige TA	Hyplas 71	Hymod Excelsior	Hymod Blue
Residue, wt% <125 µm	1.5	0.1	0.2	0.5	1.0	0.3	0.1
Particle-size distribution (psd)							
% >10 µm	2	5	3	6	na*	na	na
% <2 µm	70	78	82	77	57	92	89
% <1 µm	60	65	na	na	50	87	79
% <0.5 µm	45	na	na	na	40	80	65
MOR (dried at 100°C), MPa	3.5	7.9	4.5	9.2	6.5	7.5	8.0
Chemistry, wt %							
SiO ₂	55	53.7	54.0	60.5	69	49	53
Al ₂ O ₃	29	28.9	31.2	25.8	20	35	31
Fe ₂ O ₃	1.1	1.2	1.0	1.9	0.9	1.6	1.4
TiO ₂	1.1	1.1	1.2	1.5	1.7	1.3	1.0
CaO	0.2	na	na	na	0.1	0.3	0.3
MgO	0.3	na	na	na	0.4	0.3	0.5
K ₂ O	1.6	2.5 Alkalies	3.0 Alkalies	2.9 Alkalies	1.9	1.2	3.2
Na ₂ O	0.2	2.5 Alkalies	3.0 Alkalies	2.9 Alkalies	0.4	0.2	0.4
Carbon	2.0	2.5	0.2	0.6	0.1	0.3	0.4
LOI	12.0	12.0	9.0	8.0	5.4	12.0	9.2

Adapted from WBB Minerals Ltd. and Imerys Minerals U.K. published data sheets.

* na = not available.



Figure 14. Producers of some ball clay deposits in Asia

- Rowsley—about 15,000 tpy, mainly for local ceramics and also air-milled for the rubber industry.
- Morwell—about 6,000 tpy, mainly for sanitary ware in Melbourne; the ball clay horizon occurs between brown coal deposits.

China

WBB has been active in China for a long time and is now part of the Sibelco Group. They have carried out a great deal of exploration in China and recently acquired the Gilfair Company, which produced some 600,000 tpy of ball clays for a wide range of markets. Some small amounts of high-quality ball clay from the United Kingdom are still imported, particularly for use in sanitary ware. China is the world's leading producer of sanitary ware and tableware, so the search for high-quality ball clays continues in many parts of the country.

India

India has large resources of ball clay-type material, particularly in the Gujarat Area where Ashapura Minichem Ltd. produces 60,000 tpy. Other producing companies are Ambika Overseas Pvt. Ltd., Bhavani Minerals, and Mahavir Minerals Ltd.

Indonesia

There are a number of ball clay prospects in Indonesia, and the main one is PT Clayindo, part of the Sibelco Group. The ball clay concessions of the company are 100 km north of Pontianak (on the equator) on the island of Kalimantan (formerly Borneo). Geologically, the sequence is 4–5 m of overburden with a sequence of 10 m of light creamy brown ball clay interbedded with sandy horizons. A typical result from the area shows a fired brightness of 74, absorption of 17.5, and contraction of 3.7 at 1,120°C with iron and titania levels at 1.1 and 1.2 wt %, respectively. The silica level of 55% is reflected in the mineralogy of 73% kaolinite, 8% mica, and 19% quartz. The clay is suitable for a wide range of ceramic applications, particularly sanitary ware.

A number of ball clay deposits on the island of Belitung are being developed.

Malaysia

The largest producer in Malaysia is Unisil, which controls more than 90% of the market with up to 500,000 tpy, mainly destined for tile manufacture (locally called homogeneous tiles, which are the equivalent of gres porcellanato). The main tile producers are in Johore State with GTI (Kluang) producing 50,000 m²/day. Other producers are MML, Yilai, and Niro. The ball clay deposits are mainly situated near Kuala Lumpur, with recently discovered deposits in the Langgor Area. The Langgor Area shows extensive deposits of ball clay, which are being exploited for their sanitary-ware potential. The “B” grade clay is being exported to Taiwan and Thailand. A 20-t container for Taiwan is approximately US\$45–\$50/t CIF (cost, insurance, and freight). Up to 300 tpm are also being sold in containers to Thailand for use in tableware. The clays can be described as low-carbon, kaolinitic ball clay of medium particle size and low plasticity. The clay has low combined iron and titania, 2.2%, but alkalis are higher at about 3%. It has reasonable fired properties with 75 reflectance at 1,120°C. Rheology shows reasonably fluid clay, with the casting concentration reflecting the fine end of the PSD range. Carbon and salts are low.

The clay has potential in sanitary ware and possibly earthenware. The low carbon would make it suitable for fast-firing applications, though the low strength may detract from its use in tiles unless combined with more plastic ball clays. In general, its properties would lend themselves to a number of uses if suitable other ball clays and kaolins could be found to be a match to particular applications.

Recent exploration in Sarawak identified a series of ball clays over- and underlying coal seams in the Mukah Basin. These deposits are attracting attention from international companies because they show some potential for tiles, sanitary ware, and tableware. They are similar in quality to the ball clay deposits of the Pontianak region of Kalimantan.

Vietnam

Vinacerglass Imex is a member of the Vietnam Ceramic and Glass Corporation and is responsible for all resources for the country's glass and ceramic industries. It is interested in developing the Truc Thon ball clay deposit near Hanoi for the local sanitary-ware market.

The deposit was developed in 1964 to extract clay for refractories, and it was later realized that the clay was suitable for the developing sanitary-ware market. The area is geologically well studied and has been split into 500-m² blocks for development. The resource is given as 7 Mt of clay (includes ball clay and clay for refractories). The clay is present in a floodplain area, and the depth of clay is fairly shallow. A typical cross section is given in Table 7.

The ball clay seam is mined with local tubs, and much is sold in lump form. Some of the grade “A” ball clay is dried in the sun and bagged. There is much foreign investment in Vietnam—Inax, Kerat, Johnson, Ceasar, Laufen, and American Standard have sanitary-ware production in the country.

Thailand

WBB (Sibelco Group) and Imerys (in a joint venture with Banpu) have ball clay operations in the northern part of Thailand in Lampung Province. The Imerys deposits are at Maetan and occur as secondary deposits, laid down in seams derived from sedimentation of the weathered Triassic-rhyolitic tuffs of the region. There are 22 clay seams in the area that exhibit a range of properties from carbonaceous to siliceous ball clays with varying degrees of plas-

Table 7. Typical cross section of a floodplain area

Thickness of Horizon, m	Type of Material
4–5	Alluvial sands and soils (waste)
3–4	Colored clay (for bricks), 14–18% Al ₂ O ₃
2–3	Ball clay, 25–28% Al ₂ O ₃ ; Fe ₂ O ₃ 1.4–3.5%
1–2	Black clay, 22–25% Al ₂ O ₃ (not used)
Varies	Refractory clay, 25–28% Al ₂ O ₃

ticity and iron content. The raw-component clays are selected and mined from an open pit. The range of products is based on their casting rate, plasticity, and chemistry. Grades such as Sancast and Thaiplas S1 are produced for local markets and also some for export.

OUTLOOK AND FUTURE TRENDS

Ball clay production has steadily increased over the past few years and should continue to do so as ball clay producers look for new applications for their clays outside the ceramic industry. The ball clay industry within the United States faces little competition from imports because of transportation costs and the quality of the materials.

ADDITIONAL RESOURCES

Trade Journals

A list of selected publications related to ball clay and its end products follows:

- *American Ceramic Society Bulletin*, <http://www.ceramicbulletin.org>
- *Asian Ceramics*, <http://www.asianceramics.com>
- *Ceramic Forum International*, <http://www.cfi-web.de>
- *Ceramic Industry*, <http://www.ceramicindustry.com>
- *Ceramic Source*, <http://www.ceramicsource.org>
- *Ceramic World*, <http://www.ceramicworldweb.it>
- *Industrial Minerals*, <http://www.indmin.com/index.html>
- *International Journal of Applied Ceramic Technology*, <http://www.acers.org/act/default.asp>
- *Journal of the American Ceramic Society*, <http://www.acers.org/journal>
- *Ziegelindustrie International—Brick and Tile Industry*, <http://www.penrose-press.com>

Organizations

Ball clay and its end products fall under the purview of the following organizations:

- American Ceramic Society, <http://www.acers.org>
- Society for Mining, Metallurgy, and Exploration, <http://www.smenet.org>
- Geological Society of America, <http://www.geosociety.org>
- Clay Minerals Society, <http://www.clays.org>
- Canadian Ceramic Society, <http://www.ceramics.ca>
- European Ceramic Society, <http://www.ecers.org>

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Bentonite

Don Eisenhour and Franz Reisch

The term *bentonite* was first proposed by Knight in 1898 after he had originally named this clay *taylorite* after the site of the original mine at the Taylor ranch near Rock River, Wyoming. The name bentonite is from the Benton Shale, the formation within which the clay was thought to have occurred. The Benton Shale is named after Fort Benton, Montana, located more than 640 km to the north.

Several geologists in the early 20th century recognized that bentonite, found predominately in Cretaceous and Tertiary sedimentary rocks, was deposited as transported volcanic materials. This observation resulted in a definition based on origin. A widely quoted definition that is accepted by many geologists is the following by Ross and Shannon (1926, p. 77):

Bentonite is a rock composed essentially of a crystalline clay-like mineral formed by devitrification and the accompanying chemical alterations of a glassy igneous material, usually a tuff or volcanic ash; and it often contains variable proportions of accessory crystal grains that were originally phenocrysts in the volcanic glass. These are feldspar (commonly orthoclase and oligoclase), biotite, quartz, pyroxenes, zircon, and other various minerals typical of volcanic rocks. The characteristic clay-like mineral has a micaceous habit and facile cleavage, high birefringence and a texture inherited from volcanic tuff or ash, and it is usually the mineral montmorillonite, but less often beidellite.

This definition presents difficulties when applied to bentonite as an industrial mineral because it is based on origin and restricts the precursors of bentonite to ash, tuff, or volcanic glass. According to this definition, deposits that consist primarily of the clay minerals montmorillonite or beidellite but are of other than volcanic origin should not be called bentonite. However, many montmorillonite-rich deposits throughout the world that have non-volcanic origins are mined and sold as bentonite. Therefore, commercially, bentonites are defined exclusively on a mineralogical basis.

Grim (1973) gave the most widely used commercial definition of bentonite in a plenary lecture at the International Clay Conference (Association Internationale pour l'Etude des Argiles [AIPEA]) in Madrid, Spain. According to this definition, used in this chapter, bentonite is a clay consisting of essentially smectite group minerals, regardless of occurrence or origin. This definition

allows the inclusion of smectite clays that are sedimentary or hydrothermal in origin and are derived from nonvolcanic parent materials.

Bentonites are generally classified as either sodium (swelling) or calcium (nonswelling) based on their interlayer cations and corresponding ability to swell in water. Bentonites with Na^+ as the predominant exchangeable cation exhibit a high swelling capability in water, whereas bentonites with Ca^{++} as the predominant exchangeable cation exhibit much lower swelling ability. The term *sub-bentonite* was proposed to denote a low or moderate swelling bentonite, but it has largely fallen into disuse and is not recommended.

Within the United States “western bentonite” and “southern bentonite” are often used interchangeably with sodium and calcium bentonite, respectively. This terminology originated because the majority of calcium bentonites within the United States are located in the southern states of Mississippi and Alabama, and the higher-swelling, natural sodium bentonites are located primarily within the western states of Wyoming, South Dakota, and Montana. Other descriptive terms are based on bentonite grade such as high-yield and 13T, which have their origins in the drilling and foundry industries.

Not all bentonites fit easily into these common definitions. Some bentonites, especially those from Turkey and Australia, have Mg^{++} as the major exchangeable cation and are nonswelling in their natural form. Others, especially those with near-surface exposures that are covered with vegetation, have H^+ as their predominant exchangeable cation and are nonswelling. When dispersed in water, these natural H^+ bentonites can exhibit pH values as low as 4 (Knetchel and Patterson 1962). This is much lower than the pH of most calcium or sodium bentonites, which are typically between 8 and 10 in water.

Another type of bentonite, referred to as the potassium type, K-bentonite or metabentonite, is found in Ordovician and other Paleozoic rocks. This bentonite consists mainly of illite and mixed layer minerals and is generally assumed to have formed from volcanic ash. Smectite minerals are present only in minor amounts. This bentonite type contains significantly more potassium than the other types. The meta prefix is included in the name to denote the idea that this bentonite is the product of low-grade metamorphism or diagenetic alteration. The only known attempt to use K-bentonite was in 1928 when five or six cauldrons were mined near Dayton, Rhea County, Tennessee, for purifying lard (Gildersleeve 1946).

Table 1. Bentonite sold or used by producers in the United States, by use, *kt*

Use	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002
Domestic										
Absorbents										
Pet waste absorbents	302	455	574	607	604	773	788	862	902	899
Other absorbents	66	91	88	91	W†	W	W	W	W	W
Adhesives	W	W	W	11	15	13	14	6	2	2
Animal feed	78	97	98	65	110	77	74	47	52	42
Ceramics (except refractories)‡	24	W	W	W	W	W	W	W	W	W
Drilling mud	476	586	627	572	789	665	667	654	787	762
Filler and extender applications§	31	30	70	34	41	49	25	35	49	46
Filtering, clarifying, decolorizing	13	W	W	W	82	104	81	94	92	127
Foundry sand	733	712	745	772	901	869	888	835	746	762
Pelletizing (iron ore)**	466	509	646	674	536	529	540	500	522	536
Miscellaneous refractories	58	32	22	17	8	3	2	4	W	W
Miscellaneous††	2	55	288	242	126	80	83	67	91	117
Waterproofing and sealing	213	287	228	227	267	236	268	254	283	269
Total	2460	2850	3390	3310	3479	3398	3430	3358	3526	3562
Exports										
Drilling mud	90	34	87	102	150	65	69	56	73	59
Foundry sand	243	321	256	278	293	239	251	233	244	244
Other‡‡	72	81	89	46	101	123	121	115	129	106
Total	405	436	431	426	544	427	441	404	446	409
Grand total	2870	3290	3820	3740	4023	3825	3871	3762	3972	3971

Source: USGS Minerals Yearbooks.

* Data rounded to nearest thousand tons and may not add to totals shown.

† W = withheld to avoid disclosing company proprietary data; included with "Miscellaneous."

‡ Includes catalysts and pottery.

§ Includes cosmetics, ink, medical, paint, paperfilling, pesticides and related products, pharmaceutical, and plastics.

** Excludes shipments to Canada.

†† Includes chemical manufacturing, heavy clay products, and other unknown uses.

‡‡ Includes absorbents, fillers and extender, miscellaneous refractories, pelletizing, and other unknown uses.

HISTORY AND USE

Most of today's major uses of bentonite were developed in the 20th century. In the United States bentonite finds major uses in iron ore pelletizing, drilling muds, pet litters, and foundry sands (Table 1). Overall, global consumption follows similar trends to U.S. consumption, with the exception that use in pet litters is less, especially in developing countries. Significant secondary uses include waterproofing and sealing applications, animal feed additives, oil and grease absorbents, agricultural carriers, and filtering, clarifying, and decolorizing agents. Still smaller specialty uses of bentonite include asphalt emulsions, catalysts, paints, plastics, inks, greases, cosmetics, and pharmaceuticals.

The use of calcium bentonites can be traced back as early as 5000 BC, when they were used to cleanse and thicken woolen cloths in Cyprus (Robertson 1986). It is from this ancient use that calcium bentonites derive the name *fuller's earth*.

In the last century it was discovered that some calcium bentonites are effective at decolorizing or "bleaching" vegetable, animal, and mineral oils (Nutting 1943). This is especially true when calcium bentonites have been acid activated to improve their bleaching efficiency (Rich 1960; Torok and Thompson 1972). Acid-activated bentonites have grown in use relative to unactivated bentonites, especially for oils that are more difficult to bleach or when more highly refined oils are desired.

As used today, fuller's earth is a general descriptive term for clay or other fine-grained earthy material that is used in bleaching,

absorbent, and other related applications (for more details, see the chapter on fuller's earth in this volume). The name does not carry any specific mineralogical or compositional meaning and applies equally to minerals such as attapulgite and sepiolite. Each of these different minerals, however, is not equally suited to all applications in which fuller's earths are used. Premium products for decolorizing edible oils are largely based on acid-activated calcium bentonites.

In the United States, mining of natural sodium bentonite began in 1888 on the Taylor Ranch near Rock River, Wyoming, and in 1903 a mine was opened in Upton, Wyoming, within the bentonite beds surrounding the Black Hills. Mining of calcium bentonite began on a significant scale in the United States in Mississippi in the early 1930s (Bicker 1970). Today there are five major producers and 10 production facilities in Wyoming and South Dakota.

Significant use of bentonite as a sand bonding agent in foundries and as a drilling mud in the oil industry began in the late 1920s. The suspension and fluid loss control properties of western bentonites make them especially suitable for water-based drilling applications (Darley and Gray 1988). As a bonding agent in greensand molding, bentonite has the advantage of producing good compressive strengths when wet or dry (Anon. 1962, 1963, 1994; Sanders 1973). The natural sodium bentonites from the western United States also perform well at the elevated temperatures encountered during the pouring of molten iron and steel, resulting in good clay utilization and fewer casting defects.

Natural sodium bentonites from the western United States are recognized worldwide as performance standards for drilling, foundry, scoopable pet litters, geosynthetic clay liners (GCLs), and in a variety of other applications. These western bentonites continue to be used in markets worldwide despite the availability of local alternatives. This is especially true in applications where technical performance is essential.

Western bentonites are exported to Europe, Australia, and Chile for use in wine clarification. Significant quantities are exported to Europe and Asia for use in GCLs where long-term low permeability is desired. Many regional regulations require the use of western bentonite for GCLs in environmental and civil engineering applications. A number of public and private organizations are studying whether natural sodium bentonites are always superior in GCL applications or whether sodium-activated calcium bentonites can be engineered to achieve similar performance. For less demanding applications, sodium-activated calcium bentonites are commonly used in GCLs today.

Two other applications where western bentonites are widely used in export markets are foundries and oil-well drilling. For oil-well drilling, few bentonites in the world meet the demanding specifications set forth by the American Petroleum Institute (API) for nontreated, section-5 bentonite (Anon. 1993). For the less demanding grades, sections 4 and 6, regional sources are more commonly used. Iron and steel foundries use western bentonites to produce large, heavy-section castings. The superior thermal durability and hot strength of western bentonites are believed to be responsible for their performance advantages (Sanders and Doelman 1968).

Related to the use of bentonites for clarifying oils is their use in clarifying juice and wine. The colloidal nature and high surface area of montmorillonite are exploited in these applications to remove proteins and other submicron substances that contribute to color and opacity. Other mineral filtering aids such as silica sand, diatomaceous earth, and attapulgite work well for removing coarse particles but are relatively ineffective at removing suspended colloidal matter. For clarifying wines and juices, sodium bentonites are used much more frequently than calcium bentonites. Although local bentonites are available, wineries in Europe, Australia, Chile, and elsewhere prefer U.S. natural sodium bentonites because of their superior performance.

The ceramics industry uses bentonites to modify the flow properties of glazes and as plasticizers and extrusion aids in forming ceramic bodies. In the manufacture of both ceramics and refractories, bentonites are used at levels of 0.5% to 3.0% to improve green strength properties. Bentonites added to refractory gunning mixtures assist with sag control.

Bentonite finds some use in modifying the rheological behavior of water-based inks and paints, although attapulgites and organic modifiers are also commonly used. Organically modified bentonites are in wide spread use in oil-based inks, paints, and greases. In both water-based and oil-based applications, bentonite is used to impart anti-drip and anti-sag characteristics. It is also employed as a suspending agent for mineral pigments to improve package stability. In cosmetic and pharmaceutical applications, bentonite serves a similar function to that in inks and paints: It acts as a suspending agent in shampoos, lotions, and gels, and its high yield strength and pseudoplastic behavior allow for the creation of fluids that do not drip or run but flow easily when a spreading force is applied.

Because of their high surface areas and unique surface chemistries, bentonites have been used as catalysts in a number of chemical processes. One common application is the recovery of benzene, toluene, and xylene (BTX) compounds through UOP's (located in

Des Plaines, Illinois) Isomar process. In this process, acid-activated clay typically facilitates the recovery of para-xylene, but can also be used to enhance ortho-xylene and meta-xylene recovery as well. Smectites treated with transition metals such as copper and iron catalyze other reactions. Balogh and Laszlo (1993) describe a variety of reactions using clays, including electrophilic aromatic substitutions, addition reactions, elimination reactions, aromatization, hydrogenation, dehydrogenation, cyclization, Diels-Alder reactions, isomerization, dimerization, rearrangements, condensation, and amino acid and peptide formation under prebiotic conditions.

Cairns-Smith and Hartman (1986) describe the potential role of smectite clays in the formation of life. According to this interesting hypothesis, smectite clays may have been responsible for building the more complex molecules needed for the formation of life on earth.

PRODUCT SPECIFICATIONS

Among the industry standards available for bentonites are those used in drilling muds, foundries, absorbent granules, oil bleaching, cosmetics, and pharmaceuticals. Some standards are widely adhered to such as API standards for oil and gas drilling and United States Pharmacopeia (USP) standards for cosmetics and pharmaceuticals, whereas others such as those for foundry bentonites issued by the Steel Founders' Society of America (SFSA) are followed less rigorously. For most applications, a combination of individual customer requirements and supplier capabilities largely determine specifications. Some testing methods and specifications are described hereafter, by application.

Foundry

The SFSA provides specifications for sodium bentonites to be used as binders for mold and core sands or in preparing mold and core washes. These specifications are described under SFSA Designation 13T-86 (Anon. 1986), and bentonite products meeting these specifications are commonly referred to as 13T bentonites. The technical requirements under 13T are as follows: (1) the product moisture must be between 6 and 11 wt %, (2) the pH value must be equal to or greater than 8.2, (3) the green compression strength must be 15 psi or greater at a compactability of 46 to 51 for agreen-sand mixture containing 7% bentonite and 2.3% to 2.6% water, and (4) the methylene blue exchange capacity must be equal to or greater than 90 meq/100 g of bentonite.

In addition to standard technical requirements, SFSA 13T-86 also provides supplementary requirements that apply only if specified by the foundry customer. These include (1) a maximum exchangeable calcium content of 25 meq, (2) a liquid limit of between 600 and 850, and (3) a bulk density less than 50 g/qt.

The State Mechanical Industry Ministry of China issued foundry bentonite standards JB/T 9227-99 in 1999 (Wen 1998). These standards specify grades of bentonite based on wet tensile strength and green compression strength (Table 2).

Neither the SFSA nor Chinese foundry bentonite standards are widely adopted by foundries exactly as written. Nevertheless, they do provide good guides to the types of properties that are important and minimum requirements that are expected. In almost all cases, competitive products must meet or exceed these standards.

Drilling Mud

Specifications for bentonites supplied to the petroleum industry are set by the American Petroleum Institute under API Specification 13a (Anon. 1993). Specification 13a sets forth requirements for three grades of bentonite under sections 4 (bentonite), 5 (nontreated bentonite), and 6 (Oil Companies Materials Association [OCMA]

Table 2. Chinese foundry bentonite specifications (JB/T 9227-99) issued by the State Mechanical Industry Ministry in 1999

Based on wet tensile strengths (WTS)				
Grade	Moisture,* % maximum	Dry Size, <200 mesh	Methylene Blue Absorption, g/100 g minimum	WTS, kPa minimum
WTS-25	12	95	20	>2.5
WTS-20	12	95	20	2.0–2.4
WTS-15	12	95	20	1.5–1.9
WTS-5	12	95	20	0.5–1.4
Based on green compression strengths (GCS)				
Grade	Moisture,† % maximum	Dry Size, <200 mesh	Methylene Blue Absorption, g/100 g minimum	WTS, kPa minimum
GCS-10	12	95	20	>100
GCS-7	12	95	20	70–99
GCS-5	12	95	20	50–69
GCS-3	12	95	20	30–49

* Moisture specification 15% maximum in winter.

† Moisture specification 15% maximum in winter.

grade bentonite). Additional specifications in the United Kingdom can be found from the OCMA (Anon. 1969).

Section 4 (bentonite) requires rheological properties to be measured in a suspension of 22.5 g of bentonite added to 350 g of water. The dial reading at 600 rpm on a direct indicating viscometer must exceed 30, with a maximum yield point/plastic viscosity (YP/PV) ratio of 3. Filtrate volume must not exceed 15 cm³ and the amount of 75- μ m grit must be less than 4 wt %. Small additions of polymer extenders are permitted provided that all section 4 test requirements are met.

Section 5 (nontreated bentonite) requirements are measured in a suspension of 25 g of bentonite added to 350 g of water. Based on 600 and 300 rpm viscometer readings, the YP/PV ratio must not exceed 1.5. Sodium hexametaphosphate is then added to the suspension and the dispersed plastic viscosity and filtrate volume are determined. Minimum values of 10 cps for dispersed plastic viscosity and 12.5 cm³ for dispersed filtrate loss are required. The specific test procedures and specifications for API section 5 bentonite have been designed to ensure that high viscosities have not been achieved through enhancement with polymer extenders. Section 5 requirements further specify the absence of chemical additives.

Section 6 (OCMA grade bentonite) is described by the API as a bentonite that by the nature of its source cannot meet all the requirements of section 4. It may be treated with soda ash, polymers, or other chemicals to improve suspension performance. Rheological properties are measured in a suspension of 22.5 g of bentonite in 350 g of water. The 600 rpm dial reading on a direct indicating viscometer must exceed 30, with a maximum YP/PV ratio of 6. The filtrate volume must not exceed 16 cm³ and the amount of 75- μ m grit must be less than 2.5 wt %.

Iron Ore Pelletizing

A number of tests have been used to determine the suitability of bentonites for iron ore pelletizing (Davison 1969; Sastry and Fuerstenau 1971; Stone, Karpinski, and White 1971; Wakeman 1972). The most direct tests measure the wet and dry strengths of pellets formed by mixing iron ore powder with bentonite and water. Typically, however, producers of iron ore pellets run these direct tests more than bentonite suppliers.

The most common test used by suppliers to determine the suitability of bentonite for iron ore pelletizing is plate water absorption. This test measures the water absorption ability of a 2-g sample of bentonite placed on a porous sandstone plate in water. In North America and Europe the test is typically run for 18 hours. The amount of water absorbed is expressed as a percentage of the weight of the initial bentonite sample; for example, if 2 g of water are absorbed by the 2-g bentonite sample, the water absorption is 100%. Plate water absorption values greater than 800% are desirable. In China, IOP specification JC/T 592-1995 requires a 2-hr absorption test with a minimum value of 150% required for the highest grade, P-Q-1. In addition, the Chinese standard also requires a minimum free swell value of 15 mL/g for grade P-Q-1.

Other desirable bentonite qualities are low levels of volatile elements such as Na and K, low Si, low Cr and Ti, and high Fe. Na and K contribute to slag on the walls of blast furnaces, Si contributes to the overall slag content in the melt, and Ti and Cr alloy with iron. High iron is desirable because it contributes to iron yield rather than to slag. In North America, bentonites are typically supplied as a milled powder with 70% passing a 200-mesh screen. In Asia, products are supplied as powders milled to between 95 and 99% passing a 200-mesh screen.

Absorbent Granules

Specifications for absorbent granules provide for size, resistance to attrition, and absorption ability. One source of guidelines is provided in Federal Specification P-A-1056A, *Absorbent Material, Oil, and Water*. In the early 1970s, the American Society for Testing and Materials (ASTM) published similar specifications under C431-65, *Standard Methods for Sampling and Evaluation for Sorptive Mineral Products Used as Flo or Absorbents*, which has since been withdrawn.

In general, absorbent granules should be between 6 and 80 mesh in size, have a solubility of less than 1.5% in distilled water, and have the ability to absorb 0.8 mL of lubricating oil (or 0.9 mL of distilled water) per gram. Weidhaas and Brann (1955) describe some special tests for insecticides and other uses.

Bleaching Clays

Bench-scale tests using an approved standard as a reference determine the abilities of both natural and acid-activated bleaching earths to decolorize oils. Official natural bleaching earth standards are approved by the American Oil Chemists' Society (AOCS). The AOCS also provides testing guidelines under Official Methods Cc 8f-91, *Evaluation of Bleaching Clays and Absorbents*; Cc 8e-63, *Modified Bleaching Test for Soybean Oil*; Cc 8a-52, *Bleaching Test (cottonseed oil)*; and Cc 8b-52, *Bleaching Test (soybean and sunflower oils)* (Anon. 1998).

Specialty Applications

Bentonites are used in a variety of cosmetic and pharmaceutical applications as a thickener, a suspending and gelling agent, and a binder. Bentonites used in these applications must conform to the guidelines set forth by the USP/NF (National Formulary) (Table 3) (Anon. 2004). The two basic classifications for USP/NF products are bentonites and magnesium aluminum silicates. Bentonites are specified as dioctahedral smectites and magnesium aluminum silicates are mixtures of both dioctahedral and trioctahedral smectites.

Products in the dioctahedral category are classified as either bentonite or purified bentonite and are manufactured from montmorillonites. The magnesium aluminum silicates are subdivided into four grades, three of which (Types 1A, 1B, and 1C) are distinguished primarily by their viscosities. The fourth grade, Type IIA,

Table 3. USP/NF smectite specifications

Type	Al:Mg Ratio	Viscosity, cps	Pb, ppm (maximum)	As, ppm (maximum)	pH	Glycolated XRD (001)	Acid Demand, mL (maximum)	XRD* (060)
Magnesium aluminum silicates								
Type 1A	0.5–1.2	225–600	15	3	9.0–10.0	15.0–17.2	40	di/tri
Type 1B	0.5–1.2	150–450	15	3	9.0–10.0	15.0–17.2	40	di/tri
Type 1C	0.5–1.2	800–2,200	15	3	9.0–10.0	15.0–17.2	40	di/tri
Type 1IA	1.4–2.8	100–300	15	3	9.0–10.0	15.0–17.2	15	di/tri
Bentonite	—	—	40	5	9.5–10.5	15.0–17.2	—	di
Purified bentonite	3.5–5.5	40–200	15	3	9.0–10.0	15.0–17.2	40	di

* di = dioctahedral smectite, di/tri = mixture of dioctahedral and trioctahedral smectite.

is distinguished by its lower acid demand and higher Al:Mg ratio. The magnesium aluminum silicates are produced by blending montmorillonite with either saponite or hectorite. Although color is not specified by the USP/NF, these products are typically white with Hunter brightnesses greater than 85.

Bentonites are used in a wide range of other specialty applications. Specifications for these are typically negotiated between customers and suppliers and are not dictated by national or trade association standards.

MINERALOGY

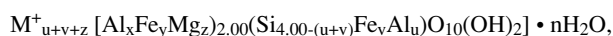
Smectite

The predominant mineral component of bentonite is smectite, which is responsible for bentonite's unique physical and chemical properties. The smectite group minerals include beidellite, montmorillonite, hectorite, nontronite, and saponite. Each mineral in the smectite group shares structural similarities but varies in chemical composition. Powder x-ray diffraction is particularly useful in identifying these various smectite minerals (Moorhead and Reynolds 1989).

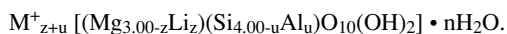
Structure

The structure of the smectite minerals is an octahedrally coordinated oxygen layer situated between two tetrahedrally coordinated silicon layers (Figure 1). These individual tetrahedral-octahedral-tetrahedral (TOT) layers are roughly 1 nm thick and are loosely held together by charge-compensating interlayer cations.

The smectite minerals are divided into two groups, dioctahedral and trioctahedral, depending on whether all three octahedral sites are occupied (trioctahedral) or only two are occupied (dioctahedral) (Güven 1988). The dioctahedral smectites montmorillonite, beidellite, and nontronite have the theoretical formula



where M^{+} represents the exchangeable cations. The theoretical formula for trioctahedral smectites such as saponite and hectorite is



Both classes of smectites display elemental substitution within the octahedral and tetrahedral sheets, and it is this substitution that is in part responsible for their unique physical and chemical properties. The magnitude and distribution of surface charge are largely determined by the number and type of substitutions within the tetrahedral and octahedral layers. The replacement of higher charged cations with those having lower charge, for example, the substitution of Al^{3+} for Si^{4+} , results in a net negative layer charge. This negative charge is counterbalanced by loosely held surface cations that are readily exchangeable.

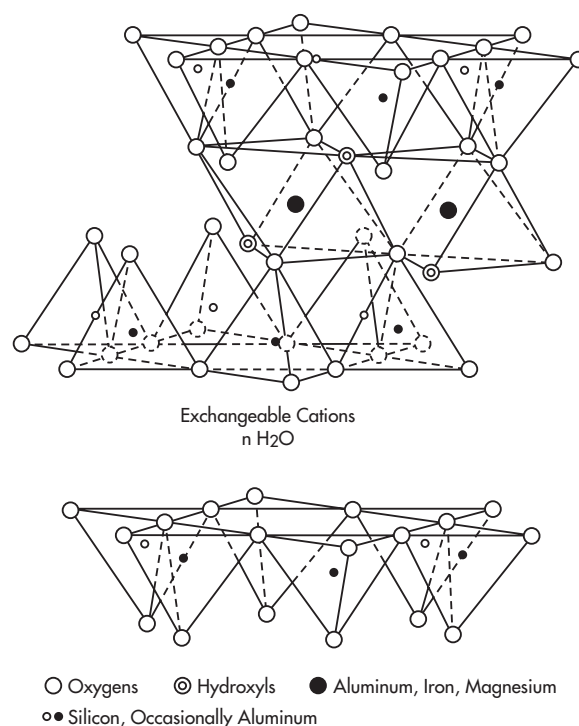


Figure 1. Structure of smectite

Exchangeable Cation Chemistry

The most common exchangeable cations in smectites are sodium, calcium, magnesium, hydrogen, and potassium. Along with the exchangeable cations, water molecules also exist between the TOT layers. The type of exchangeable cation present influences the nature of this interlayer water. Sodium allows one or more layers of water in the interlayer space whereas calcium allows only two layers.

The ability of smectites to exchange cations is described as the cation exchange capacity (CEC) and is typically expressed in milliequivalents per 100 g of clay (meq/100 g). Smectites exhibit cation exchange capacities between 60 and 170 meq/100 g, with values of 100 to 120 being typical. Bentonites commonly exhibit lower CECs than pure smectites because of the presence of nonclay minerals. The exchange capacities of bentonites are influenced by pH and, if iron is present within the structure, Eh (Stucki, Golden, and Roth 1984). Changes in Eh (oxidation-reducing potential) cause iron in smectites to change oxidation state and correspondingly result in changes in CEC.

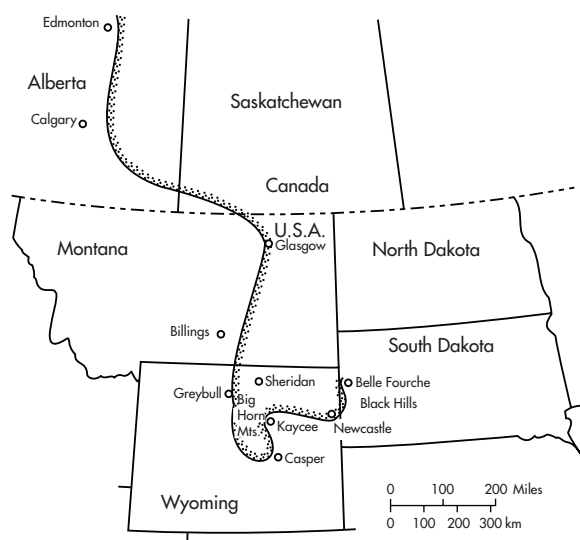


Figure 2. Western U.S. bentonite outcrop

The influence of iron on oxidation state on CEC can be seen in bentonites in Wyoming and South Dakota. Bentonites in this region can be gray or yellow, depending on the oxidation state of iron. Gray bentonites contain comparatively more Fe^{2+} whereas yellow bentonites are richer in Fe^{3+} . The yellow, or weathered, bentonites have historically exhibited superior colloidal properties. The reasons for this have been a subject of some debate. Knetchel and Patterson (1962) proposed that the superior properties may be related to an increased level of exchangeable calcium. Elzea and Murray (1990) suggest that oxidation of iron results in a reduction in surface charge, a corresponding decrease in exchangeable calcium, and an overall increase in the Na/Ca ratio.

Sanders and Doelman (1968) report observations similar to those of Knetchel and Patterson, that in weathered yellow outcrops calcium levels increase relative to sodium rather than the reverse. Because an increase in Ca/Na ratios appears generally accepted, it is likely that the improved performance characteristics of weathered yellow clays are related to either reduction in layer charge or a process of physical delamination.

The type of exchangeable cations greatly influences the behavior of smectite particles in aqueous suspensions (Foster 1953; Van Olphen 1977; Alther 1986; Lagaly 1989; Wolfbauer 1977). Sodium smectites display greater swelling and superior colloidal properties relative to calcium smectites.

Other Minerals

Other minerals found in bentonite can be classed in three categories: (1) those of volcanic origin, (2) secondary minerals that form in situ as a result of diagenesis and weathering, and (3) those that are of detrital origin. Typical volcanic minerals include feldspars, biotite, quartz, apatite, zircon, magnetite, and amphiboles. Occasionally unaltered volcanic glass is also present.

Minerals of low-temperature origin are poorly ordered opaline silica (Elzea, Odom, and Miles 1994), zeolites, calcite, gypsum, various iron sulfate and oxide minerals, and other clay minerals, including kaolinite and illite. Detrital minerals are the least common and can consist of any rock-forming minerals that are found in sedimentary environments. These minerals rarely exceed 10% of a commercially viable deposit.

OCCURRENCE

Bentonites are found in both marine and non marine environments ranging in age from Jurassic to Pleistocene. These beds can be very extensive geographically, range in thickness from several centimeters to tens of meters, and are usually parallel with the over- and underlying strata. Bentonites also occur as small, lens-shaped deposits. Other less common types of bentonite deposits are those that grade into unaltered host rock.

Bentonites are found in a range of colors, the most common being gray, yellow, olive green, brown, gray-blue, and white. Bentonites have a characteristic soapy texture and waxy appearance. Sodium bentonites often display a typical "popcorn" texture on weathered outcrops. Weathered calcium bentonites have an "alligator skin" texture.

Origin

The most common mode of formation of bentonite is through the in situ alteration of volcanic ash or tuff. A less frequent origin of bentonite is from the hydrothermal alteration of existing igneous rocks. The parent rock type for the majority of bentonite deposits was siliceous and ranged from dacitic to rhyolitic in composition.

The alteration of volcanic ash to smectite is a hydration reaction that requires magnesium and produces excess silica and alkali ions. Bentonite is most commonly found in marine strata, and the alteration of ash in contact with seawater is the most common environment of deposition of commercial bentonites. Other modes of formation include genesis through contact with alkaline lake and groundwaters.

Numerous forms of mineralogical, chemical, and textural evidence show that some bentonites formed through alteration of volcanic ash. Mineralogical evidence includes the observation that bentonite beds often contain euhedral minerals characteristic of volcanoclastic rocks. Chemically the major element and rare earth chemistry of bentonites is consistent with a volcanic origin (Elzea and Murray 1990). Observations under both optical and scanning electron microscopes reveal relict glass shards that have been replaced by smectite. The presence of unaltered glass shards in some deposits provides the strongest evidence of a volcanic precursor.

The time at which alteration of the ash to smectite occurs has been disputed. Theories that alteration of ash begins immediately on contact with seawater and that alteration begins shortly after the ash has settled to the seafloor or lake bottom have been proposed. Others believe that alteration takes place after burial. The Wyoming bentonites have shown to have been altered after burial within the top several hundred meters of subseafloor sediment. This alteration was caused by contact with diagenetic pore fluids evolved from Mowry seawater (Elzea and Murray 1990).

Distribution of Deposits

United States

Western Bentonite. Western or Wyoming bentonite is mined in three major districts in the western United States encompassing Wyoming, Montana, and South Dakota (Figure 2). These districts accounted for more than 90% of western bentonite mined in the United States in 2004.

The Black Hills District is the easternmost of the three districts and production is centered near Colony, Wyoming. This district extends south to Upton, Wyoming, north west to Alzada, Montana, and southeast to Belle Fourche, South Dakota. This area produces high-quality sodium bentonite that is primarily used in the foundry and drilling mud industries. In the past decade a large

amount of bentonite also has been mined for use as scoopable cat litter. Four processing facilities currently manufacture sodium bentonite products from this district.

The central Wyoming district is on the eastern edge of the Big Horn Mountains near the towns of Casper and Kaycee (Figure 2). One plant near Casper processes clay from this area.

The third district is along the western edge of the Big Horn Mountains. Bentonite mines are near Tensleep, Lovell, Greybull, Worland, and Thermopolis, and processing facilities are near Lovell, Greybull, Worland, and Thermopolis.

Western bentonite is mined from approximately eight beds and the majority of these are located within the Cretaceous Mowry Shale. The Mowry Shale is an organic-rich marine shale that was deposited along the Western Interior Seaway. The Mowry Shale is overlain by the Belle Fourche Shale and Frontier Formation, both of which contain commercially exploited bentonite beds. Bentonite is also mined from several beds in older formations in the Big Horn Basin.

All of the Wyoming bentonite beds are interstratified with marine sediments, except for the Newcastle bed mined in the Black Hills District. The Newcastle bed is limited in geographic extent and is believed to have been deposited in fresh water.

Southern Bentonite. Southern, or calcium, bentonite is mined in Texas, Mississippi, and Alabama. The primary uses for southern bentonite are as a bonding clay for foundry sands, a refining agent for oils and fats, an additive for animal feeds, and absorbents. This area is the second most productive bentonite mining district in the United States after Wyoming.

Deposits of southern bentonite are found throughout the Gulf Coast region and are located within formations of Upper Cretaceous to Middle Tertiary age. Commercially developed bentonites in Mississippi are produced from the Eutaw Formation (Upper Cretaceous), the Ripley Formation (Upper Cretaceous), and the Vicksburg Formation (Tertiary). Calcium bentonites mined in Alabama are located in the Ripley Formation. Texas contains extensive bentonite deposits, which are found in the Jackson and Gueydan Formations of Tertiary age.

Fuller's Earth. The majority of fuller's earth produced in the United States is mined from the Paleocene Porters Creek Formation. Processing plants are located along the edge of the Mississippi Embayment outcrop area in an arcuate band from Mississippi north to the southern tip of Illinois and then south through Missouri. The Porters Creek Formation ranges in thickness from 3 to 40 m in the north (Thomas 1981) to up to 150 m in Mississippi (Hughes 1958) and contains an upper weathered zone that is up to 12 m thick. Pyrite is concentrated in the underlying black to dark gray clay (Reisch 1992). Minerals present in this formation are calcium-magnesium smectite, opal C-T, kaolinite, illite, and trace amounts of halloysite and clinoptilolite.

Fuller's earth is also mined in the Miocene Monterey Formation in the southwestern corner of the San Joaquin Valley near Taft, California. The fuller's earth mined here is used predominantly for cat litter and industrial absorbents. Although the Monterey Formation is several hundred meters thick, mining is conducted only in those areas where the bulk density is low.

Other locations where fuller's earth is mined and processed are the Hawthorne Formation near Ocala, Florida, and the Twigg's Clay Member of Barnwell Formation near Wrens, Georgia.

Hectorite. Hectorite is a relatively rare magnesium-lithium silicate with in the smectite group. The majority of hectorite is mined from Tertiary age deposits near Hector, California, which is the type locality for this mineral. These deposits are believed to be altered alkaline lake sediments.

Hectorite is also located in a deposit in Amargosa Valley, Nevada. This deposit is an average of 4.6 m thick, covers a few square kilometers, and contains approximately 25% hectorite and 75% calcium carbonate. West of McDermitt, Nevada, an area consisting of hundreds of square kilometers contains pure to impure hectorite beds and lenses that are associated with volcanic sediments, zeolites, and carbonates; it has been commercially mined since 1986 (Odom 1992).

Other Deposits. Although bentonite production in the United States is predominantly from the Wyoming and Gulf Coast districts, there are a number of small bentonite producers in other parts of the country. Desiccant grade bentonites are mined from a deposit near Chambers, Arizona; this bentonite has also been used as a bleaching earth. Deposits near Vici, Oklahoma, have also been used as desiccant grade material. Sodium bentonite is mined near Adrian, Oregon, and is used in civil engineering and drilling applications. Bentonite deposits in Utah are used in the civil engineering and pet litter markets. Many local producers also supply bentonite for use as a binder in animal feed.

Canada

Bentonite deposits in western Canada are in Alberta, Manitoba, British Columbia, Saskatchewan, and the Northwest Territories. The deposits are found in Cretaceous- and Tertiary-age sediments and are predominant in the Upper Cretaceous marine sedimentary horizons (Grim and Güven 1978). These bentonite beds are often located with shales and limestones and also can occur as partings in coal beds. The Canadian bentonites are predominately calcium bentonites, although they are the same age as bentonites from the western U.S. district. Sodium bentonites are present but are much less common.

Sodium bentonite is mined and produced in Saskatchewan. Commercial products from this area include clays for drilling muds, civil engineering, foundry greensand molding, and animal feeds.

Mexico

Bentonite and fuller's earth are mined in Mexico, primarily in the central region, which contains a large amount of volcanic sediments. Many of the bentonites mined in Mexico are of a mixed calcium-sodium type. Calcium-type bentonites are concentrated in Hidalgo and the majority of sodium bentonite mining is conducted in Durango. Production of both calcium and sodium bentonites totaled more than 415 kt in 1999. In 2004, bentonite production was estimated at 450 kt (Anon. 1995).

South America

Brazil. Bentonite is present in the states of Minas Gerais, Rio Grande Sul, Santa Catarina, Paraíba, Paraná, and São Paulo of Brazil. The majority of these bentonite deposits are not commercially viable because of a high percentage of nonclay minerals. The fairly pure bentonite deposits in the states of Paraná and São Paulo supply more than 90% of bentonite mined in Brazil, which totaled 220,000 tons in 1998 (Russell 2000), making it the largest bentonite producer in South America.

Argentina. Bentonite is found in the provinces of La Pampa, San Juan, Mendoza, Neuquén, and Río Negro of Argentina. Natural sodium bentonite deposits are located in Río Negro and Neuquén. Argentina is the second largest bentonite producer in South America.

Peru. Bentonite deposits are commercially developed in Callao, Ica, and Piura in Peru. Calcium bentonites are the dominant type of bentonite deposit in Peru, although natural sodium bentonite deposits are found in Piura.

Chile. Bentonite mining in Chile is concentrated near Bocanegra, about 60 km east of Arica. Calcium bentonite supplies the local fishmeal pelletizing industry. Acid-activated bentonites are also produced in Lima.

Europe

United Kingdom. Deposits of calcium montmorillonite in England are referred to locally as fuller's earth. These deposits are present in Upper Cretaceous- and Jurassic-age sediments and are mined in Bedfordshire, Oxfordshire, and Surrey.

Germany. Calcium bentonite is extracted in Bavaria from deposits near Mainburg, Mossburg, and Lanshut. These bentonites are located in lenses found in the Oligocene to Miocene section between the Upper Marine Molasse and Upper Freshwater Molasse (Harben and Kusvart 1996).

Greece. The Greek island of Milos contains very large bentonite deposits, some greater than 30 m thick. These deposits have formed by the alteration of Lower Pleistocene volcaniclastics (Christidis and Scott 1996). Along with the United States, Greece is one of the largest exporters of bentonites.

Italy. Bentonites from Italy are mined predominantly on the island of Sardinia and have formed by hydrothermal alteration of trachytes and trachytic tuffs (Grim and Güven 1978).

Spain. Bentonite deposits in Spain are located near Madrid and Almeria. Calcium, natural sodium, and sodium exchanged bentonites are all produced in Spain. Many companies in Spain mine bentonite as a smaller part of their main operations, which involve the production of hormite clays.

Turkey. Numerous deposits of bentonite are present in Turkey, including white bentonites and desiccant-grade calcium bentonites. White bentonites exported to western Europe are mainly used as pet litters and desiccants, and in the production of detergent granules.

Africa

Morocco. The major exploitable bentonite deposits in Morocco are located southwest of Nador and together are estimated to have reserves totaling 1.8 Mt.

South Africa. Bentonite deposits are located in the Koppies district of the Free State and the Heidelberg area of Western Cape. Small deposits are present in the KwaZulu-Natal Province. Acid-activated bentonites are also produced in South Africa.

Australia

The continent of Australia contains many bentonite deposits, including natural sodium. Calcium bentonites are present in Queensland and New South Wales, and sodium bentonites are mined at Gurulmundi in New South Wales.

Asia

India. Indian bentonite reserves contain both calcium and sodium deposits, and the majority of reserves are located in Rajasthan and Gujarat. These bentonites are used for both iron ore pelletizing and foundry greensand molding. Lesser amounts are used for drilling, civil engineering, and pet litters. Indian bentonites are commonly dark red to brown in color and are high in structural iron.

Japan. Bentonite deposits in Japan are of the calcium, sodium, and acid, or hydrogen types. Some white bentonites are of high quality and are used in nanocomposite applications. Almost all bentonites produced in Japan are consumed internally.

China. Bentonite is mined in nearly every province of China; the leading producing provinces are Shandong, Sichuan, and Liaoning.

Bentonite types are both calcium and sodium, although natural sodium bentonites are comparatively rare and of low quality. Mining methods include open pit and underground. Although recent investments by major bentonite companies have resulted in the establishment of larger-scale operations, the majority of bentonite producers are small and local.

DEPOSIT EVALUATION

Exploration

Exploration for bentonite involves using geological knowledge and field investigations. The initial step in exploration is examining the geological environment. An understanding of the basic requirements for bentonite formation narrows the possible settings. Bentonite most commonly forms through the aqueous alteration of volcanic ash. In addition the predominant environment of post-depositional alteration is marine in nature. Bentonites are largely restricted to formations of Cretaceous and Tertiary age. Using these factors, a typical bentonite-forming environment will be an area of past volcanic activity that was located near a substantial body of water.

The next step in exploration is field investigation of a potential deposit. At this time the target area is examined for the presence of bentonite in outcrop. Once the presence of bentonite is confirmed the nature of the deposit is determined via surface mapping combined with drilling. The data from drill logs and maps allow a general assessment of the reserve volume and quality.

After a deposit has been confirmed as viable, other factors are taken into consideration before further expenditure in detailed drilling, testing, and mapping. The thickness of the overburden, distance to major transportation routes and markets, and governmental permitting requirements all must be taken into account.

Mineralogical Evaluation

Examining the mineralogical components of a deposit is an important part of deposit characterization. A thorough understanding of the physical and chemical properties of the clay minerals present will enhance understanding of the deposit, allowing for proper economic utilization. Beneficiation of clays is an increasingly important process as many of the higher quality deposits become depleted. Detailed knowledge of the physical and chemical properties of a clay can be used to design processes for optimum utilization. As higher technology processes continue to be refined, clay minerals are increasingly required to meet more demanding specifications.

Analytical methods used in the study of clay minerals include x-ray diffraction, differential scanning calorimetry, infrared spectroscopy, and zeta potential measurements. Other methods are used to determine particle size distribution, surface area, and interlayer cation chemistry.

Appraisal of Field and Laboratory Results

Bentonite testing consists of a combination of both standard and customer-specified tests. Typical standard tests include rheology testing, as outlined by the API, and foundry bond testing, as specified by the American Foundrymen's Society. ASTM test procedures cover free swell, liquid absorbance, and water permeability. Individual companies also conduct special test procedures designed to satisfy individual customer requirements.

In addition, numerous test procedures are set forth by varying organizations for specialized markets. Examples of such tests are bleaching oil procedures set forth by the AOCS and purity requirements outlined by the USP/NF.

After the relevant data on a deposit are gathered, the information is synthesized with the spatial data on the location of drill

holes. Maps of the deposit are generated, giving a detailed analysis of the deposit that includes clay thicknesses, grades, and overburden depths. This information is used to calculate the expected reserve of the various grades of bentonite. Estimating reserve is one of the first and most important phases of deposit evaluation, but other factors must be taken into account before mining can begin. Overburden amounts and type, distance to processing facilities, transportation issues such as roadways and right-of-ways, and the various legal and environmental permitting requirements all must be accounted for before mining can begin.

MINING AND PROCESSING

Mining

The most common method of mining bentonite is the open pit method. This involves removing overlying material to expose the desired commodity, in this case bentonite. Bulldozers, scrapers, and excavators, and often a combination of these types of equipment, remove the overburden. In a typical bentonite mine the topsoil and subsoil are first removed and stockpiled separately for redistribution during pit closure and land reclamation, and the overburden is then removed. In a typical Wyoming bentonite mine a deposit is mined in stages: After the bentonite is removed from the first area, the overburden from the adjacent area is placed in the void left by the removal of the bentonite and this sequence continues as mining progresses. Scrapers, front-end loaders, or excavators extract the bentonite and load it into trucks for transport to the processing facility.

Western bentonite overburden thicknesses range from zero up to 10 m. Mineable bentonite beds range in thickness from less than 1 m to up to 2 m. A general rule of economic recovery of bentonites requires that the ratio of overburden to clay thickness be less than 10:1, although this ratio may be exceeded where other logistic or market factors are favorable.

Although most bentonite mining uses open pit methods for extraction, some underground mining is practiced. Underground mining methods are used extensively to mine bentonites in Durango, Mexico, and in many locations in China.

Processing

As mined, most bentonites have a moisture between 25 and 35 wt %. Processing the clay usually requires some combination of field drying and plant drying. In arid regions, field drying alone can reduce moistures to less than 12 wt %. Coal-fired rotary dryers are commonly employed at a processing plant when additional drying is required. Final product moistures typically range between 7 and 12 wt %. Care must be taken to avoid overdrying bentonites because this can result in reduced performance.

After drying, bentonites are sized by passing the ore through a combination of roll crushers, screens, and roller mills. Where extremely fine particle sizes are required, air classification is often used either during milling or as a separate stage of processing. Polymers to improve viscosity and fluid loss are typically added either directly before or after milling. Polymer additions vary depending on the application, but levels between 0.25 and 1.50 lb (0.1 to 0.7 kg) per ton of clay are typical. Long-chain water soluble polymers are most commonly used to enhance the performance of bentonites.

Soda ash is typically added either in the field or at the plant before drying. In the field, soda ash is added as stockpiles are built or on clay that has been spread out to dry. Both dry and wet additions of soda ash are common in field operations. Plant additions of soda ash are typically made to wet clay using a paddle mixer to uniformly distribute the components. Water may be added to improve

the reaction between soda ash and clay, but excessive water is avoided because of the higher drying costs associated with higher moistures. In some operations, pug mills and extruders help mix soda ash and clay. The more aggressive mixing by extruders has the added benefit of improving clay performance through mechanical delamination.

For high-end cosmetic and pharmaceutical products, water washing commonly removes impurities and improves brightness. In this process, bentonites in low-solids slurries are subjected to a series of wet screening, hydrocyclones, and centrifugation to remove nonclay impurities. Soda ash additions are made before drying on rotary drums to produce flake products or by spray to produce powdered products. An additional fine milling step sometimes further reduces particle size to less than 20 μm .

To produce acid-activated clays, sulfuric or hydrochloric acid is added to a clay slurry and allowed to react for several hours. Pressure filtration removes residual acid from the clay. An alternative method for producing acid-activated bentonites involves the formation of "noodles," which are then acid-leached and washed without filter presses. The rinsed acid-activated clays are then dried and ground to the desired particle size. Acid activation typically increases Brunauer Emmett Teller (BET) surface areas from less than 10 m^2/g to more than 250 m^2/g . This method of surface area measurement is based on the physisorption and desorption of nitrogen.

ORGANOCLAYS

In the second half of the 20th century it was discovered that smectite clays could be organically modified to make them function well in low-polarity solvent systems such as mineral oils, toluene, xylene, and diesel fuel. The basic technology involves exchanging Ca and Na cations with cationic surfactants, especially quaternary amines. This exchange process converts hydrophilic smectites into those that are organophilic (hydrophobic).

Although both types of smectites (hydrophilic and organophilic) function by delaminating to form colloidal size particles, the mechanisms for dispersion are quite different. In aqueous systems, sodium smectites disperse through the hydration energy of water and are electrostatically stabilized as a result of their negative charges. In contrast, electrostatic and enthalpic forces do not dominate in nonpolar systems, so the primary driving force for dispersion is entropic.

Organoclays have found a wide variety of uses in low-polarity systems, and new applications are constantly being developed. A particular area of recent focus has been the development of organoclays for use as functional fillers in plastics. Numerous commercial applications of clay-polymer composites have appeared in the past few years.

Applications

Paints and Coatings

Organoclays serve three primary functions when used in solvent-based paints and coatings: (1) anti-settling, (2) anti-sag, and (3) anti-drip. In high-end coating applications finely ground wet-process organoclays ensure a smooth and uniform surface finish. In lower-end coating applications such as traffic paints, coarser ground dry-process organoclays are more commonly used. Typical use levels in paints are between 0.3 and 1.1 wt %.

Printing Inks

In printing inks, organoclays provide stable viscosity, control misting, and can improve water resistance. High purity and fine grinds are required in this application. Typical use levels in printing inks are between 0.2 and 3.0 wt %.

Lubricants and Greases

Water-washed organoclays that are free of abrasive grit are used in the manufacture of greases. Organoclays are especially used to thicken high-temperature greases because of their thermal stability. One potential weakness of organoclays in greases is their poor interaction with some corrosion inhibitors. These anticorrosion additives can have a detrimental effect of an organoclay's ultimate viscosity. Typical use levels in greases are between 5 and 10 wt %.

Drilling Fluids

Although both organobentonites and organohectorites are used in oil-based drilling applications, the majority of the volume is in low-end dry-process organobentonites. These low-end organoclays do not require the fine grinding required for paint grades and easy-dispersing grades. The high shearing encountered in the drilling process provides enough energy to disperse even coarser grades of organoclay.

For deep well drilling where greater thermal stability is required, organohectorite is used in place of the more cost-effective organobentonites. Bentone 38 (Elements Specialties, Inc., Hightstown, NJ) is the primary product used in these high-temperature applications. For quite some time Bentone 38 was the only suitable product on the market. Alternatives, however, are now becoming available. Typical use levels in drilling fluids are between 2 and 5 wt %.

Adhesives and Sealants

Organoclays are principally used in adhesives and sealants to prevent running or sag during the drying or setting process. Organoclays are used not only because of their rheological properties but also because they typically do not negatively affect the physical properties of the system. As an example, organoclays are used in polysulphide sealants for the construction industry to maintain slump resistance in vertical joints during curing. Typical use levels in adhesives and sealants are between 1 and 3 wt %.

Ceramics and Refractories

Organoclays are used as a binder in the manufacture of some refractory bricks and monolithics, especially where the presence of water in the binder system is detrimental. An example is calcined dolomite refractories, where an oil-based binder system prevents the hydration of the lime and magnesium oxide.

Organohectorite is sometimes preferred in the manufacture of monolithics because of its higher thermal stability in the range of 200° to 400°C. In some applications organobentonites do not maintain enough viscosity in this temperature range to prevent sag during firing. Higher-temperature thermal stability is a general characteristic of organohectorites. Typical use levels in ceramics and refractories are between 0.3 and 1.5 wt %.

Consumer Products

Wet-process organohectorites and organobentonites are both widely used in cosmetics and personal care products, especially fingernail lacquers, antiperspirants, lipstick, sunscreens, and eye products. Hectorite treated with a trialkylaryl ammonium cationic surfactant is widely used in fingernail lacquers because of the medium-to-high polarity solvents used in their formulations.

This market has increasingly shifted a way from using dry organoclays toward using mastergels. Mastergels are organoclays that have been pre-dispersed in commonly used solvents such as mineral oils, SD 40 alcohol, lanolin oil, cyclomethicone, or combinations of these. Mastergels have grown in popularity in the personal care industry because of their ease of use.

In response to customer requests, organoclay suppliers recently introduced products based on surfactants not derived from animals. Examples include a vegetable-derived quaternium-18 organobentonite and a vegetable-derived stearyl ammonium organobentonite. Typical use levels in personal care products are between 0.3 and 1.5 wt %.

Material Requirements

Organoclay systems require three basic components to function properly: (1) clay, (2) a cationic surfactant, and (3) a polar activator. Conventional organoclays incorporate two components, clay and surfactant, into the organoclay product, and the end user adds a polar activator. Self-activating or self-dispersing organoclays combine all three components, clay + surfactant + activator, in a single product.

Because of the volatility of some polar activators like methanol and acetone, they cannot be incorporated directly into a single product, so self-dispersing organoclays typically contain a different type of polar activator than is used in conventional organoclay systems. Although self-dispersing organoclays offer added convenience, in many applications they also have somewhat lower gel strengths than conventional organoclays. Consequently a number of users still prefer conventional organoclays to the newer, self-dispersing grades.

Clays

The type of clay used in the production of an organoclay is as important for the final performance as the surfactant and the polar activator. No simple correlation appears to exist between a clay's performance as an organoclay and its performance as an untreated, water-based, rheological additive. Consequently conventional tests of free swell, viscosity, cation exchange capacity, and plate water absorption do not directly predict a clay's performance potential as an organoclay.

Bentonites from the Black Hills region of South Dakota and Wyoming have been widely used in the manufacture of both wet and dry-process organoclays. To date, the only commercially available organohectorites are based on hectorite mined from Hector, California.

Surfactants

The majority of organoclays are surface modified by reacting bentonite or hectorite with a tetraalkyl ammonium cationic surfactant. These are used in solvent systems based on mineral spirits, hexane, toluene, xylene, styrene, alkyds, and vegetable oils.

The second most common organoclay surface modification is achieved by reacting a smectite clay with a trialkylaryl ammonium cationic surfactant. This surface treatment produces an organoclay that will disperse in higher polarity solvents than organoclays produced with a conventional dimethyl ditallow quaternary ammonium surfactant. Common systems that use a trialkylaryl ammonium organoclay are epoxies, polyesters, polyamides, polyurethanes, acetone, methyl ethyl ketone, ethyl acetate, ethylene glycol ether, propanol, and ethylene glycol.

Polar Activators

Polar activators facilitate the dispersion of organically modified clays and help achieve stable gel strength and high gelling efficiencies. Most self-dispersing grades either have some form of polar activator incorporated into the organoclay during production or have an excess of surfactant loading. Table 4 lists types of polar activators and typical amounts required based on the weight of organoclay.

Processing

The two basic methods of manufacturing organoclays are dry processing and wet processing. The dry process produces low-end organoclays and the wet process produces high-end organoclays. In both processes, the addition level of surfactant is critical. The optimum level of surfactant is usually between 27 and 34 wt %, although some self-dispersing grades have surfactant loadings >40 wt %. For any given clay, the optimum level must be maintained within $\pm 1\%$ or performance can be degraded. Undertreatment is usually more detrimental than overtreatment.

The drying temperature and final moisture are also important factors. Exposing organoclays to temperatures $>100^\circ\text{C}$ can be detrimental to performance. Similarly, over or under drying can also be detrimental. Optimum final product moisture should be in the range of 1% to 3%.

Dry Process

In the dry process, warm surfactant is added to 200 mesh clay (with or without a small amount of water) to form a dough. For best performance, the dough is thoroughly mixed and (preferably) extruded under high shear. The wet organoclay is then dried and ground to the desired particle size. In addition to reducing grit, grinding to a finer particle size improves the dispersibility of the final product.

Wet Process

In the wet process, the clay is dispersed in water at a total solids level between 2% and 5%. The resulting clay slurry is then hydrocycloned and centrifuged to remove nonclay impurities. In a separate mix tank, the surfactant is dispersed in warm water (50° to 80°C) at a level of 3% to 8%. The surfactant/water mixture is then added to the clay slurry under high shear or strong agitation. The resulting organoclay suspension is then filtered to (a) increase the solids level and (b) remove excess Na and Ca salts produced by the reaction of the surfactant and clay. The filter cake may be washed one or more times to remove additional salts. The cake is then dried and ground to the desired particle size. To improve the rate of dispersion, high-end organoclays are commonly milled to a mean particle size of between 1 and 10 μm .

FUTURE TRENDS

An area of active research in the past decade has been the use of smectites as functional fillers in polymers. In these applications, individual smectite particles are dispersed within a polymer matrix to form a polymer-clay composite material. Because the thicknesses of the dispersed clay platelets are approximately 1 nm, the composite materials formed are commonly referred to as *nanocomposites*.

The steps involved in making smectites suitable for nanocomposites are similar to those for making organoclays for conventional applications such as greases and printing inks. Smectites are beneficiated to remove other mineral impurities and then surface modified with a surfactant to make them disperse within the host polymer. Organoclays designed for use in nanocomposites primarily differ from conventional organoclays in their types of surface modifications and their greater levels of purity. Smectite-based nanocomposites have the potential to improve the thermal and mechanical properties of engineering plastics, increase chemical resistance, act as flame retardants, and decrease the permeability of films.

A number of surface-treated smectite products have been introduced into the market by leading organoclays manufacturers or through alliance partners. The overall use of smectite-based nanocomposites is currently limited but is expected to grow as markets adapt to this new technology.

Table 4. Chemical polar activators commonly used with conventional organoclays

Activator	Percentage*
Methanol (95%)/water (5%)	33
Propylene carbonate (100%) [†]	33
Propylene carbonate (95%)/water (5%)	33
Ethanol (95%)/water (5%)	50
Acetone (100%) [†]	60
Octylphenoxy polyethoxy ethanol [†]	75

* Percentages based on weight of organoclay.

[†] When a water-free polar additive is desired.

Over the past decade, the use of GCLs has continued to show strong growth and new bentonite-based liners continue to be developed. Efforts are being made to extend the effective lifetime of liners and to improve their resistance to a variety of environmental contaminants. Investigations are also taking place to better understand the performance differences between natural sodium bentonites and sodium-activated calcium bentonites. The results of these investigations could influence GCL specifications set forth by regulatory bodies.

A significant amount of research has been conducted on the synthesis of pillared clays (Schoonheydt et al. 1999; Gil, Gandia, and Vincente 2000; Cool and Vansant 2004). The unique mesopore dimensions and high pore volumes of pillared clays have demonstrated potential viability in several adsorption and catalytic applications involving relatively large molecules of high value. Commercial adoption of pillared clay technologies, however, has been slow to develop. This has been in large part because of their high manufacturing cost relative to conventional adsorbents such as zeolites and because of difficulties involved in producing materials that have sufficient selectivity and reproducibility for demanding adsorption and catalytic applications. It remains to be seen whether the unique characteristics of pillared clays will begin to be exploited more widely in commercial applications.

The unique surface chemistries and high surface areas of smectites continue to make them a focus of many research efforts. Their colloidal properties and nanoscale dimensions are likely to be increasingly exploited as emerging technologies focus on nano- and mesoscale interactions and processes.

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Common Clays and Shale

Karan S. Keith and Haydn H. Murray

INTRODUCTION

Common clays are a naturally occurring, fine-grained material composed predominately of hydrous aluminum silicates. The term *common clay* encompasses a wide variety of clay types, including fine-grained rocks such as shale. Common clays and shale are a useful geologic material because they typically exhibit plastic behavior when wet. This material can then be formed into desired shapes and fired to produce a product with rock-like hardness. Common clays and shale are the most widespread ceramic materials. Products made from these clays include items such as structural and face brick, drain tile, vitrified pipe, quarry tile, flue tile, conduit, pottery, stoneware, and roofing tile. Large quantities of common clays are also used to make construction materials such as lightweight aggregate and portland cement. They are used as filler in paint and other products, for packing dynamite blast holes, and for plugging oil and gas wells that are no longer in use.

GEOLOGY

Mineralogy

Common clays occur in a variety of environments and in many different rock types across all time periods of the geologic record. The source material includes glacial clay, soils, alluvium, loess, shale, weathered and fresh schist, slate, and argillite. Fireclay and kaolin are sometimes considered common clays, particularly when used in the manufacture of structural clay products. Mineralogically, common clays are highly varied, although the most common constituent is usually one of the members of the mica mineral group. Mica clays include illite, sericite, muscovite, and biotite. Other frequently occurring clay mineral components of common clays are kaolinite, smectite, mixed-layer clays, and chlorite. Quartz and other detrital minerals are typical nonclay minerals present in rocks mined for common clay.

Illite is one of the most abundant clay minerals found in sediments and sedimentary rocks and one of the most prevalent minerals in common clay resources. *Illite*, a term introduced by Grim, Bray, and Bradley (1937), is mica-type clay mineral that was named after an abbreviation for Illinois. Illite is a low-temperature mineral formed at the earth's surface. It is a hydrated potassium aluminum silicate (Figure 1) in which some iron is usually substituted for aluminum in the structure. Illite is similar in structure to smectite, the main difference being that in illite the interlayer cation is potassium and in smectite it is sodium, calcium, or magnesium.

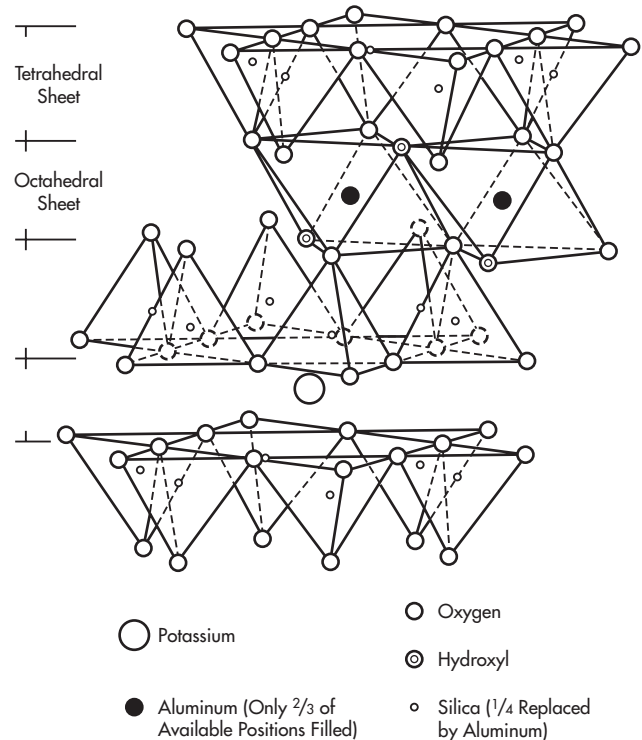


Figure 1. Structure of illite

Because of the similarity in structure, it is common to have smectite interlayered with illite, which is termed a *mixed-layer* clay. Smectite is an expandable clay, and if the mixed-layer clay material contains significant quantities of smectite, its presence can lead to excessive shrinkage during drying, in addition to other problems.

Clays and shale from the Pennsylvanian strata in the central and eastern portions of the United States have an excellent range of properties for making structural ceramics and low-grade refractory shapes. Commonly these strata have a refractory underclay or fireclay beneath a coal bed and a red-firing, illite-chlorite-rich roof shale above the coal (Hughes 1993). The roof shale is sometimes upwashed and coarsening, which allows producers to create shale or fireclay blends

that have adequate plasticity for forming the material. Additionally, there are often enough sand- and silt-size nonclay minerals to open the body and speed burnout during firing.

Physical and Chemical Properties

Common clays have a wide range of physical properties, making them applicable in many different structural products. These physical properties include plasticity, green strength, dry strength, drying and firing shrinkage, vitrification range, and fired color. The properties desired vary with the structural clay product made. For example, clay used in making conduit tile must be very plastic and have high green and dry strengths and uniform shrinkage. These properties do not have to be as closely controlled in manufacturing drain tile or common brick.

Plasticity is defined as the property of a material to undergo permanent deformation in any direction without rupture under stress beyond that of elastic yielding. *Fat* clays are clay materials that have a high plasticity; *lean* clays have low plasticity. Many factors can influence the plasticity of a clay material, including mineralogy, particle size, particle shape, organic matter, soluble salts, adsorbed ions, and the amount and type of non-clay minerals present.

Green strength and dry strength are important properties of clays used in structural applications because most structural clay products are handled in the manufacturing process and must be strong enough to maintain their shape. *Green strength* refers to the strength of the clay material in the wet or plastic state, while *dry strength* is the strength of the clay after it is dried. Dry strength depends on the proportion of fine particles present; the shape of the individual particles; the degree of hydration of the clay fraction; the method of forming the ware; and the rate and thoroughness of the drying. The presence of a small amount of smectite, which occurs in very fine hydrated particles, generally increases dry strength. Green strength is influenced by many of the same variables as plasticity.

Drying and firing shrinkages are critical properties of clay used for structural clay products. *Shrinkage* refers to the loss in volume of a clay material as it is dried or fired. Drying shrinkage depends on the water content, the character of the clay minerals, and their particle size. Most plastic clays shrink appreciably with drying, often producing cracking and warping. Clays with low plasticity, such as sandy clay, have low shrinkage but can produce a weak porous body. An excess amount of smectite minerals (10% to 25%) commonly causes excessive shrinkage, cracking, and slow drying. Firing shrinkage of the raw clay depends on the density of the material, volatiles that are present, the types of crystalline phase changes that take place during firing, and the dehydration characteristics of the clay minerals.

Vitrification (or glass formation) is a process of gradual fusion in which some of the more easily melted constituents produce increasing amounts of liquid as the temperature is increased. This liquid produces glass as the material is cooled, and the glass is the bonding material in the final fired product. The temperature range of vitrification during firing is a very important property of clays and shale used in structural clay products. Some clay has a narrow vitrification range, requiring close monitoring of kiln temperatures during firing. Clays consisting primarily of illite, smectite, or chlorite have a lower vitrification temperature than kaolinite-rich clay. Mineral impurities such as calcite and feldspar lower vitrification temperatures by acting as fluxes. Temperature and duration of firing will determine the degree of vitrification attained. The amount of shrinkage and porosity required in the final product most commonly dictates the extent of vitrification.

Uniform color is an essential property of many structural clay products. The color of a final fired product is influenced by a variety of conditions: the state of oxidation and particle size of the iron minerals; the firing temperature and degree of vitrification; the proportion of alumina, lime, and magnesia in the clay material; and the composition of the gases in the kiln during the burning operation. High-grade white-burning clay contains less than 1% Fe_2O_3 , buff-burning clay ordinarily contains 1% to 5% Fe_2O_3 , and red-burning clay contains 5% or more Fe_2O_3 . Although several factors also affect product color, finely divided iron-bearing minerals are the primary materials influencing color in the final fired product.

Mineralogy of the clay or shale deposit can most easily be determined by x-ray diffraction. The type and proportion of clay minerals present directly influence the amount of iron-bearing minerals in the material. A raw material that is predominantly illite becomes red when fired and gets hard at relatively low temperatures. Products that could be made from this material include red bricks, drain tile, and building tile. The presence of kaolinite in a raw material generally results in material that burns light or white and is hard to fuse. Products made from these clays are light or buff bricks and refractory brick.

PRODUCTION AND MARKETS

Common clays are widely distributed, usually easily located, and are often used in products that do not require elaborate processing. Typically, common clays and shales are dug from open pits, and these pits must be near the processing plants to minimize production costs. Usually both the raw material and the finished products are heavy and the profit margin is low, so production costs must be controlled. Most products made from these materials are processed and marketed in a similar manner to refractory clays. Common clays and shale require little beneficiation. Typically they are crushed or ground only before pugging and extrusion. Physical contaminants such as concretions are removed by dry screening. Beneficiation for clays needed in ball clay or kaolin applications may occur in the form of drying or air flotation. Clays used in refractories are often blended to meet product standards. Figure 2 is a generalized flowsheet for processing clays used to make structural clay products.

In 2003, approximately 160 companies in 41 U.S. states produced common clays and shale. In states not reporting production, common clays and shale probably were mined and sold for construction applications by companies not participating in the U.S. Geological Survey canvass of producers. Common clay production in the United States, at the mine, was 23.2 Mt (a slight increase from 2002) with a value of \$149 million. This increase was the result of strong demands from the construction market. Major domestic uses for common clays are distributed as follows: 56% brick, 17% cement, 17% lightweight aggregate, and 10% other uses.

The average price for all common clays and shale sold in the United States and Puerto Rico in 2003 was \$6.45/t. The price of common clays and shale sold for lightweight aggregate production in 2003 was estimated to be \$13.70/t. The price of lightweight aggregate products ranged from \$30 to \$50/t for most applications.

Leading producer states of common clays and shale in 2003 were, in decreasing order: North Carolina (2.4 Mt); Texas (2.16 Mt); Alabama (2.02 Mt); Georgia and Ohio (1.31 Mt each); Missouri (1.05 Mt); California and Oklahoma (1.03 Mt each); South Carolina (1.02 Mt); and Kentucky (925 kt).

Sales or use of common clays and shale increased to 23.2 Mt in 2003, matching production. The major markets were building brick (12.8 Mt), production of lightweight aggregate (4 Mt), and portland cement clinker manufacture (3.95 Mt). Sales of lightweight aggregate

can be subdivided into concrete block (2.37 Mt), structural concrete (908 kt), highway surfacing (364 kt), and miscellaneous lightweight aggregates (361 kt). Other markets include drain tile, floor tile, flue linings, pottery, refractory products, roofing granules, sewer pipe, and structural tile.

The largest user of common clays and shale is the brick manufacturing industry. Production of bricks increased from 8.47 million in 2002 to 8.6 million in 2003, whereas shipments of brick increased from 8.04 million in 2002 to 8.54 million in 2003. This increase was the result of continued demands from the construction sector.

The demand for clay floor and wall tile also increased in 2003. Production increased from 622,000 floor tiles and 649,000 wall tiles in 2002 to 652,000 floor tiles and 672,000 wall tiles in 2003.

Production of vitrified clay sewer pipe and fittings decreased to 143,000 units in 2003 from 159,000 units in 2002, whereas shipments increased to 151,000 units in 2003 from 139,000 units in 2002. The increase in shipments resulted from using stockpiles for clay pipe and tile products (Virta 2004).

RESEARCH AND TESTING

Developing and testing most common clay products demands preparing test pieces of specific dimension, and drying and firing properties (Klinefetter and Hamlin 1957; Clews 1969; Grimshaw 1972). Fired test pieces are evaluated for shrinkage, warping, cracking, permeability, modulus of rupture, and compressive strength. Color and soluble salt content are also important properties for some clay products.

A collaborative effort between the Illinois Clean Coal Institute, the Illinois Department of Commerce and Community Affairs, researchers at the Illinois State Geological Survey, and local brick manufacturers is ongoing in researching the combined use of coal fly ash and local clays and shale in brick manufacturing. Development of a commercially viable brick product could result in a value-added use for the millions of tons of waste fly ash produced each year.

In 2002 the Illinois State Geological Survey, sponsored by the Illinois Clean Coal Institute, began a 2-year study to locate and map common clays and shale resources that have high potential for use in producing fly ash-supplemented brick. This research was done in an effort to provide a market for fly ash, a by-product of coal-derived power generation, and to expand existing markets. Using by-product wastes such as fly ash generally requires clay materials with a fine particle size. The researchers defined areas that were best suited for development of a clay or shale resource within a 50-mile radius of four major coal-fired power plants in Illinois. Results of this study are under consideration for the possible development of a new brick manufacturing operation that would use by-product fly ash and local clay and shale resources in the brick production process.

REGULATORY CONSIDERATIONS

The U.S. Environmental Protection Agency (EPA) issued its emission standards for brick and structural clay products manufacturing under its maximum achievable control technology (MACT) standards. These new standards are expected to reduce emissions of hydrocarbons, hydrogen chloride, hydrogen fluoride, and trace metals by 2.3 ktpy, a 35% reduction from current emissions. The standards specify acceptable technology for controlling pollution and also limit plant kiln design capacity (Virta 2004).

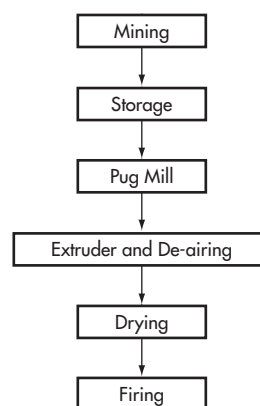


Figure 2. Typical process flowsheet for structural clay product manufacturing

OUTLOOK AND FUTURE TRENDS

The market in common clays and shale has remained nearly unchanged for the past 5 years. The primary markets for common clays and shale products are residential and commercial construction. Products used in construction include brick, drain tile, lightweight aggregate, quarry tile, and structural tile. Strong growth in these segments should sustain the common clays and shale market for the near future. The demand for other products may fall short of this growth rate. Based on recent growth trends, the sale and use of common clays and shale should remain steady for the next several years.

The market for heavy structural-clay products still faces strong competition from cement, wood, glass, plastics, aluminum, and other metals. Growth in this market is always limited by the heavy weight of these products, which limits their market range and increases production costs. The cost of fuel for transportation can have a major effect on industry growth, and thus the most economical mines and plants are often located near one another and ideally near large metropolitan markets.

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Fuller's Earth

Sam M. Pickering Jr. and Fred G. Heivilin

INTRODUCTION

Fuller's earth is a general term for industrially versatile smectite or palygorskite-sepiolite clays (hormites) with high surface area and strong sorptive, binding, gelling, thickening, or decolorizing ability. Fuller's earth has been in common use from perhaps biblical or at least medieval times, when such clays and earths were used for "fulling," or cleaning raw wool to remove greasy lanolin and dirt before the wool was spun, dyed, and woven. The term *fuller's earth*, when used for such a wide variety of industrial clays, has no specific compositional, market, or mineralogical connotation.

Fuller's earths are composed of various combinations of absorptive clay minerals, often with varying amounts of impurities such as silica (at times in the form of fossil diatoms), kaolinite, illite, zeolites, clay-size micas, and carbonate minerals. In general, such clays of marine sedimentary origin in the southeastern United States are commonly called *fuller's earths*, whereas in the American West clays originating by alteration of volcanic ash are typically termed *bentonites*.

Mineralogy, crystallinity, crystal habit and shape, particle size, and crushability are all critical to the sorptive, binding, thickening (gelling), cation exchange capacity (CEC), specific gravity, dusting, deodorizing, and decolorizing abilities of commercial-grade fuller's earth clays. Therefore, these important factors have a profound effect on the refined product's specific industrial uses, market applications, pricing, and customer acceptance.

NOMENCLATURE

Although fuller's earth is a widely used commercial term, it has often been inconsistently applied to a variety of smectites, hormites, bentonites, zeolites, impure diatomites, and other such clay occurrences. The essence of the American Geological Institute's (AGI's) *Dictionary of Geological Terms* definition of fuller's earth is that it is a very fine grained, earthy substance with high water absorptive capacity and ability to refine and decolorize edible oils; it differs from ordinary clay in its higher water percentage and lack of plasticity (AGI 1962). The AGI also applies this term to fuller's earth clays without reference to any particular chemical or mineral composition, texture, or geological origin.

Given that this definition allows considerable overlap that could include many different types and occurrences of other clay materials, more specific fuller's earth definitions may be of interest. Ampian (1985, pp. 158–159) stated that the term fuller's earth "has

neither a compositional nor a mineralogical connotation, and the substance is defined as a nonplastic clay, usually high in magnesium, that has adequate decolorizing and purifying properties." Although the term *nonplastic* is often used, it is seldom specified whether it is applied to fuller's earth clays in the raw moist state, after partial drying or in a semicalcined condition.

In the 6th edition of *Industrial Minerals and Rocks*, Elzea and Murray (1994, p. 234) used the term fuller's earth as "more or less a catchall for clay or other fine-grained earthy material suitable for bleaching and absorbent and certain other uses." In a like manner to the AGI usage, they also state that fuller's earths have "no compositional or mineralogical meaning." Elzea and Murray also gave a historical outline of fuller's earth use, which can be summarized as use in antiquity for cleansing and fulling wool; use by the late 1800s for decolorizing and purifying mineral and edible oils; use in the early 1900s for petroleum processing; and use in the last half of the 20th century as an oil absorbent, cat litter, and agricultural chemical carrier granules, replacing petroleum purification as the dominant use. In the mid- to late 1900s, fuller's earths began to be widely used for adsorptive purposes as either natural or acid-activated clays for bleaching mineral or edible oils (Nutting 1943).

Bentonites are similar clays that may overlap with fuller's earths in both commercial application and mineralogy. To simplify the distinction between the two clay types, however, the AGI (1962, p. 49) defined bentonite as "a clay formed from the decomposition of volcanic ash and is largely composed of the clay minerals montmorillonite or beidellite." They specifically restrict the use of the term bentonite to clay that was "produced by decomposition of volcanic ash and not from the decomposition of any other substances." It is interesting that some southeastern fuller's earth clay producers refer to their products used in the foundry sand market as "bentonites," which may serve to obtain a freight-rate advantage over the western bentonite producer's eastern sales.

Some clay researchers explain the origin of many of the southeastern fuller's earth deposits as wind-blown volcanic ash from the west, but they have never been able to establish a volcanic source for the presence of hundreds of feet of eastern clay deposits. The present authors (also see Merkl 1989) regard the southeastern smectitic-hormitic clay deposits as having been deposited by normal, nonvolcanic sedimentation in quiet water basins under very low energy in highly saline, anoxic-reducing environments.

Table 1. A historical long-term trend record of U.S. fuller's earth production and average U.S. free on board (f.o.b.) selling prices

U.S. Production*	1940	1950	1960	1970	1980	1990	2000
Short tons, <i>st</i> [†]	146	395	407	980	1,529	2,541	3,201
Metric tons, <i>t</i>	133	359	370	891	1,390	1,880	2,910
\$/st	12.21	26.45	22.55	23.73	49.82	88.00	75.09

Source: Buckingham and Virta 2003.

* Note that U.S. production, unlike statistics from other nations, is of actual refined product tons, not crude clay tons.

† All U.S. domestic sales of bulk fuller's earth product are made by the short ton (2,000 lb).

Table 2. U.S. fuller's earth sales by market use, 2002

Market Application	Sales, <i>st</i>
Pet waste absorbent (cat litter)	1,738,000
Oil and grease absorbents	449,900
Fertilizer pelletizing binder	152,900
Pesticide and herbicide carrier	112,200
Animal feed pelletizing binder	89,700
Filtering, clarifying, and decolorizing	69,630
Fillers, extenders, binders, and drilling mud	64,680
Miscellaneous	290,400
U.S. export	33,990
2002 yearly total sales	3,003,000

Source: Virta 2004.

PRODUCTION

U.S. Geological Survey (USGS) published records (Virta 2004) show that worldwide annual 2002 fuller's earth production was some 3,900,000 t, of which the United States produced and sold approximately 70%. As has been discussed, however, nomenclature of industrial smectite and hormite clays is subject to considerable confusion.

In gathering U.S. and foreign mineral production statistics, the USGS, by policy, does not attempt to precisely identify the type of clay being mined but rather classes each mining company's production based only on what the companies themselves report that they mine (R.L. Virta, personal communication). For several examples, the following instances are rather typical:

- Calcium montmorillonite may be referred to as calcium bentonite in some parts of the United States but is called fuller's earth in England (Harben and Bates 1990).
- In the Florida–Georgia fuller's earth district, near the town of Attapulgis, the clay being mined is informally referred to as attapulgite rather than the mineralogically more accepted term palygorskite. Similarly, palygorskite occurs in two very different crystal habits—as “mountain leather” type material in hydrothermal vein environments and as sorptive gelling clay in anoxic-reducing, semimarine sedimentary deposits.
- Attapulgite (palygorskite) and sepiolite may both be reported by the USGS as fuller's earth production in the United States (Heivilin and Murray 1994).
- Calcium montmorillonite may be referred to by the USGS as “southern bentonite,” “Mississippi bentonite,” or “Texas Bentonite,” although there may be little or no evidence of its volcanic origin.
- Large tonnages of sorptive clays produced for cat litter products in Spain and Senegal are variously referred to as sepiolite, meerscham, and attapulgite in the same publication

(Newnan 2003) and as both fuller's earth and attapulgite (Virta 2004).

U.S. fuller's earth production tonnage and product prices (exclusive of bentonites) have grown with the national economy over the past 70 years, as reported by Buckingham and Virta (2003) in thousands of tons and average selling price in Table 1.

The USGS (Virta 2004) lists U.S. production of processed fuller's earth products for 2002 as 3,003,000 st (2,730,000 t), which sold for \$246 million (or an average 2002 price of \$81.92 per processed short ton). This total production was from 12 listed states: 5 companies in Georgia; 3 companies each in Florida, Mississippi, and Nevada; 2 each in California and Virginia; and a single company each in Kansas, Illinois, Missouri, Oregon, Tennessee, and Texas. Additionally, the USGS (Virta 2004) reported U.S. 2002 total fuller's earth sales by generalized market application (Table 2).

Fuller's earth is such a versatile industrial minerals material that many of its commercial uses do not fit conveniently into such simple categories, so this listing should be regarded as reflecting only generalized market segments. Also, by law the USGS is required to avoid listing production statistics for mineral market uses served by only one or two producers because that would divulge confidential production and sales information. This practice has the effect of putting much of specialized production into the miscellaneous category. Similarly, the USGS (Virta 2004) reports estimated 2002 world fuller's earth production from market economy countries (France, India, Iran, Japan, and Turkey unreported; Table 3).

HISTORICAL U.S. PRODUCTION AND PATTERNS OF USE

Native Americans were reported to have used fuller's earth and bentonite for cleaning blankets and clothing before European arrival in the 15th century. During the Revolutionary War, soldiers stationed near Perth Amboy in New Jersey used Woodbridge fire clay to clean their buckskin clothing. In the early 1800s, fuller's earth was discovered in association with an iron ore bed near Kent, Connecticut. During the Civil War, fuller's earth was used to bleach sugar near Falls City, Texas.

The first documented commercial fuller's earth deposit in the United States, which is still being mined today, was discovered in 1893 near Quincy, Florida. The Owl Commercial Co. (predecessor of the present makers of White Owl cigars) made the discovery during their attempt to make burnt brick from clays on their Quincy tobacco plantations. Because of its high content of smectite, the clay was unsuitable for brickmaking. One of the Alsatian farm workers in the area, however, recognized the Quincy clay as similar to fuller's earth, which was being mined in Germany. Two years later, his observation led to development of the first U.S. mine for fuller's earth for processing mineral oils. Also, fuller's earth had been mined slightly earlier on a small scale in Arkansas in 1891 (Miser 1913) and tested for use in refining cottonseed oil.

The U.S. demand for acid-activated fuller's earth for edible oil and petroleum refining and decolorizing expanded rapidly until it

peaked at about 317,000 st in 1930. At that time, this was about 90% of total U.S. fuller's earth production. After 1930, the use of fuller's earth for petroleum refining decreased because of the availability of alternative oil refining methods.

After that time, U.S. oil refining use of fuller's earth declined until it reached a uniform rate of 35,000 to 40,000 st/y for edible oils only. Using fuller's earth as a waste oil absorbent and floor-sweep type of clean-up agent, however, began before World War II and, by the 1950s, its use as a carrier for herbicides and pesticides had become more prominent. Cat litter production began in 1952, and it has grown rapidly since then.

In the district between Quincy, Florida, and Attapulgus, Georgia, the excellent gelling properties of palygorskite (attapulgite) fuller's earth were discovered and developed for salt water drilling mud, as a joint binder taping compound for sealing the seams of construction wallboard, and for other applications requiring a thickened gelling clay. These uses for gelling fuller's earth products developed to replace sales lost when use for petroleum refining declined. The Florida–Georgia mining district today is the world center for gelling fuller's earth clay production.

What is now by far the most prominent American use for fuller's earth, as a pet waste absorbent product (cat litter), began to grow rapidly in the 1950s. At first, cat litter was made from oil absorbent product that had been crushed to finer than $3/4$ -in. size, semicalcined in countercurrent rotary kilns, milled and screened, and packaged for retail sale. Today, cat litter is typically dried to only 4% to 15% moisture, which results in improved absorption, reduced dusting, and lower energy cost.

In the early 1990s, clumping cat litter became very popular. Blending western bentonite or clumping agents with eastern fuller's earth causes liquid waste to form clumps that can easily and neatly be taken from the litter box with a perforated scoop. This leaves only unused clean granules in the litter box, minimizing waste and enabling easy handling of a formerly messy and unsanitary chore. Today, many clumping cat litter products are up to 100% western sodium bentonites.

GEOLOGY

Mineralogy

Typically, fuller's earth is a marine or semi marine sedimentary clay variably composed of the clay mineral groups smectite and hormite. Tables 4 and 5 summarize these closely similar types of clay minerals.

In 1862, Savchenkov first used the term *palygorskite* to define a vein-type hydrothermal "mountain leather" clay mineral from the Palygorsk locality in the Ural Mountains of Russia (Hey 1975), where it was mistaken at first for a variety of asbestos.

J. de Lapparent first termed the highly absorptive gelling clays from Decatur County, Georgia (United States), and also those from an area near Mormoiron, France, with the mineral name *attapul-gite*, because he thought those clays quite different from palygorskite. The new name was applied to gelling clays occurring near the small southern Georgia town of Attapulgus. More recently, however, x-ray diffraction proved the two clay types to be the same mineral (Bailey et al. 1971). Although first applied later than palygorskite, the name attapulgite is still in common informal use in the Florida–Georgia mining district where the crystal length-to-diameter ratio does not exceed 10:1 (Merkel 1989).

In 1774, Glocker first applied the name *sepiolite* for a clay mineral later called "meerschau" by Werner in 1788. Haüy in 1801 described the same type of low-density white magnesium silicate clays as *ecuame de mer*, which Brochant in 1802 also termed *talcum plasticum*. Today, this type of magnesian clay mineral is

Table 3. World production of fuller's earth, 2002

Producing Nation*	Production, t
Algeria	3,521
Argentina, estimated	1,500
Australia, attapulgite	6,000
Germany (unprocessed)†	500,000
Italy	30,000
Mexico	150,000
Morocco, smectite	42,243
Pakistan	15,000
Senegal, attapulgite	176,454
South Africa, attapulgite	7,900
Spain, attapulgite, estimated	90,000
United Kingdom, estimated product	140,000
United States	2,730,000
Rounded world total	3,890,000

Source: Virta 2004.

* Excludes centrally planned economy countries.

† Crude rather than processed product tons of clay.

Table 4. Smectite group minerals

End-Member Mineral	Crystal System	Chemical Composition
Montmorillonite	Monoclinic	(Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ •nH ₂ O
Beidellite	Monoclinic	(Na,Ca _{0.05}) _{0.33} Al(Si ₄) ₄ O ₁₀ (OH) ₂ •nH ₂ O
Nontronite	Monoclinic	Na _{0.33} Fe ₂ (Si,Al) ₁₀ (OH) ₂ •nH ₂ O
Hectorite	Monoclinic	Na _{0.33} (Mg,Li) ₃ Si ₄ O ₁₀ (F,OH) ₂
Saponite	Monoclinic	(Ca/2,Na) _{0.33} (Mg,Fe) ₃ (Si,Al) ₄ O ₁₀ •4H ₂ O

Source: Roberts, Campbell, and Rapp 1990.

Table 5. Hormite group minerals

End-Member Mineral	Crystal System	Chemical Composition
Palygorskite*	Orthorhombic and monoclinic	(Mg,Al) ₂ Si ₄ O ₁₀ (OH)•4H ₂ O
Sepiolite	Orthorhombic	Mg ₄ Si ₆ O ₁₅ (OH) ₂ •H ₂ O

Source: Roberts, Campbell, and Rapp 1990.

* Informally termed attapulgite in the Florida–Georgia, Spain, and Senegal mining districts.

known as sepiolite and is found more abundantly in the northern extent of the Florida–Georgia basin than more southerly concentrations of attapulgite near Quincy.

The reader is referred to the Bentonite, and Palygorskite and Sepiolite chapters of this book for a more detailed discussion of the mineralogy of the smectite group and hormite minerals, respectively.

Origin

Fuller's earth clay deposits in the eastern United States are found in marginal marine sedimentary units that formed in restricted, anoxic, shallow, low-energy, reducing, and often hypersaline conditions. Such depositional environments favor formation of magnesian montmorillonite, palygorskite (attapulgite), or sepiolite.

Alternatively, sorptive calcium montmorillonite fuller's earth deposits have been formed in Nevada in Pliocene freshwater lakes with as much as 40% siliceous diatom tests. In south-central

California, what is now the Miocene Antelope Shale was originally deposited as diatomite and then diagenetically altered by deep burial to a form of absorbent opal CT.

Other inert, nonabsorptive, accessory minerals in fuller's earths can include dolomite, calcite, quartz (sand, silt, biogenic opaline CT, or diatomite), gypsum, and assorted heavy minerals. Finely divided fossil or organic plant matter can color the fuller's earth gray or bluish gray; oxidative weathering alters the clay to a cream, tan, green, pink, or yellowish tint.

Physical Properties

Mineralogy of fuller's earths determines their most effective potential use. Montmorillonite is a type of clay mineral that shrinks when dried and may swell when rewetted. Highly adsorptive when dried, this mineral is used in granular animal litter, in floor-sweeping compounds, and as a carrier for insecticides, herbicides, and so forth.

The extremely fine particle size, high CEC, and tight packing of attapulgite- and montmorillonite-rich fuller's earths make them useful to increase "stickiness" and promote high green strength in ceramic dinnerware; to provide adhesion and plasticity in metal foundry molding sands; as an adhesive binder to form pellets of taconite iron ore, agricultural fertilizers, and so forth; and to form an impermeable seal or slurry barrier for isolation of sanitary landfills and hazardous waste disposal sites.

Bleaching clays with or without acid activation need a particular pore size and porosity to clean and decolorize edible oils. There are only two such actively mined fuller's earth clay deposits in the United States—in northeastern Mississippi where acid activation (the clay slurried with acid) is necessary and in the south Georgia district near Meigs, where clays bleach naturally or with only acid addition to the dry powdered product.

The presence of attapulgite in elongate needle-shaped or acicular habit crystals is indicative of superior gelling or thixotropic behavior when slurried with water or liquid polymers. Such fuller's earths can be used for oil-field drilling muds, which retain their integrity as thick and viscous gels, even in the presence of saline formation brines. Magnesian fuller's earths can also be used in thickened or gelling form to produce nondripping paint, to thicken liquid detergents, for wallboard joint cement and spackle compounds, and for other specialty applications.

In the Florida-Georgia fuller's earth mining district, attapulgite commonly occurs in two distinct forms known as short- and long-length crystalline material. The higher gelling long-length clays are found in the southern part of the district and are stratigraphically restricted to the Mid-Miocene age Dogtown Member of the Hawthorn Formation of northwestern Florida. Dogtown attapulgitites are typically longer in crystal habit than 10 μm and are associated with the most favorable gel-strength clays. The slightly younger Meigs Member clays contain short attapulgite crystals less than 10 μm long and are more prevalent in the northern portion of the fuller's earth mining district in southeastern Georgia near Ochlocknee.

Sepiolite clay also occurs in needle-like crystal habit in the more northerly Meigs Member and remains stable at relatively higher temperatures. Thus sepiolite-rich fuller's earth products can be useful as drilling muds for maintaining borehole circulation when completing geothermal production wells.

DISTRIBUTION OF MAJOR U.S. DEPOSITS

Southeastern United States

Fuller's earth deposits of commercial quality and accessible for shallow open-pit mining are mostly found in several districts in the

southeastern United States, where relatively low-energy, warm, restricted coastal marine conditions were prevalent during late Mesozoic and Cenozoic times.

These southeastern fuller's earths are found in three main stratigraphic formations:

1. In the Mid-Miocene Dogtown and Meigs members of the Hawthorn Formation in the mining district between the towns of Quincy, Havana, and Dogtown in the panhandle of north Florida, and Attapulgus, Reno, Calvary, Cairo, Ochlocknee, and Meigs in southwestern Georgia
2. In the Late Eocene Twiggs Clay Member of the Barnwell Formation in the area east of Wrens in Jefferson County, Georgia
3. In the Late Paleocene Porters Creek Clay between Cairo and Mounds in Pulaski County at the southern tip of Illinois, and in the towns of Ripley and Blue Mountain in Tippah County, Mississippi

The Florida-Georgia District

A narrow depositional trough trends southwest to northeast across the Florida Panhandle region from the town of Quincy to near the Georgia towns of Attapulgus, Meigs, and Ochlocknee (Herrick and Vorhis 1963). This restricted basin, variously termed the Gulf Trough or the Apalachicola Embayment, has localized fuller's earth deposits in the Miocene-age Hawthorn Formation that dominate U.S. production of both granular and gelling-grade industrial clays.

Suggestions have been made that fuller's earth clays in the Florida-Georgia District originated from altered volcanic ash (such as in Reynolds 1970); more recent research (Thomas 1981), however, has shown no indication that these marine and semi-marine clays were deposited in any conditions other than normal, nonvolcanic, reducing environments in shallow sedimentary basins.

Gelling-grade magnesian attapulgite (Figure 1) is much more concentrated in the Dogtown Member of the Hawthorn Formation at the narrowest southern end of the trough or basin; and the smaller percentages of sepiolite and shorter-crystal-length attapulgite- and montmorillonite-mixed clays of the Meigs Member are more abundant toward the northern end. The Florida-Georgia area underlain by this Miocene-age trough has been continuously and extensively mined for various grades of fuller's earth for more than a century.

This depositional trough is thought to have begun as a considerably older graben structure that served as a major ocean current seaway throughout much of the early and mid-Tertiary but was broadly uplifted in the Miocene when much of what is now Florida was raised by the Peninsular Arch (Herrick and Vorhis 1963; Huddleston 1993). During the mid-Miocene, the trough was uplifted and cut off from open ocean circulation; it became a series of discontinuous, small to extensive, evaporitic basins rich in magnesian salts, where dolomitic limestone, attapulgite/palygorskite, and sepiolite were deposited.

The Virginia District

Two fuller's earth producers in east-central Virginia mine a rather heavy, marginal-grade diatomaceous mudstone for cat litter in the Miocene Calvert Formation (Hosterman and Patterson 1992). This material, although not of superior quality, has a considerable freight advantage in shipping to the population centers in northeastern cities.

The Mississippi Embayment District

A wide Coastal Plain sedimentary embayment or open-fronted basin extends inland along the course of the Mississippi River as far

north as Cairo and Mounds, Illinois. This continuous outcrop belt of the Late Paleocene-age Porters Creek Formation from Ripley and Blue Mountain, Mississippi, to Mounds and Cairo contains many fuller's earth deposits that are as much as 370 ft thick.

These Paleocene-age calcium montmorillonite clays have less desirable higher-density and lower-absorbency characteristics than clays from the Florida–Georgia district. Their freight advantage to the large midcontinent market area, however, and their ability to blend with western swelling bentonite to provide good liquid-clumping capacity allow their extensive use in the cat litter trade. Some companies blend the weathered light-colored clays with darker, unoxidized clays to produce an attractive “salt and pepper” colored product from the Porters Creek clay district.

The U.S. Western District

Different types of fuller's earth are produced in the western United States, such as at California's San Joaquin Valley, where absorptive mixtures of opal-CT altered from diatomite are present. Two high-grade fuller's earth deposits in Nevada, composed of mixed montmorillonite and diatomite, have been proven for quality and passed standard validity exams for granular cat litter and oil absorbent, but they have not yet been brought to the market. Some sepiolite gelling clay is found in east-central California, but it is of marginal quality and sold mainly in the West Coast market.

EXPLORATION METHOD

Fuller's earth exposed in surficial outcrops is commonly too weathered and oxidized by soil-forming processes to have sufficient quality for industrial use. New fuller's earth deposits are often discovered by widely spaced core drilling near areas where the clay was mined or near outcrop exposures that look promising.

Truck-mounted rotary drilling rigs of the type developed for placing explosive charges for early oil-field geophysical exploration—such as the 500 and 1250 models built by Failing, Gardner-Denver/Mayhew, and DSM—are used for the drilling depth of 100 to 200 ft common in fuller's earth exploration. Double-tube core barrels with built-up hard metal bits are used, and the core is extruded with water pressure from the drill rig's mud pump or with compressed air. Typically, NX-size core of about 2 1/8-in. diameter is recovered; rinsed and trimmed; marked accurately by property code number, hole grid location, and depth in the hole; and transported in boxes or bags to the company laboratory for extensive quality testing.

When an area of core holes tests favorably in the laboratory, accurately spaced core-drilling campaigns are begun on a surveyed grid of 400 to 800 ft. As the shape, extent, and quality of new clay deposits are proven, grid drilling is narrowed to spacings of 200 and 100 ft before overburden stripping is begun.

After the commercial clay surface is exposed, closer spaced drilling may be done using air-pneumatic or auger methods, or the area may be sampled with a mining backhoe. Regulated wetlands, endangered species areas, and archaeological sites are avoided wherever possible. Lately, however, mitigation is needed for wetland areas that must be crossed by haul roads or those underlain by high-quality fuller's earth that the company wishes to mine.

Fuller's earth quality is posted from drill and laboratory testing results on carefully scaled grid maps, which are used for mine planning, government permitting, and future clay reserve tonnage calculations. These mine planning maps show overburden thickness and type, clay thickness and commercial quality, location of property boundaries, and regulated wetland areas.



Figure 1. Foliate texture of high-magnesian attapulgite gelling-grade fuller's earth from the Florida–Georgia District near the axis of the Gulf Trough depositional embayment. This texture develops shortly after the raw clay is exposed for mining and is thought to be an indicator of high gelling strength. (Knife, for scale, is 10 cm long.)

CLAY QUALITY CHARACTERISTICS

Special Characteristics

The fuller's earth industry, particularly perhaps in North America, has become accustomed to applying special terms to different properties of clays and their products. These terms may not be familiar to those outside the industry, so some simplified explanations may be helpful, as follows:

- *Clumping clays* are those clays with clumping agents or a high content of western sodium bentonite; they have become very popular for clumping or scoopable-type cat litter products. The bentonite absorbs liquid wastes, which clump in discrete lumps that can be neatly scooped from the litter box, leaving only clean litter behind. Bactericides are needed to improve long-term odor reduction in western bentonite clumping cat litters.
- *Dusting clays* are those clays that are unsuitable for granular products because they break down too finely upon crushing or during shipping, handling, or use. In cat litters, a high dusting clay product causes mudging, tracking outside the litter box, and a dirty cat.
- *Heavy or high-density clays* is a term used for cat litter products that are denser than about 40 lb/ft³. These products typically are lacking in absorption, take up more room in the cat

box, are inconvenient for the retail purchaser to carry, and commonly do not control odors as well as lighter clays.

- *Gelling clays* is a term used for clays that have a high slurry viscosity at low percent solids; these clays are used as a thickening agent for wallboard-tape joint cement, nondrilling paints, drilling muds (especially palygorskite, used to maintain circulation when drilling in brine formations), and liquid detergents, and as a fine pulp retention aid in paper manufacture, liquid fertilizer suspensions, adhesives and sealants, putties and glazing compounds, and other industrial applications. Gelling viscosity is typically measured on Fann or Brookfield viscometers. Gelling behavior and viscosity can be enhanced by extruding the moist clay to align the needle-shaped crystallites or by adding calcined magnesium oxide.
- *Granular clays* refers to products that are carefully crushed and screened to a narrow range of chip sizes, often listed such as "4–20" (passing through a U.S. Standard 4-mesh screen and retained on 20 mesh). The granule size controls product surface area and liquid or gas absorption in the animal litter.
- *Slaking clays* are those clays that, after drying, break down to mud when wetted with water or oils. Slaking is a very undesirable quality in granular fuller's earth products because it decreases odor control and increases liquid buildup in cat litter and causes unsafe slippery conditions when used as a floor-sweep compound type of oil absorbent product. Slaking is caused by dispersion of the surface of the clay granules to form a slick surface, in which the clay crystallites are uniformly negatively charged and consequently repel each other. Paradoxically, although slaking is undesirable behavior in granular fuller's earth products, it is essential in gelling clays.

Quality Testing

Companies that produce fuller's earth test their exploratory drill core and quality control samples against a variety of published and unpublished product specifications that are important to their customers. Fuller's earth product specifications are set by the type of market use intended. The initial critical quality factor is the percentage of coarse inert impurity materials, commonly termed *grit*, that contaminate the clay deposit. Grit specifications for the maximum allowable nonabsorptive minerals present in crude clays can range from 5% to as much as 15%. Some of the coarser grit material can be partly removed by air separation at the whizzer during dry milling or by oversize screening when producing granular products.

Dry calcined MgO can be added to the raw clay during processing to improve gelling, viscosity, and thickening behavior. It may be necessary to extrude the moist clay for crystallite alignment or to allow for a seasoning time of up to 2 weeks to allow the MgO to have its maximum desired effect.

Granular fuller's earth products commonly must be composed of a narrow size range of chip particles, with very little fine dust-size material allowed. Dusting behavior can be a problem with many of the softer or more frangible absorbent fuller's earth products. When dried or semicalcined and then crushed to a granular or chip-sized product, the finer mesh sizes of clay may need to be removed and discarded to meet the customer's particle-size specifications. De-dusting boxes and liquid polytetrafluoroethylene addition may be used to reduce airborne dust immediately before packaging. Slaking is also a quality problem, where the clay granules break down when wetted and form an impermeable, nonabsorbent muddy mass.

The American Petroleum Institute (Anon. 1969) lists drilling mud specifications. Specification P-A-1056A, published by the U.S. General Services Administration, describes tests for floor-sweep-type absorbent granules. The American Oil Chemists' Society

(Anon. 1958) describes edible oil bleaching tests. Weidhaus and Brann (1955) describe testing for the various types of insecticide, carrier, and dusting diluents.

Product Performance Standards

The following are general guidelines for specific fuller's earth products intended for particular market applications.

Granular products intended for cat litter should be light in color with a loose packaged density of less than 50 lb/ft³, and when crushed they should produce a minimum of fine dust-size material. Low bulk density is especially important for high-quality consumer cat litter; the purchaser will select generous-size packages that weigh as little as possible.

The same low bulk density, however, will increase per-ton shipping cost in railcars and export containers. Litter granule size usually ranges from about 4 to 30 Tyler screen mesh, and liquid absorptivity ranges from 50% to 120% without slaking or granule breakdown. Cat litter products are typically dried to 10% to 15% moisture, and western bentonite is commonly added to absorb liquid waste into easily removed, scoopable clumps.

Granular oil-absorbent fuller's earth products vary in density from 22 to 52 lb/ft³, with non-slaking oil absorption ranging from 50% to 100%. Hard granules, low dusting, and high adsorption ability all bring a premium price for this type of product, which is generally sold at 0% moisture.

Agricultural granules for use as carrier agents for liquid insecticides, herbicides, bactericides, nutrients, and fungicides are generally sold in screen sizes ranging from 24 to 48, or 30 to 60 Tyler mesh, with minimal dusting or slaking allowed. These products are commonly produced from Porters Creek Clay in the midcontinent Mississippi Embayment area and are dried to 0% moisture.

Gelling-type fuller's earth products are tested by measurement of slurry viscosity at low clay solids percentages. The most widely used viscometers are the low shear Brookfield unit at 100 rpm or the high shear Fann unit at 600 rpm, depending on customer preference and market application. Clay slurry viscosity can be tested with either fresh or supersaturated saline water.

Magnesium-rich attapulgite fuller's earth clays retain good gel strength under saline conditions, whereas sodium- or calcium-based montmorillonite gelling products break down in the presence of salt water. Therefore, attapulgite fuller's earth is selected as a high-gelling drilling mud for oil and gas exploration when expecting saline formation conditions. For such drilling use, a 600-rpm clay testing 30 Fann units will equate to 100-bbl yield units of properly thickened mud per ton.

Bleaching fuller's earth clays are used to purify and remove discoloring agents from edible oils and liquid products. These products must have very specific pore sizes and shapes to absorb impurities properly while allowing the clarified liquid to filter easily through the clay. The only U.S. fuller's earth products suitable for this use are produced in the Jackson Area of Mississippi and the Meigs to Ochlocknee mining districts of Georgia. These specialty clays are dried to no less than 10% moisture, ground to finer than 325 mesh, and acid treated or soaked for enhanced activation.

Fuller's earth used for sports turf or lawn growth aids (for athletic playing fields or golf courses) is usually dried hard at high temperature to light red, making granular products similar in size to cat litter. These products loosen soils for better drainage and more effective use of plant nutrients.

MINING

Fuller's earth is mined by open-pit methods (Figure 2). Generally, mine planning and permitting, followed by overburden excavation,

are based on core drilling on grids of 50 to 100 ft and careful clay quality testing. Overburden is, whenever possible, backfilled into nearby previously mined-out pits and sloped to blend in with the original, premining terrain. After the overburden is removed, closer spaced drilling using compressed air or auger sample return is frequently done on 50 to 25 ft spacing for effective mine quality control.

Overburden is stripped with backhoe excavators and off-road haul trucks, or dozers and scrapers, often by local independent contractors (Figure 3). The clay itself is excavated with backhoes, front-end loaders, or scrapers. Because the sedimentary fuller's earth was deposited in horizontal layers or strata, quality control is much more reliable if the clay is mixed during mining by vertical excavation (such as with hydraulic backhoes). This vertical mining averages out the horizontal layering of quality variations and delivers better-blended crude clay to the stockpile or processing plant. Acceptable overburden thickness can range from only a few feet or meters to more than 100 ft, depending on the mining district, ore zone thickness, clay quality, and the market value of products produced.

Highway haul trucks transport the crude clay from the property; they must meet complex state and interstate regulations for haul weight, individual wheel load bearing, spillage, tracking mud onto the paved road surface, and so forth. Thus, there is a real cost and efficiency advantage to mining near enough to the clay processing plant so that mine-run crude clay can be hauled by very large off-road trucks on privately owned roads, where regulated load limits do not apply. After a fuller's earth plant has operated for a few decades, however, it is likely that most or all of the nearby acceptable quality clay deposits have already been mined out.

Mine Permitting and Regulation

Proposed fuller's earth mines must be approved and permitted by state and local agencies. Each mine permit process addresses reclamation, air quality, stormwater runoff, local zoning, and other regulatory issues. The permit process can be very different from state to state, and may vary considerably through time in an individual state. Careful attention should also be paid to wetlands, county zoning regulations, Native American tribal customs and practices, proximity to historic homes or buildings, parks, natural areas, wildlife sanctuaries, or endangered species regulations.

Mine permitting must also deal with land and mineral ownership and leasehold rights, mine water control, highwall slope stability (typically laid back to between 0.5:1 and 2:1 angles), adjacent property setback, and so forth. Mineral rights on privately owned lands are commonly leased from the landowners, and royalties for extracted clay are paid by the ton or cubic yard.

Failing to obtain a satisfactory lease contract, mining companies may purchase clay properties outright or buy the deeded, severed minerals only and leave surface and timber ownership to the landowner. On federal lands, the U.S. Bureau of Land Management or the U.S. Bureau of Indian Affairs must handle mineral leasing or placer claims in accordance with the General Mining Act of 1872 and their own particular standards and regulations.

Mined Land Reclamation

Once mining is completed, the mined-out pits are backfilled and leveled with overburden from a nearby or adjacent cut, or developed into fishing ponds. The disturbed land is restored to attractive, stable, noneroding, less than 3:1 slopes. Cover crops of pasture grass and select tree seedlings are planted on the reclaimed land to leave little or no hint that the property had ever been mined. Individual states, and in some cases also a county or smaller local permitting agency, control regulation of such privately owned disturbed mining lands in the United States.



Figure 2. Typical open pit fuller's earth mine near Ochlocknee, Georgia, showing the excavated surface of the minable clay under approximately 20 m of overburden. Ore zone thickness is approximately 4 m.

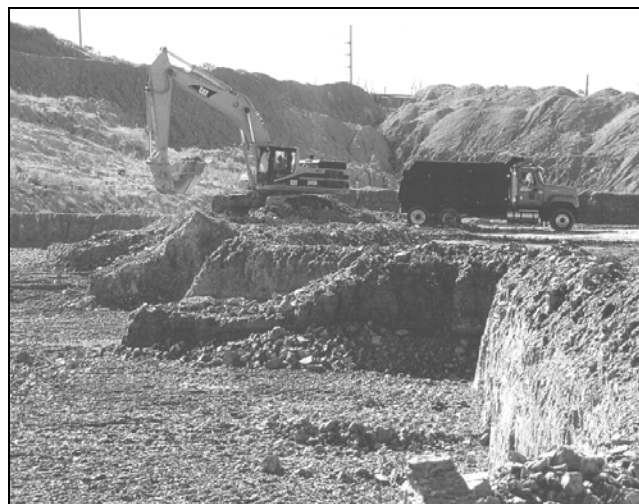


Figure 3. Mining fuller's earth clay after overburden has been removed and hauling by highway truck to the processing plant. Note overburden in the background that has been backfilled to fill the previously mined-out pit.

CLAY PRODUCT PROCESSING

Fuller's earth is an unusually versatile mineral that can be processed to meet a rather bewildering variety of product specifications for sales to a wide range of differing market uses. Crude run-of-mine fuller's earth is typically crushed and semidried with a shredder or hammer mill, Raymond mill, Williams mill, or Imp mill for bleaching and gelling products.

The clay may be dried to 10% to 15% moisture or semicalcined. Care is taken not to overheat and reduce pore size, absorption, or CEC, and alter mineralogy to make cat litter, bleaching and oil-adsorbent material, agricultural chemical carriers (for pesticides, herbicides, etc.), jet fuel filtration agents, or turf improvement products.

Various-sized granular products can be screened to make any product from 4 by 12 mesh, 30 by 60 mesh, or even as fine as 60 to 90 Tyler mesh specifications. Finer clay products can be ground

and air-float separated to finer than 200 mesh, 325 mesh, or even ultrafine –6- μ m material. The moist clay can be “pugged” (extruded) to align elongate crystals and improve gelling properties.

MgO may be added to improve product viscosity and gelling characteristics. There is not agreement in the industry on whether adding MgO causes actual attapulgite crystal needle growth after a few days’ residence in the clay product, or if the MgO simply results in an improved surface charge on the existing clay crystal-lites that results in better gel performance.

PRODUCT HEALTH AND SAFETY CONSIDERATIONS

Crude fuller’s earth clay is checked by scanning electron microscope, transmission electron microscope, x-ray diffraction, and x-ray fluorescence chemical analysis for the presence of industrial fibers of possible asbestiform characteristics, cristobalite, trace metals, and other possible hazardous elements. Because some fuller’s earth products may be used for processing animal and human foods, all products and additives used must meet food-grade standards. Several examples of possible hazardous situations that have affected fuller’s earth operations are as follows:

- Development of East Gate, Nevada, mordenite for cat litter use was halted because of the presence of erionite fibers in the crude clay and overburden.
- Use of fuller’s earth cat litter in California was challenged because of the presence of crystalline silica. It was necessary to obtain a “Safe Use Determination” by the Sorptive Minerals Institute to enable the sale of most types of cat litter in the state.
- The National Institute for Occupational Safety and Health (NIOSH) conducted a health study to ensure that the type of elongate crystals in palygorskite in the Florida–Georgia fuller’s earth district did not constitute an asbestiform mineral health hazard.

PRODUCT PACKAGING, TRANSPORT, AND MARKETING

Finished granular fuller’s earth products such as cat litter, oil absorbents, and floor-sweep compounds are sold in consumer-attractive paper or plastic packages of 5 to 50 lb or in metric sizes for export markets. Cat litter packaging has evolved from unweighed filling of semicalcined clay into hand-stapled bags in 1952 to fully automated bag-filling units that shrink-wrap bundles which are then conveyed onto automatically stretch-wrapped pallets for warehousing and then loading onto trucks or railcars.

Agricultural chemical carriers, jet fuel filtration products, bleaching clay granules, anticaking or dry-flow agent clay powders, specialized drilling muds, and gelling or thickening agents are shipped in 40- or 50-lb paper bags, polypropylene bulk big-bags, bulk truckloads, or railcars.

Some export fuller’s earth products are shipped overseas in large metal shipping containers, covered barges, or bulk ship holds. Although the industry packaging trend is toward nearly complete automation, some fuller’s earth products continue to be hand-bagged and -palletized.

Finished fuller’s earth products may be distributed to a market radius of only a few hundred miles for typical high-density, low-absorption cat litter or to worldwide markets for high-grade bleaching clays. Order size can range from barge load or shipping cargo bays, or 80- to 120-truck load special promotions, to individual pickup truck loads destined for the local hardware store. Generally, the main tonnage of fuller’s earth products is shipped to market in truckloads, railcars, or in metal shipping containers.

Individual fuller’s earth customers can be hardware stores, municipal or hazardous waste landfills, city or university athletic fields for turf enhancement granules, jet fuel purification facilities at major airports, or multibillion-dollar distributors for chemical, grocery, or discount consumer sales outlets.

Product sales go through regional or national distributors or directly to the wholesale or retail customer. Fuller’s earth products are sold in the neighborhood grocery store in attractive small packages for household cat litter or to a paint manufacturer for use as a thickener and antidrip agent.

The overall trend in the fuller’s earth industry is to develop new products that better satisfy the particular customer’s needs and allow a higher added-value price over standard or commodity grades. New product development research must consider fuller’s earth mineralogy, physical and chemical specifications, existing patent rights, customer service and packaging preferences, and extra processing and energy cost requirements before launching innovative higher-value products.

The future of the U.S. fuller’s earth industry depends on developing and patenting new special-use products and reaching new types of market applications.

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Kaolin

Robert J. Pruet and Sam M. Pickering, Jr.

INTRODUCTION

Kaolin is a global industrial mineral primarily used as (1) a pigment to improve the appearance and functionality of paper and paint, (2) a functional filler for rubber and plastic, (3) a ceramic raw material, and (4) a component for refractory, brick, and fiberglass products. Other lower-volume uses for kaolin include chemical manufacture, civil engineering, agricultural applications, and some pharmaceuticals. The limited availability of suitable raw material, extremely competitive market conditions, and the technological complexity of kaolin processing and kaolin product functionality creates a high barrier of entry in to kaolin production. Rock and soil containing kaolin minerals occur over wide areas on most continents, but large high-purity kaolin deposits that are capable of supplying large processing facilities and are accessible to global transportation infrastructures are rare. Therefore, the majority of the world's kaolin is mined from sedimentary kaolin deposits located in the United States and Brazil and from primary kaolin deposits in the United Kingdom and Germany. The large size of operations in these regions is driven in part by demand in the paper market for large volumes of consistent quality pigment and by the need to cover the large fixed cost base that is required to mine and process kaolin ore into marketable product.

Definitions

Kaolin is a white or nearly white clay comprising naturally occurring kaolin group minerals. It is distinguished from other industrial clays containing high levels of kaolin minerals—such as ball clay and fire clay—by its whiteness, fine particle size, and kaolin group mineral content (Table 1). The white color of kaolin can occur natu-

rally or result from extensive processing to remove color-bearing minerals and organic compounds that adsorb certain wavelengths of visible light. A second component of kaolin's white appearance is derived from its fine particle size, which causes light to scatter. In most commercial products, kaolin contains particles with an equivalent spherical diameter that is generally finer than 2 μm , though some grades of kaolin products contain particles about 10 μm in size. The term *hydrous kaolin* generally refers to processed kaolin product that contains kaolin minerals with their structural water or hydroxide component. *Calcined kaolin* refers to the thermally processed kaolin exposed to temperatures higher than 450°C to form metakaolin, or to temperatures higher than 1,000°C to form high temperature minerals such as mullite, spinel, and cristobalite.

Crude kaolin ore deposits are contained in a variety of kaolinitic rock types. *Primary kaolin* generally describes a kaolin ore altered from an igneous or metamorphic rock that was kaolinized in situ by hydrothermal or weathering processes. Varieties of primary kaolin are China-clay rock and residual kaolin. Saprolite can be residual kaolin that forms from the weathering of felsic igneous and metamorphic rocks. *Sedimentary kaolin* is a kaolin ore formed through sedimentary depositional processes. *Secondary kaolin* is sedimentary kaolin comprising transported mineral particles. Though the term sedimentary kaolin was originally synonymous with secondary kaolin, it is clear that many kaolin ores deposited as sediments have undergone some postdepositional kaolinization of other minerals or recrystallization of kaolin minerals (Pruett 1993; Hurst and Pickering 1997). The primary or sedimentary origin of a kaolin deposit influences the exploration, mining, and processing methods used to manufacture a kaolin product (Figure 1). A variety

Table 1. Features that distinguish kaolin from ball clay and fireclay

	Kaolin	Ball Clay	Fireclay
Occurrence	Altered rock, sedimentary rock	Sedimentary rock	Sedimentary rock
Processing	Unprocessed, air-float, water-washed, delaminated, calcined	Unprocessed, air-float, some slurry	Unprocessed, calcined
Properties	White or nearly white, clay particle size	Highly plastic clay, contains some organic matter and/or swelling clay	Low in alkalis, calcium, and iron; high alumina and silica; does not deform at high temperature
Use	Pigment, filler, ceramic, refractory	Ceramic, refractory	Refractory
Synonyms	China clay, paper clay, white clay, <i>bolus alba</i>	Pipe clay	Firestone, pot clay, refractory clay, sagger

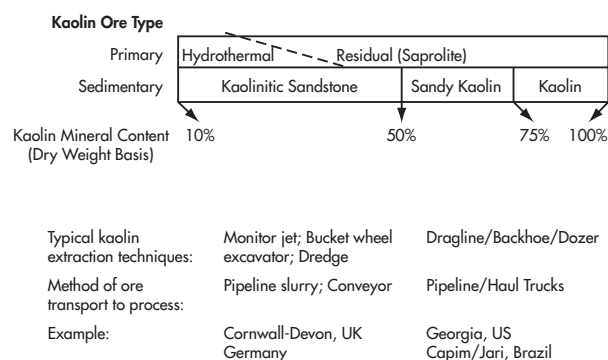


Figure 1. Relationship between kaolin mineral content and extraction method for kaolin ore types

of terms (Table 2) are used to describe rock types that contain kaolin minerals in sufficient concentration to be used or considered as kaolin ores or are associated with kaolinized rock units.

GEOLOGY

Mineralogy

Kaolin minerals are dioctahedral 1:1 phyllosilicates having a sheet of silicon atoms in tetrahedral coordination with four oxygen atoms and a sheet of aluminum atoms in octahedral coordination with two oxygen atoms and four hydroxide molecules (Figure 2). The basal oxygen atoms of the tetrahedral sheet form a crystal face, and the apical oxygen in the silica sheet are shared with aluminum. The remaining two thirds of oxygen in the octahedral sheet are shared with hydrogen (i.e., hydroxides) and form the opposing crystal face. Hydrogen bonding between the basal oxygen of the tetrahedral (T) sheet and hydrogen of the octahedral (O) sheet in an adjacent layer define a cleavage plane that enables delamination of kaolinite into flat platy particles. The difference between kaolinite, dickite, and nacrite is related to differences in the stacking order of unit layers. Kaolinite has a single tetrahedral-octahedral (TO) layer; dickite has a two TO-stacking unit layer with higher structural order than kaolinite; and nacrite has a six TO-stacking unit layer and ordered distribution of octahedral vacancies forming a crystal with rhombohedral symmetry. Halloysite has two layers of water between each TO layer in its hydrated form. Hydrated halloysite is also referred to as 10Å-halloysite, indianite, and endellite. Dehydrated halloysite is called 7Å-halloysite or metahalloysite.

Kaolinite is the most common kaolin mineral and has the greatest industrial importance. The kaolinite crystal lattice shows a range of defect concentrations and isomorphous substitution of iron for aluminum in the octahedral sheet and perhaps aluminum for silicon in the tetrahedral sheet (Schroeder and Pruett 1996). The terminology to describe kaolinite defects is confusing and discordant. Kaolinite crystal defects were initially described as well-crystallized or poorly crystallized, terms used by Grim (1953), which changed in the scientific literature to well-ordered or poorly ordered, and evolved to high-defect or low-defect, which is currently favored by mineralogists publishing in academic journals such as *Clays & Clay Minerals*. In the patent literature, industrial mineralogists and technologists typically use the terms well-crystallized or poorly crystallized, as originally used by Grim.

The Hinckley index is a method recognized by industry for measuring the relative levels of defects in kaolinite powders. The Hinckley index of kaolin is calculated using x-ray powder diffraction patterns (Figure 3). High-defect kaolinite has broad x-ray peaks,

a low Hinckley index (<0.6), and is called poorly ordered or poorly crystallized kaolinite. Low-defect kaolin has sharp x-ray diffraction peaks, a high Hinckley index (>0.7), and is called well-ordered or well-crystallized kaolinite. Hinckley index relates generally to the physical properties of kaolin, particularly to particle size. Kaolin with a high Hinckley index is typically coarse particle size (<70 wt % <2 µm), whereas kaolin with a low Hinckley index is typically fine particle size (>80 wt % <2 µm).

The accessory mineral content of kaolin is a result of its geological origin and the separation processes used for beneficiation. Primary kaolin ore from different deposits or even the same deposit generally show a wide variation in mineralogy that is controlled by the degree of alteration by weathering and hydrothermal processes. Primary kaolin contains significant amounts of nonkaolin minerals that are resistant to alteration. Common minerals that resist alteration processes are quartz, muscovite, tourmaline, and zircon. The margins of primary kaolin deposits can have sharp boundaries or can gradually change into less-altered rock that shows only partial feldspar and mica alteration. Rock that is partly kaolinized can have some host minerals from the parent rock, such as feldspar or biotite, or some minerals that are first series products of chemical alteration, such as halloysite, illite, vermiculite, or smectite.

Sedimentary kaolin typically does not contain high concentrations of unstable or labile minerals from the parent source rock (Figure 4), and the content of minerals such as quartz and mica in commercial deposits is low because coarse sand- and silt-sized particles were separated from clay during sediment transport. The fine silt- or clay-sized fractions that make up the bulk of sedimentary kaolin deposits contain impurities such as anatase, illite, smectite, hydroxyl-interlayer vermiculite, and mixed-layered clay minerals. Sedimentary kaolin that is associated with oxidized sediments contains iron oxide and iron hydroxide minerals that are common in soil environments such as hematite and goethite. Sedimentary kaolin that is associated with reducing anoxic depositional environments will generally contain organic matter and may contain iron sulfides such as pyrite, marcasite, or both.

Clay-sized titania minerals such as anatase are common in sedimentary kaolin and are uncommon in primary kaolin. Anatase and its precursor pseudorutile are weathering products of ilmenite and titanium-bearing biotite mica inherited from the parent rock (Schroeder, Pruett, and Melear 2004). The chemistry of anatase appears to reflect its precursor minerals (ilmenite, micas) by having minor levels of iron and trace levels of chromium, zirconium, and niobium substituting for titanium, thus causing the mineral to have a brown to tan color which detracts from the whiteness of kaolin products. Leucogene originating from ilmenite typically occurs as coarse aggregates that can be removed by standard gravity separation or magnetic separation processes, whereas anatase resulting from biotite mica alteration is typically finely disseminated in the kaolin ore and responds well to flotation or selective flocculation for removal.

OCCURRENCE

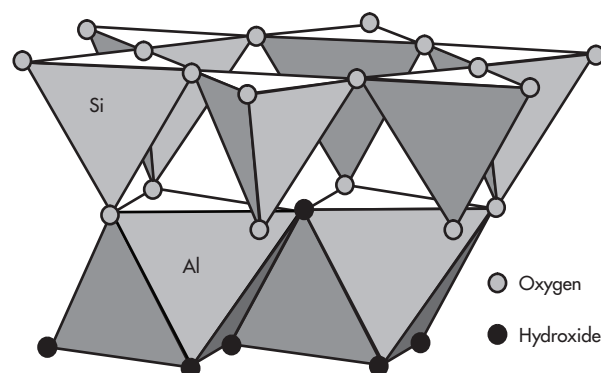
Kaolinite is a very widespread mineral across the earth's surface, especially as a major component of soils in humid subtropical and tropical areas. Kaolin deposits (Ross and Kerr 1931; Patterson and Murray 1984) of sufficient purity, brightness, whiteness, and suitable mineral-water slurry viscosity, however, are rather rare.

In general, kaolin deposits can occur as the following:

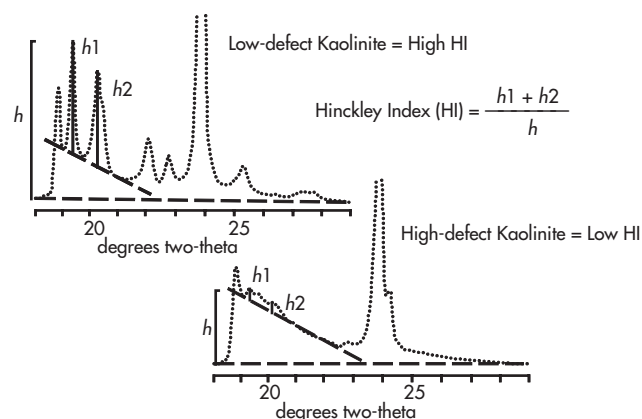
- Sedimentary bodies with fairly to extremely low "grit" content in various stages of oxidation and recrystallization
- Residual weathering blankets or funnel-shaped hydrothermal alteration zones along fracture patterns from much older aluminous rocks such as granites

Table 2. Kaolin rock terms and definitions

Terms Generic to Kaolin	
Kaolin	A rock mass containing principally kaolinitic clays that are low in iron, and usually white or nearly white in color (Ross and Kerr 1931)
Tonstein	Kaolin composed of volcanic ash that was partly or fully altered to kaolin minerals and is commonly associated with coal deposits.
Terms Typically Related to Primary Kaolin	
China stone	Partly kaolinized granite that is harder than China-clay rock
China-clay rock	Granite showing the highest degree of kaolinization where all feldspar has altered to kaolinite and can readily be broken apart by hand
Cornish stone	China stone
Lithomarge	A smooth indurated variety of kaolin containing a mixture of kaolinite and halloysite
Saprolite	Weathered igneous or metamorphic rock showing primary relict texture that can have a high kaolin mineral content
Terms Typically Related to Sedimentary Kaolin	
Ball clay	Highly plastic secondary clay containing kaolinite and used for ceramics
Fireclay	A clay, typically containing kaolin minerals, with a high silica and alumina content; used as a refractory because it will not deform at high temperature
Flint clay	Kaolin that is smooth, tough, flintlike, and breaks with a pronounced conchoidal fracture
Hard kaolin	A term original used for kaolin used to fill hard rubber that originates from fine-particle-size kaolin deposits located in the Georgia–South Carolina kaolin district. Hard kaolin also occurs in northeastern Brazil. It has a low Hinckley index and tends to break with some difficulty in a rough irregular fracture.
High-alumina kaolin	Kaolin containing minor amounts of hydrous alumina minerals such as gibbsite, boehmite, or diaspore
Kaolinitic sandstone	Sandstone containing significant and potentially separable amounts of kaolin minerals. The sand-sized particle content is >50% by volume or mass.
Sandy kaolin	Kaolinitic sediments generally containing between 5 and 50 wt % sand-sized particles
Soft kaolin	A term originally used for kaolin used to fill soft rubber that originates from coarse-particle-size kaolin deposits located in the Georgia–South Carolina kaolin district. Soft kaolin has a high Hinckley index, tends to be massive, and breaks with a smooth conchoidal fracture.
Underclay	A clay that underlies a coal bed representing a soil from the coal swamp flora. Underclay is commonly kaolinitic and can be a source of ball clay or fireclay.

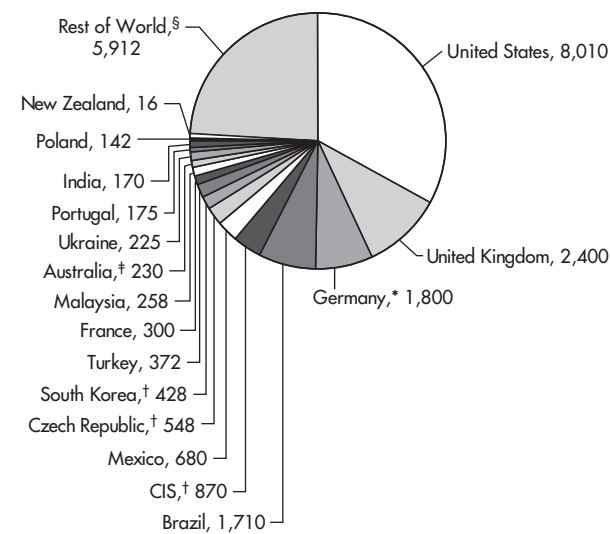


Adapted from Grim 1953.

Figure 2. Kaolinite crystal structure**Figure 3. Hinckley index formula with examples of calculation for low-defect and high-defect kaolinite from x-ray powder diffraction spectra collected from random-oriented, pulverized kaolin powders**

Mineralogy	Weathering	Transport/ Deposition	Alteration	
		Distance → Higher Higher ← Energy	Early (reduction)	Late (oxidation)
Quartz	→	→		
Muscovite	→	→		
Feldspar	→	→		
Kaolinite, low-defect	→	→		
Halloysite	→	→		
Kaolinite, high-defect	→	→		
Biotite	→	→		
Ilmenite/Magnetite	→	→		
Pseudoturbite	→	→		
Anatase	→	→		
Hematite	→	→		
Goethite	→	→		
Organic matter	→	→		
Pyrite	→	→		
Marcasite	→	→		

Figure 4. Sequence of mineral changes from a granite that are associated with (1) weathering, (2) transport and deposition, (3) early stage of postdepositional alteration, and (4) late stage postdepositional alteration for kaolin in central, middle, and eastern Georgia, United States



Modifications from the USGS numbers including the following:
* German kaolin production taken from *Minerals Yearbook 2002*.
† Assumed 15% beneficiated, dry product recovered from crude kaolin.
‡ Includes ball clay.
§ Modified to reflect adjusted volumes for CIS, Czech Republic, and South Korea; and deletion of volume from Columbia.

Figure 5. World production, kt (as compiled by the U.S. Geological Survey [USGS], 2002)

- Weathering alteration deposits of feldspar-rich (arkosic) sedimentary rock

The most prominent world kaolin mining districts are in the United States (southeastern), Brazil (northern), the United Kingdom (Cornwall–Devon), and Germany (Bavaria and Saxony). The volume of beneficiated kaolin produced from these four districts is shown in Figure 5. Kaolin production from some other countries is reported using different metrics such as crude tons mined (Commonwealth of Independent States [CIS], Czech Republic, and the Republic of Korea), or includes ball clay (Australia) or common clays (Colombia). The prominence of U.S., Brazilian, U. K., and German kaolin production is both in terms of volume and quality of beneficiated product that reaches global pigment and filler markets as opposed to local commodity markets where kaolin is sold as inexpensive mineral filler or as a structural component in brick.

United States

In the southeastern United States, kaolin has been mined since colonial times in the upper Coastal Plain areas of Georgia and South Carolina. These deposits are composed of deltaic sediments of Late Cretaceous to Early Tertiary age that represent the Oconee Group (Figure 6).

The major sedimentary units here are cross-bedded, fining-upward coarse- to fine-grained quartz sands which originated as outwash from weathered Paleozoic to Precambrian granitic rock bodies contained in the Piedmont and Blue Ridge provinces of the Appalachian Mountains. Lens-shaped clay accumulations were formed by sediments deposited in low, swampy areas on the advancing delta

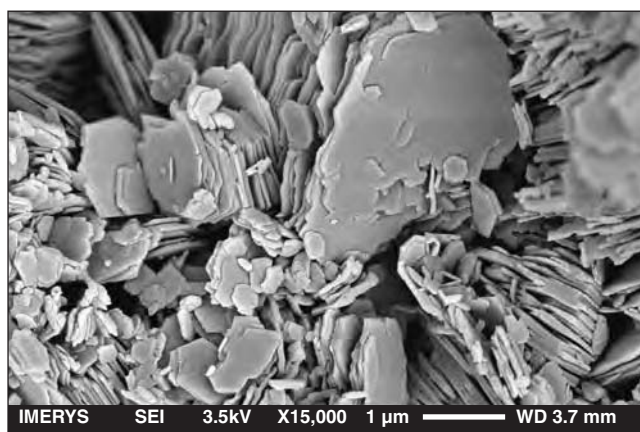
Section (thickness not proportional)	Age	Group	Formation	Member	Description of Stratigraphic Units, Including Their Role in Groundwater Oxidation–Recrystallization of Kaolins
	Late Eocene	Jackson or Barnwell	Twiggs Clay	No formal stratigraphic term yet applied.	Smectite fuller's earth, denies recharging oxidizing groundwater access to kaolin beneath unless breached by erosion.
			Clinchfield Sand	Treadwell and Riggins Mill	Fine-grained sand with occasionally abundant marine vertebrate fossils (shark and other fish teeth and bones, etc.).
	Early–Middle Eocene	Oconee	Huber	Jeffersonville*	Fining-upward aquifer sand sequences capped by hard, only partially altered, finer-particle-size, higher-iron kaolin lenses.
	Late Paleocene			Marion*	Soft gray to black unoxidized kaolin and lignite lenses in clayey sands, few to no commercial-quality kaolin deposits.
	Latest Cretaceous		Buffalo Creek*	Not Yet Subdivided	Many fining-upward aquifer sand sequences, capped by soft coarse kaolin lenses that are currently the most heavily mined.
	Late Cretaceous	No formal stratigraphic term yet applied.	Pio Nono	No formal stratigraphic term yet applied.	Arkosic clayey sand with no kaolin lenses, contains no known commercial kaolin deposits. Coarse gravel at base.
	Paleozoic and Pre-Cretaceous	No formal stratigraphic term yet applied.	Piedmont "Basement"	No formal stratigraphic term yet applied.	Metamorphic–igneous complex; weathered granites, gneisses, and phyllites. These crystalline rocks were sources for commercial kaolins.

LEGEND: fk = Finer particle size hard kaolin (both unoxidized and oxidized).
ck = Coarser particle size soft kaolin (both unoxidized and oxidized).
kl = Gray kaolins and lignites.
— U — = Profound unconformity.
- - - U - - - = Subtle unconformity.

*Stratigraphic unit that produces important tonnages of commercial grade kaolins.

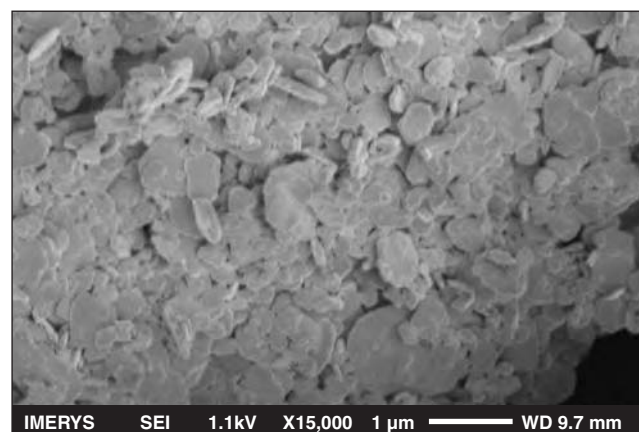
Adapted from Pickering and Avant 1999.

Figure 6. Stratigraphy of the Georgia kaolin district



Courtesy of IMERYS.

Figure 7. Electron photomicrograph showing the fracture surface of coarse kaolin crude that is representative of Cretaceous kaolin deposits in Georgia



Courtesy of IMERYS.

Figure 8. Electron photomicrograph showing the fracture surface of fine kaolin crude that is representative of fine Tertiary kaolin deposits in Georgia

Table 3. Comparison of typical sedimentary characteristics for soft, coarse-particle-size kaolin deposits with those for hard, finer-particle-size kaolin deposits

Typical Characteristics of Sedimentary Kaolins	Soft Kaolin	Hard Kaolin
Texture of crude clay fracture surfaces	Breaks easily into smooth, conchoidal surfaces	Tough, breaks less easily, rough, earthy, hackly surfaces
Larger trace fossils	Burrows and trace fossils very scarce to absent	Common, mainly intertidal trace fossil burrows
Microscopic fossil types of dominant plant pollen and spores	Mainly pollen of upland, back-deltaic, and continental aspect	Trace bacteria, more marine pollen, dinoflagellates, and hystrichospherids
Typical deagglomerated crude clay particle size	Coarser than about 65% to 70% finer than 2 μm	Finer than about 80% to 90% finer than 2 μm
Clay particle crystal habit or morphology	Coarse books, stacks, and vermiforms in a matrix of euhedral thin crystallites, more recrystallized	Vermiforms, books, and stacks very rare or absent, only thin submicron single crystal plates, less recrystallized
Crystallite particle packing relationship	Open, porous, interlocking face to edge packing	Tight, little pore space, face to face packing
Crystal cleavage, ability to produce delaminated products	Coarse vermiforms and books cleave and delaminate well for high aspect ratio products	Hardly delaminates at all, crystal plates are too fine and thin
X-ray diffraction patterns	Well-resolved peaks in the 020, 110, 111, 021, and 021 bands, low crystal defect kaolinite	Poorly resolved peaks in the 020, 110, 111, 021, and 021 bands; diffuse pattern; high crystal defect kaolinite
Hinckley index	High Hinckley index, two phase mixture	Low Hinckley index, single phase
Clay chemistry after deagglomeration removal of detrital minerals	Fe and Ti low, increase with decreasing crude particle size, lower alkali metals	Fe and Ti higher, often same, or increase with decreasing crude particle size, slightly higher alkalis
Accessory detrital mineral suites	Altered muscovite abundant, detrital heavy minerals more mature but less abundant	Muscovite scarce, coarser anatase more abundant, immature heavy minerals
Moist crude clay bulk density and specific gravity	1.2–1.3 st/yard ³ , specific gravity 1.3–1.6	1.3–1.4 st/cu yd, specific gravity 1.6–1.7
Aqueous slurry viscosity at highest-solids concentration	Generally Hercules higher and Brookfield lower	Generally Hercules lower and Brookfield higher
Georgia, geological age, and stratigraphic occurrence	Older, in Georgia in Cretaceous Buffalo Creek Formation or early Paleocene Marion Member	Younger, in Georgia from Early to Middle Eocene Jeffersonville Member of the Huber Formation
Northern Brazil occurrence	Rio Capim District, Para State	Rio Jari District, Amapa State
Depositional environment	Fluvial upland back-deltaic, mostly fresh water	Coastal, marginal marine, often brackish or saline

Adapted from Pickering and Hurst 1989.

front and also in the less saline back-delta areas. These lens-shaped clay units were deposited during several worldwide episodes of marine transgression and highstand along the fall line in Georgia and South Carolina. This process of deposition and the role of weathering and bacterial alteration are more thoroughly described in Elzea Kogel et al. (2000) and Elzea Kogel et al. (2002). Domkowski (1992) suggested that the older Cretaceous coarse kaolin (Figure 7) was derived from weathered granitic and gneissic source

rocks, and the Early Tertiary fine-particle-size kaolin (Figure 8) from phyllic meta-volcanic source rocks. In general, Table 3 describes soft and hard kaolin and holds true for kaolins in both Georgia and the eastern Amazon region of Brazil.

Because the river deltas were heavily overgrown with thick plant cover, the clays were laid down with a considerable organic content of decaying vegetation. The resulting clay deposits were originally rather dark organic, pyritic mud, and usually cap distinct,

Table 4. Comparison of the typical weathering alteration characteristics of reduced and oxidized types of sedimentary kaolins from Georgia

Typical Characteristics of Sedimentary Kaolins	Reduced, Unoxidized Kaolins, Protected from Recharging Fresh Groundwater	Oxidized Kaolins, Well Exposed to Recharging Fresh Groundwater
Moist clay color or shade	Pale gray to brownish gray	Pale pink to cream
Main impurity materials	Dark organic matter, pyrite	Hematite, anatase, and goethite
Stratigraphic and geomorphic occurrence	Typically down-dip, beneath a thick cover of impermeable overburden	Generally up-dip areas, where thick overlying impermeable overburden was eroded away
Amount and type of organic matter	More abundant, readily oxidized	Less abundant
Valence state of iron minerals	Fe ²⁺ , ferrous	Fe ³⁺ , ferric
Extent of recrystallization	Can be lower Hinckley index	Can be higher Hinckley index
Types of industrial processing required to produce well-whitened paper coating clay products	Ozone oxidation or thermal calcination to remove dark organic matter; can be unresponsive to reduced-acid leaching and magnetic separation	Ozone oxidation for removal of dark organic matter not needed, responds well to reduced acid leaching and magnetic separation

Adapted from Pickering, Hurst, and Elzea 1997.

fining-upward, cross-bedded sand depositional sequences. Subsequent weathering oxidation and microbial alteration naturally beneficiated these dark detrital clays to their present near-white purity and appearance (Table 4), perhaps accompanied by extensive in-situ recrystallization of the coarser particle-size Cretaceous kaolin. The table applies to either the soft, coarse, and older clays, as well as the hard, fine, and younger clays. Both the Rio Capim and Rio Jari sedimentary kaolins of the eastern Amazon region of Brazil fit into the well-oxidized side of the table.

In recent years, an attempt has been made to open a primary kaolin district in the Georgia Piedmont near Sparta, Georgia. This venture is developing some exceptionally white and bright high-grit residual kaolin, which has formed as a weathering blanket over the extensive mid-Paleozoic Sparta granite batholith. Feldspars in the Sparta granite have been altered in situ, first to halloysite, which then is transformed to very coarse kaolinite. Because the kaolinite particles were not exposed to the effects of erosion, river transport, and sedimentary deposition, the clay is relatively pure after extensive de-gritting. Potential advantages of this new venture include very high brightness and whiteness, very coarse particle size, and favorable mining conditions with easily excavated low overburden. The main disadvantage of the Sparta primary kaolin is the much higher content of quartz and mica particles.

Smaller volumes of kaolin are mined in several other states in the United States. In the high alumina-clay district near Andersonville, Georgia, and Eufula, Alabama, mixed kaolin and gibbsitic bauxite are mined to produce refractory brick, castings, bodies, and grogs. In the Central Valley of California, refractory-grade kaolin is mined from cross-bedded kaolinitic sands of the Eocene Ione Formation (Bates 1945). The Ione kaolin is a relatively minor by-product of industrial and construction quartz sand production. Somewhat similar kaolinitic sand deposits of the Late Paleocene age Wilcox Formation are mined near Kosse, Texas, where the kaolin is calcined to produce a rather white pigment material. Near Edgar, Florida, similar kaolinitic sands of the Miocene Fort Preston Formation are mined for a popular kaolin product used by art and hobby potters.

Brazil

The fastest-growing kaolin-producing district worldwide is in the eastern Amazon region of northern Brazil (Figure 9). Here sedimentary kaolin is found in coarse deposits along the Capim River south of the Amazon and in very fine particle-size deposits on the east side of the Jari River north of the Amazon (Pickering and Linkous 1997; Pickering 1994). The coarse particle-size kaolin units in the Capim River area occur in the Late Cretaceous age Ipixuna Formation and

are found in grabens located along the southeastern margin of the Cameta Sub-basin (Rossetti and Santos 2003). Rossetti and Santos also propose a lower Tertiary age for the Barreiras Formation, which is the unit containing kaolin along the Jari River. Thus it appears that the eastern Amazon region sedimentary kaolins of Brazil were deposited during the same global sea level highstands that enabled deposition of the Georgia kaolin.

The Jari kaolin deposits were first developed by Ludwig in 1976. The Jari deposit is now mined and processed by Caulim da Amazônia, S.A. (Cadam) to manufacture an ultra-fine glossing pigment for paper coating. Since that time, Cadam's Felipe mine has grown steadily to become what is probably the largest single kaolin mine worldwide in terms of kaolin product volume. This kaolin deposit is unusual in that the main stratum is nearly 35 m thick with very little overburden. The kaolin particle size is very fine, with low grit content, enabling a very high recovery from crude clay. The mine east of the Rio Jari is connected to the processing plant at Munguba, on the west side of the river, by a pipeline beneath the river. The Rio Jari is deep and wide enough at Munguba to permit large ocean-going ships to berth directly at the plant site and load directly with kaolin for worldwide export.

South of the Amazon River are two rapidly growing kaolin operations located west of the Rio Capim. Barges can navigate the Rio Capim, but this river is too shallow for the ocean-going ships that transport kaolin. Both of the Capim producers, Rio Capim Caulim, S.A. (RCC) and Pará Pigmentos S.A. (PPSA), have built the longest kaolin slurry transport pipelines in the world (each >150 km) from their mining areas to the processing plant (RCC) and dryers (RCC and PPSA) near Barcarena, west of Belém. Each drying facility is connected by conveyor to mooring platforms in the river where ships can be loaded with either dry or slurry kaolin products for worldwide export or for domestic use in southern Brazil.

Some advantages of the Brazilian deposits are the following:

- Superior kaolin ores of low grit, very pure kaolin of high brightness and whiteness, with favorable viscosity and paper-coating characteristics
- Access to deep water ship transport to worldwide customers
- Low overburden ratios and relatively simple mining conditions
- Abundant supplies of process water
- Relatively low labor rates
- Major nearby hydroelectric power supply, in the case of the Capim area

For these reasons and others, in recent years the Brazilian kaolin industry has grown rapidly while the other main world producers have experienced considerably less growth (Figure 10).

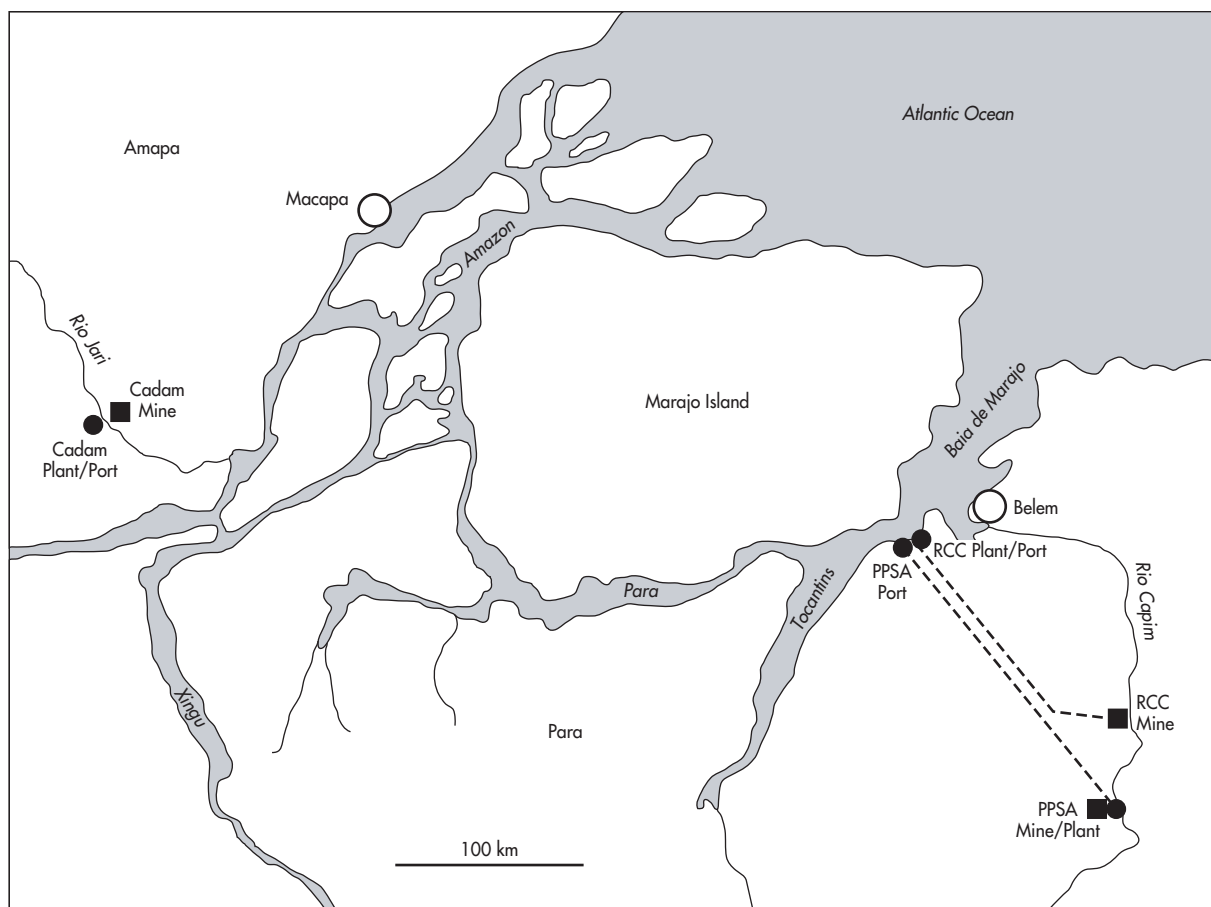


Figure 9. Location of sedimentary kaolin mines with associated pipelines, wet process plants, and ports in northern Brazil near the mouth of the Amazon River

United Kingdom

Primary kaolin has been mined for centuries from hydrothermal alteration deposits in the southwestern United Kingdom, in Cornwall and Devon. Production is from altered fracture zones in the Variscan age Cornubian granite near St. Austell and Tregonning. The kaolin is quite coarse in crystal size, and recovery rates are 8% to 20% because of the very high content of coarse grit. Accessory minerals include quartz, unaltered feldspar, muscovite and biotite mica, tourmaline, topaz, apatite, fluorite, zircon, cassiterite, wolframite, rutile, hematite, and turquoise. The hydrothermal kaolinizing fluids have followed joints, fractures, and faults in the parent granite, often along north-south and northwest-southeast orientations.

The result is roughly funnel-shaped kaolinized deposits dipping steeply and tapering downward to depths as great as several hundreds of meters. As would be expected, the most extensive kaolin deposits were found in areas where major fracture zones intersect or overlap (Exley 1959, 1976; Bristow 1977). Alteration fluids were apparently meteoric in origin, recharging the groundwater system, which has set up slow convection cells carrying the low-temperature hydrothermal fluids (Durrance et al. 1982; Fehn 1985). Bristow (1993) has proposed that the heat source to drive the groundwater convection cells was from radioactive decay from uraninite, apatite, zircon, monazite, and xenotime associated with the granite.

Kaolin in Cornwall-Devon is typically mined using a monitor directed at kaolinized zones along the rock fracture systems. The

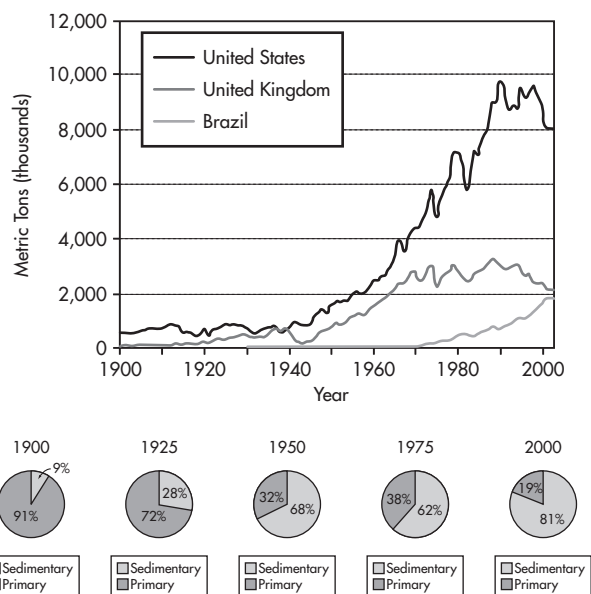


Figure 10. Kaolin production from Brazil, the United Kingdom, and the United States, 1900–2002

resulting kaolin slurry drains to the lowest portion of the pits, from which it is pumped up to the degritting equipment. Refined by hydroseparators and cyclones, the degrittied kaolin slurry is pumped to the processing plants to produce kaolin products for the paper filling and coating, paint, adhesives and sealants, rubber, tiles, plastics, and ceramics industries (Manning 1995).

Germany

Sedimentary kaolin is mined from Tertiary age feldspathic-kaolinitic sandstone in the Hirschau and Schnaitenbach areas of Bavaria, in southwest Germany. The sediments were derived from granitic source rocks in the Naab Basin Mountains and are preserved in an east-west trending half-graben. The deposit averages about 76% quartz, 12% feldspar, and 12% kaolin. The quartz has an average grain size of 1 mm, the feldspar about 0.1 mm, and the kaolin about 2 μ m; economic separation depends upon efficient size fractionation.

Overburden is removed and raw ore mined by bucket-wheel excavator and transported by conveyor belt to the adjacent production plant. The ore is mixed with water and dispersant chemical by chain stirrers in stone-lined vats. The sand is removed by screening, and the slurry is refined to remove fine quartz and feldspar. Kaolin recovery is 12% to 16% by weight from the raw ore. The feldspar and quartz sand concentrates are cleaned and sold to local glass industries. The kaolin concentrate is further processed, and the product is used for applications such as paper filler and coater; paint, plastic, rubber filler, and pigment; and ceramics.

In northwest Saxony in southeastern Germany, between Dresden and Leipzig, primary kaolin derived from the alteration of volcanic ignimbrites and porphyritic andesites of the Bohemian Massif are extensively mined. These kaolins are used as pigments in paper, paint, and plastic; as filler in rubber; and as raw material in fine art ceramics and porcelains. Kaolin altered from pitchstone, felsite, and quartz porphyry has been mined at Seilitz, near Meissen, continuously since 1764 (Murray 1989).

INDUSTRIAL PROPERTIES

Chemical Properties

Theoretically, kaolin contains just alumina, silica, and structurally bonded hydroxides (Table 5). However, natural processes form kaolin minerals and cause some iron substitution for aluminum in proportion to iron content of the bulk rock. Low concentrations of mineral impurities not removed by mineral processing will increase the content of the element oxides associated with those impurities. K_2O and MgO levels are typically elevated in proportion to mica content. MgO , CaO , and silica levels are typically elevated in proportion to smectite content. TiO_2 content is proportional to anatase and rutile content. Iron content is influenced by a wide assortment of iron-bearing minerals or iron-substituted kaolinite. Where a high degree of alteration has occurred, alumina and loss on ignition (LOI) at 1,050°C are elevated if gibbsite or boehmite occur in the ore. Commercial specifications related to the chemistry of kaolin products are standard when kaolin is used in ceramic, fiberglass, and refractory applications. The lower concentration of alkaline elements and higher concentration of alumina in kaolin make the material more refractory.

Hydrous kaolin is hydrophilic and can be dispersed at high solids (~70%) in water-based systems, making it an excellent pigment mineral for paper coatings and water-based paints. The aluminum-oxygen and silicon-oxygen bonds in the kaolin mineral layers form a chemically inert particle that is resistant to chemical attack through a wide pH range. This chemical resistance enables kaolin to be used as a filler pigment for acid, Kraft, and alkaline

Table 5. Examples of chemical assay results for wet-processed kaolin products manufactured in Brazil, the United States, and the United Kingdom

	Theoretical	Brazil (Capim)	Georgia (Middle)	United Kingdom (Cornwall)
	wt %			
SiO_2	46.54	44.80	45.70	46.20
Al_2O_3	39.50	38.30	37.60	39.00
Fe_2O_3	0.0	0.51	0.46	0.38
TiO_2	0.0	0.55	1.41	0.01
MgO	0.0	<0.05	0.03	0.16
CaO	0.0	<0.02	0.08	0.05
Na_2O	0.0	0.13	0.26	0.03
K_2O	0.0	<0.02	0.05	0.55
LOI @ 1,050°C	13.96	14.40	14.00	13.80

paper. The absence of an interlayer charge gives kaolinite a very low cation exchange capacity, which is important when high electrical resistance is desired in a material, such as for wire and cable insulators. The kaolinite edge and face surfaces have a net electrostatic charge that is pH dependent (Conley 1996). The octahedral edge of the kaolinite particle has a positive charge below a pH of about 4.5 and becomes negative at a pH of about 11 or higher (Figure 11). The tetrahedral edge of the kaolinite particle becomes more negative at a pH of about 7 or higher. Therefore, kaolin-water systems typically flocculate at a pH of about 6 and lower and are dispersed at a pH of about 6 or higher in the presence of dispersing chemicals (Figure 12). Dispersion is further discussed under Feed Preparation in the Processing section.

Physical Properties

Pure kaolinite is soft and white, has a naturally fine particle size and platy shape, and can be dispersed in water into a fluid slurry with >70% solids. These physical properties make it an excellent white pigment for applications such as paint and paper coatings where whiteness, gloss, and coverage are important. Commercial specifications for the physical properties of kaolin products are standard where kaolin is used as a pigment or functional filler. Each market application has its own specific set of properties measured and reported on the kaolin product certificate of analysis (COA). In general, kaolin physical properties cited on a COA for pigment and filling applications fall into four categories: color, particle size, viscosity of a clay-water slurry, and abrasiveness.

Color

How color and whiteness are reported depends on the market application specific to a geographic region. Brightness is a measure of light reflectance relative to a specific white standard at a specific wavelength. In North America brightness is measured using *Test Method 534, Brightness of Clay and Other Mineral Pigments (d/0° diffuse)* from the Technical Association of Pulp and Paper Industry (TAPPI) and is reported in GE units. GE brightness is reported relative to an MgO standard at 457 nm and is measured using a technical brightness tester. Kaolin pigments with brightness ranging from 84 GE to 88 GE units are considered standard brightness grades; >89 GE units are considered high brightness grades. In Europe, brightness is measured using ISO Standard 2470, *Paper, Board, and Pulp—Measurement of Diffuse Blue Reflectance Factor (ISO Brightness)*, and is reported to pigment consumers in ISO units. The Hunter *L-a-b* color system is used to report pigment reflectance and

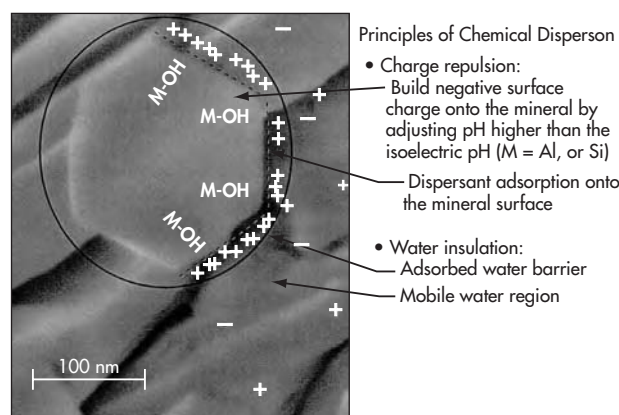
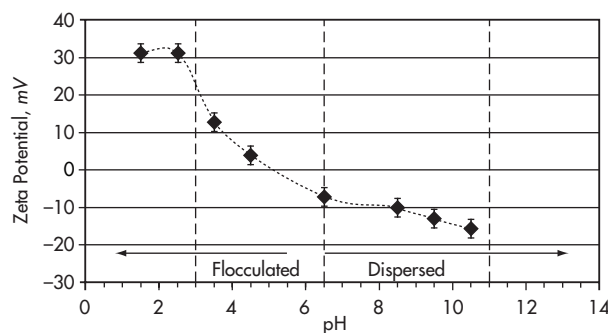


Figure 11. Scanning electron photomicrograph of a kaolinite particle with diagram showing surface charges that influence dispersion of kaolin particles in aqueous systems



Adapted from Yuan and Pruett 1998.

Figure 12. Zeta potential (Z^0) versus pH for coarse Georgia kaolin that has the Z^0 corrected to show the theoretical kaolinite zero point charge at pH 4.8

shade. L is a measure of reflectance on a scale from zero (none) to 100 (total); a measures redness (positive) or greenness (negative); and b measures yellowness (positive) or blueness (negative). Absence of color is indicated by a zero value in the a and b scales. Several standards also report whiteness and yellowness as a function of light absorption across the visible light spectrum.

Particle Geometry

Particle-size specifications relate to the overall distribution of particle size and to maximum concentrations of coarse particles. Kaolin used for paper applications has particle size measured by a gravitational settling technique such as the SediGraph (Micromeritics Instrument Corporation, Norcross, Georgia). Particle size measured by gravitational settling reports an equivalent spherical diameter that matches well with cut point targets on centrifuges. Particle size may be reported as a mass percent below $2 \mu m$; for example, a No. 1 coating clay will typically have 90 wt % of particles $< 2 \mu m$. Other markets may specify the products in terms of median diameter (d_{50}) and maximum top size. The particle size distribution can be expressed as a particle size at two or more points in a range of particle sizes or can be expressed as a steepness or sorting coefficient that describes the narrowness of a particle-size distribution. A kaolin pigment particle-size distribution can be engineered to

yield $0.3 \mu m$ pores in a paper coating, a pore size optimal for scattering light and higher opacity.

Maximum top size is the largest particle diameter measured by a specified particle-size instrument, which could be a gravitation-settling or laser light-scattering device. Hegman grind is also a measure of maximum top size. Laser instruments can report a platy particle's absolute diameter, absolute thickness, or somewhere in between as a function of particle orientation to the light source. Residue specifications are another parameter related to particle size that provides the application's tolerance to coarse particles inherited from the ore or incidental to processing. Residue is typically expressed as a mass percent age or parts per million (ppm) greater than a specific screen mesh size.

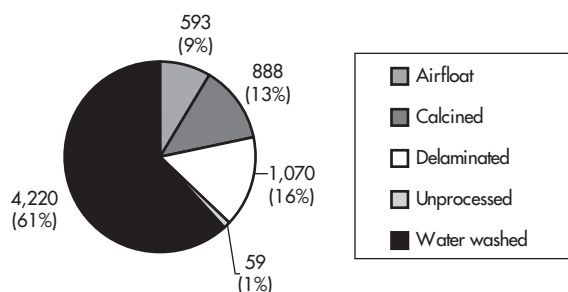
The platy shape of kaolin is an important property that influences coverage, gloss, and printability of a coating. There is no agreed industry standard for reporting kaolin particle shape. The platy shape of individual kaolinite particles is expressed as an aspect ratio, which is the average of a particle's diameter divided by its thickness. An average aspect ratio can be reported for a population of particles. Measurement of the average aspect ratio on kaolin is tedious and expensive because a statistically meaningful ratio requires the measurement of a large population of individual particles using a transmission electron microscope or similar instrument (Vander Wood, Pruett, and Boltin 1995). Kaolin producers and consumers take different approaches to approximating aspect ratio. Some use microscopy, others use a combination of surface area and particle-size measurements. IMERYS developed its own proprietary technology for measuring the shape properties of particles. Some manufacturers of laser light-scattering, particle-sizing instruments claim to measure aspect ratio, but these techniques need to compensate for a range of particle orientations and are highly influenced by particle dispersion.

Rheological Properties

The rheological properties of a kaolin-water suspension can be reported as flowability, viscosity concentration, slurry solids, or fluid viscosity at a specific shear rate. Flowability is expressed as a percentage of solids in the minimum amount of water needed to make a dispersed clay system fluid. Viscosity concentration and slurry solids indicate, respectively, the slurry water content at set viscosity and the recommended water content to make a fluid kaolin suspension fit for use when applied to material handling and to a customer's application. Viscosity concentration is reported as percent solids when an optimally dispersed kaolin suspension is made down to 500 centipoise at 100 rpm measured using a No. 3 spindle on a Brookfield viscometer (Brookfield, Middlebrook, Massachusetts), the standard instrument used to measure low-shear viscosity of clay-water suspension. Brookfield viscosity is expressed in centipoise at a specified solids concentration, rotational speed (10 to 100 rpm), and spindle dimension (typically 1 to 3).

The Hercules viscometer (Kaltec Scientific, Inc., Novi, Michigan) is used to measure the high-shear behavior of a clay-water suspension (TAPPI method T-648). The Hercules instrument applies a shear rate from 0 to either 1,100 rpm or 4,400 rpm. The instrument changes the shear rate from 0 rpm to as high as 4,400 rpm and back down to 0 as it measures the torque (from 1×10^4 to 1.8×10^7 dynes-cm) applied to the clay slurry in a sample cup. Results can be reported in centipoise or more commonly, where the pen exits the chart, in "dynes" or rpm. When the torque equals 1.8×10^7 dynes-cm, an rpm value between 0 and 4,400 at 18 dynes is reported. When the torque is below 18 dynes, the dynes at 4,400 rpm are reported.

The solids concentration of the clay slurry is reported with the bob used and the shear rate or shear stress measurement. The



Source: USGS 2002.

Figure 13. Types of processed kaolin sold in 2002 by producers in Georgia, kt

measurement made by the Hercules viscometer also describes kaolin slurry as Newtonian, dilatant (shear thickening), or thixotropic (shear thinning).

Information published in previous editions of *Industrial Minerals and Rocks* on the subject of high-shear kaolin rheology has focused on the need for kaolin products that are very fluid under the extreme high-shear conditions found under the blade of modern paper blade coaters. However, the evolution of paper-coating technology, combined with a better understanding of how kaolin properties add value to coatings in terms of appearance properties, have changed, to some degree, the premise that premium kaolin products need to have dynes rheology at slurry solids >71%. For example, metered size press (MSP), curtain, and spray coaters no longer apply paper-coating colors using a blade to level the coating onto paper moving at very high speed. The engineering of paper-coating pigments to provide more even coverage at lighter coat weights or to provide higher opacity at heavier coat weights requires some compromise to rheological properties at high shear. High shear viscosity can be increased when features such as higher aspect ratio particles are engineered into kaolin products to improve coverage or when a more tightly controlled particle-size distribution is used to improve light scatter and opacity. Kaolin pigment fluidity, however, does have an important role in enabling the paper coater to maintain a manageable water balance in the coating color relative to machine-drying capabilities and to economically ship kaolin slurry by truck, rail, or ship.

Abrasiveness

Kaolin used as a pigment or functional filler must be soft and non-abrasive to prevent excessive wear on equipment used during processing or application. The abrasiveness of kaolin is typically measured on dispersed slurry at 15% solids using an Einlechner Abrasion Tester (Einlechner, Kissing, Germany) with the measurement result reported as weight of screen loss after a specified number of revolutions (mg loss/100,000 rev). Factors that impact abrasiveness are Mohs hardness of the mineral and particle size. As kaolinite is very soft, the occurrence of hard particles such as quartz and feldspar in the kaolin product will increase its abrasiveness. The top size and median particle size of the kaolin slurry also influence abrasiveness.

TECHNOLOGY

Processing

Kaolin processing is technically complicated and a costly barrier for entry into many markets where purity, consistency, handling characteristics, and appearance are valued properties. Most kaolin processing is performed in the wet state for pigment, functional

filler, and specialty mineral applications. Kaolin processing is typically performed in the dry state for refractory and ceramic applications where bulk chemistry is important but where purity, handling, and appearance characteristics may be less stringent. The USGS tracks worldwide kaolin production by country, how U.S. kaolin is processed, and how kaolin is used for both domestic and export consumption (see, for example, <http://minerals.usgs.gov/minerals/pubs/commodity/clays>). The USGS reports kaolin processing in several categories: airfloat, calcined, delaminated, unprocessed, and water washed (Figure 13). Dry-processed kaolin includes airfloat processed and refractory-grade calcined categories. Wet-processed kaolin includes water-washed, delaminated, and pigment-grade calcined categories. The term *slip* is used in reference to a low-solids kaolin mineral-water suspension that is wet processed to remove impurities or to engineer particle size and related characteristics. The term *slurry* refers to a final product that is a high-solids and dispersed kaolin mineral-water suspension containing chemicals to prevent unwanted particle agglomeration, gelling, settling, or microbiological growth.

Feed Preparation

Blunging is a process where dry-mined kaolin ore is made down into a mineral-water suspension with water in a range of 35% to 70% solids (Murray 1980). The kaolin blunger is simply a tank with an impeller near the bottom. Blunging is the first step in feed preparation for wet-processed sedimentary kaolins and dry-mined primary kaolins. It is not used where kaolin is wet mined with water-jet monitors. Many blungers are located at the head of pipelines that transport clay slip to the processing operation. Pipelines may then extend tens of kilometers, as in the case of the Georgia kaolin operations, or hundreds of kilometers, as in the case of the kaolin operations in the Capim District of northern Brazil.

The purpose of blunging is mechanical disaggregation of the rock to separate particles and chemical addition to keep particles dispersed. There are two facets of chemical dispersion of kaolin particles:

1. pH adjustment to induce a negative charge on both kaolinite particle edges and faces
2. Use of dispersant chemicals to increase the negative charge on mineral surfaces and thereby increase particle repulsion

The choice of pH used to disperse the kaolin slurry is partly dependent on downstream processes utilized for beneficiation. Typically, pH is adjusted to around 6.5 or 7.0 using sodium carbonate (soda ash). Chemical dispersants can be classified as inorganic or organic. Common inorganic dispersants used for kaolin processing include sodium silicate, tetrasodium polyphosphate (TSPP), and sodium hexametaphosphate (SHMP). The most common organic dispersant used in kaolin processing is sodium polyacrylate. The choice of dispersants used for primary dispersion is based on (1) the ability to disperse the kaolin particles, (2) the tolerance by downstream beneficiation processes, and (3) cost. Conley (1996) provides an excellent review of the principles and practices of chemical and mechanical dispersion.

Refining, Degritting, and Desanding

The concentration of kaolin clay from crude is called refining or desanding. The purpose of refining is to concentrate the kaolin minerals from the other major rock-forming minerals by particle-size separation, thereby making it one of the first steps in kaolin beneficiation. Refining is aimed at removing sand- and coarse, silt-sized particles. The particle size target in the refining process largely depends upon the particle-size distribution of nonkaolin mineral

impurities in the ore. Desanding is the first process step when kaolin is extracted from a primary deposit using a monitor, as in the case of the Cornwall and Devon deposits (Pemberton 1989). The term *grit* is used for particles greater than 44 μm (3.25 mesh), so desanding is the process of de-gritting. Kaolin ores that have high kaolin contents, such as commercial sedimentary kaolin in Georgia and Brazil, have de-gritting steps early in the process that are typically performed after bunting.

The processes used for refining are a function of gangue particle size and content. In Cornwall and Devon, where gangue particles are large and the major component of the ore, clay-bearing materials washed from the pit walls collect in sediment ponds near the pit bottoms. Gravel pumps move the clay-bearing materials from the sediment ponds to a spiral classifier or a bucket wheel desander. The spiral classifier is similar to the drag-box (sandbox) used for removing sand from sedimentary kaolin deposits. This process equipment enables coarse sand particles to settle into a concentrate that can be mechanically removed and enables the kaolin slip containing fine particles to overflow the trough and proceed to the next process. Screens are located throughout the kaolin refining and beneficiation process to remove coarse residues. Screens with very coarse mesh size may be utilized after desanding. Fine sand- and silt-sized particles are removed using hydroseparators and hydrocyclones.

Classification and Fractionation

Classification is synonymous with fractionation, the grading of particles too small to be screened according to their size, shape, and density by control of their settling rate through a fluid medium (USBM 1997). The continuous bowl-type decanter centrifuge, a major advance in kaolin processing in the 1930s, permitted the production of >80% <2 μm kaolin pigments used for paper coating (Murray 1980). The decanter centrifuge has a solid-wall bowl containing a helical screw inside the bowl that rotates at a slightly different speed. Sedimentation occurs inside the bowl, and the screw removes the coarse fraction to the discharge on one end of the rotating assembly while the fines-bearing slip discharges over a weir on the opposite side. The disc nozzle centrifuge is another type of centrifuge used for kaolin processing that has a finer cut size for production of ultra-fine kaolin products.

Brightness Beneficiation

Kaolin beneficiation processes include a range of advanced process technologies such as magnetic separation, selective flocculation, flotation, reduced acid leaching, and oxidative bleaching. Physical separation processes, such as magnetic separation, selective flocculation, and flotation, concentrate kaolin while removing nonkaolin particles, the majority of which are discoloring impurities such as iron oxides, iron hydroxides, titania minerals such as anatase, tourmaline, and micas or abrasive impurities such as quartz and feldspar.

The high-intensity magnetic separator (HIMS) has been used in Georgia and Cornwall for kaolin processing since the 1970s (Mills 1977; Clark 1985). Removal of paramagnetic impurities from kaolin requires that a dispersed kaolin slip slowly pass through a high magnetic field with high field gradient and multiple collecting surfaces. The conventional HIMS is an electromagnet that surrounds a central canister that may be 2.1 m (84 in.) or 3.1 m (120 in.) in diameter with an effective depth of about 51 cm (20 in.). The canisters are filled with a matrix of stainless steel wool. In the 1980s, superconducting magnet technology was introduced for processing kaolin. The main benefit of superconducting magnets is their lower energy consumption, smaller size, and higher field strength that is about 5 Tesla versus about 2 Tesla for a conventional HIMS. Super-

conducting HIMSs are further divided into static and reciprocating magnets. The static superconducting magnets use the same operating principles as a conventional HIMS, where the magnetic field acting on the canister is cycled on and off to allow flushing of magnetic impurities from the canister several times per hour when the magnetic field is eliminated. Reciprocating magnets typically have a higher duty cycle because the magnetic field is constant, and a movable dual canister allows one canister to be in the magnetic field while the other canister is flushed to purge captured impurities (Stadtmuller, Goode, and Riches 1988; Stadtmuller et al. 1997).

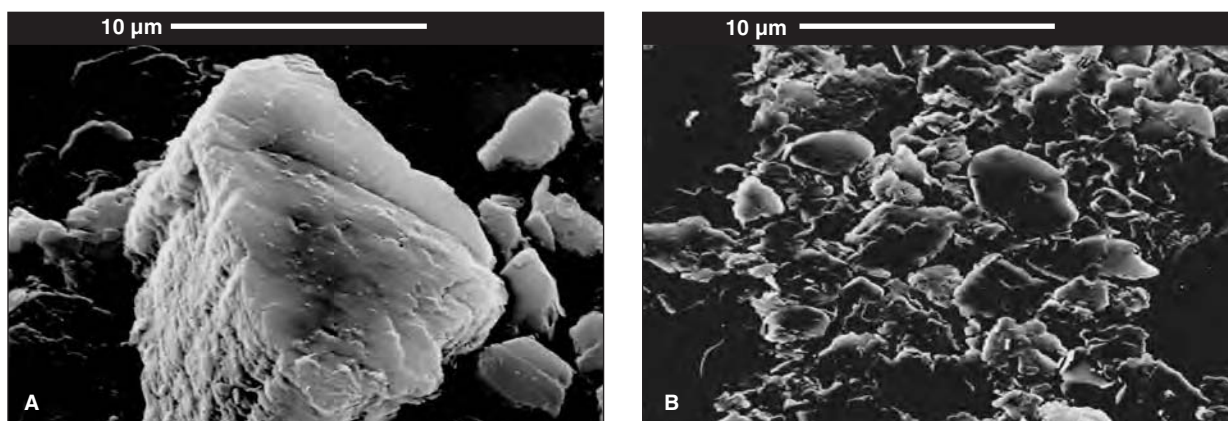
The objective of selective flocculation is to aggregate specific mineral particles into large agglomerates while leaving the remaining mineral particles in a dispersed state to permit mineral-mineral separation by gravitational settling. All Georgian and some Brazilian wet kaolin processors use selective flocculation to remove anatase, which contains some iron in the natural state. The selective flocculation process developed by Maynard (Maynard, Millman, and Iannicelli [1969] and Maynard [1974]) is the most common process and requires the blunged kaolin slip at approximately pH 6.5 be (1) overdosed with sodium hexametaphosphate and sodium silicate, (2) conditioned with sodium chloride, (3) aged to allow anatase particle aggregation, and (4) flocculated using a water-soluble, strongly anionic, high-molecular-weight polyacrylamide polymer to form anatase flocs that will settle in a thickener. Several improvements have been made to the selective flocculation process including those described by Shi (1986); Behl, Willis, and Young (1996); and Garforth et al. (2000).

Reverse froth flotation was introduced to kaolin processing in the early 1960s (Greene and Duke 1962; Grounds 1964; Cundy 1976; Yoon and Hilderbrand 1986) to remove anatase from sedimentary kaolin ore. Sedimentary kaolin flotation entails adding a carrier such as ground calcium carbonate (ground limestone) or divalent ion such as calcium or barium chloride to a dispersed kaolin slip to aggregate anatase. The slip is then conditioned with a collector such as fatty acid that coats anatase particle surfaces, making these surfaces hydrophobic so that the anatase will attach to air bubbles.

Reduced-acid leaching and oxidative bleaching are chemical treatments applied to kaolin slurries to improve brightness and shade. The use of reduced-acid leaching to remove soluble iron oxides such as hematite and goethite from kaolin slips has been around since the 1930s. Sodium hydrosulfite (sodium dithionite) is added to a clay slip that has been acidified with sulfuric acid to pH of 3. The sodium hydrosulfite creates a reducing chemical environment that promotes the dissolution of iron oxides and iron hydroxides. The low pH keeps the iron in solution until it can be removed in the liquid phase from the clay slip by filters. The dissolution and removal of iron oxide and iron hydroxide minerals that absorb light on the blue portion of the visible light spectrum increase brightness and decrease yellowness. In the 1970s, oxidative bleaching by ozone gas was introduced as a cost-effective method of brightness improvement. The ionization of the oxygen or dry air in the ozone generator creates ozone, which is then bubbled through ozone contact towers that allow the gas to oxidize organic matter contained in the clay slurry.

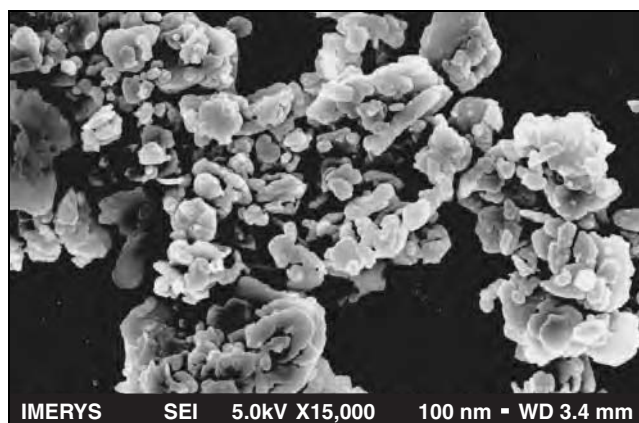
Wet Grinding and Delamination

Kaolin processors use grinding to reduce particle size and to help obtain mineral liberation for mineral separation processes. Delamination is the cleaving or parting of kaolinite stacks into finer platy particles (Figure 14). During the mid-1950s, the delamination process was initially by extrusion of coarse kaolin. In the late 1950s, the U.S. Bureau of Mines (USBM) developed attrition grinding of



Courtesy of IMERYS.

Figure 14. Electron photomicrographs showing (A) kaolinite stacks prior to grinding and (B) kaolinite plates after delamination and classification to a delaminated kaolin product



Courtesy of IMERYS.

Figure 15. Electron photomicrograph showing calcined agglomerates composed of sintered kaolin particles. Porosity of the calcined kaolin agglomerate imparts opacity and light-scattering properties.

clay slurries using sand or other media to delaminate and separate fine kaolinite platy particles (Feld et al. 1960). Delaminated products show value in paper coating because they have good sheet coverage and printability.

Dewatering

Dispersed kaolin clay slurries are typically shipped by tanker truck, rail, or ship at about 60% to 70% solids, depending on product type. Kaolin slip solids in the processing operation can range from 5% to 70%, depending on mining and blending technology. Kaolin slip solids are typically between 15% and 35% at the leaching stage, which occurs after physical separation of impurities, particle classification, and grinding. Most dewatering technologies require obtaining a flocculated kaolin slip in preparation for reduced-acid leaching. Kaolin particles are flocculated when pH is adjusted to <5 and chemicals such as alum and high molecular weight polymers are added to aid dewatering. Thickeners, centrifuges, rotary vacuum filters, and pressure filters are then used to dewater flocculated slip (Murray 1980; Leung 1988). Dewatering a dispersed kaolin slip is possible with use of centrifuges, membrane filters, evapora-

tors, and back mixing with dried clay. The limitations of filtration technologies and the need to add water to redisperse flocculated slip typically allow only evaporating and back mixing with dry clay to increase slurry solids to 65% to 70%. The spray-dry back-mix process involves addition of spray-dried clay to slurry in a mixing tank in a proportion required to raise slip solids to the appropriate amount for shipping.

Drying

Kaolin can be dried using several types of dryers: spray, rotary, tray, fluid bed, and apron. The spray dryer is the most common dryer technology used by U.S. and Brazilian kaolin producers. Spray drying involves feeding slip to an atomizer located at the top of a heated chamber. Atomized droplets of slip quickly dry into beads about 0.25 to 1 mm in diameter with a moisture content between 1 and 3 wt %. The other dryer technologies previously mentioned are fed undispersed filter cake. The apron dryer is a common process for making acid-lump type products that contain low levels of dispersant. A band conveys a 2.5 to 15 cm (1 to 6 in.) bed of shredded or extruded filter cake on a perforated apron through a tunnel-like chamber containing hot gases. Dried product can be loaded bulk into road, rail, or sea containers or packaged into 50-lb or 1-t bags. Dried product can be milled or pulverized to a powder form to help further reduce moisture content and improve ease of product makedown into slurry for intended applications.

Calcination

Calcination is a thermal process that causes kaolin minerals to transform to other amorphous or crystalline phases. The phase transformations that occur during calcination are the dehydroxylation of kaolinite to metakaolinite at about 500°C and crystallization of metakaolinite into mullite above 1,000°C. Calcination can increase the brightness of kaolin by burning off organic matter and structures the clay into aggregates (Figure 15). Calciners used by the kaolin industry include the horizontal rotary kiln and vertical Herreshoff. Milling is typically used on the calcined product to break up coarse agglomerates and residue.

Georgia Kaolin Processing

Georgia kaolin is most commonly processed in the slurry form by a variety of advanced beneficiation methods (Pruett 2000). Typically, the wet-process plant first blends kaolin from several mines to

enable production of a specific range of products. The kaolin is blunged into slurry that is then centrifuged to make products having a range of particle sizes, which then may be whitened and brightened by chemical reduction leaching, oxidation bleaching, HIMS, selective flocculation, froth flotation, thermal calcination, and other proprietary methods. The refined kaolin products may be shipped to North American customers as high-solids slurry in tank cars or dried for worldwide export. In typical years, approximately two thirds of Georgia kaolin production is used in North America, and one third is exported, mostly to customers in Western Europe and southeastern Asia (Figure 16). About two thirds of the kaolin produced in the Georgia district by wet slurry processing is used as a pigment for coating fine printing papers (Figure 17) for use in magazines, catalogs, and annual reports. These slurry-processed products may also be used as a pigment extender in paints, plastics, adhesives, and sealants; for various ceramic, refractory, and catalyst raw materials; and as an inert binder in pharmaceuticals. Export kaolin products may be shipped in bulk, in polypropylene big-bags, or by large metal shipping containers.

A rather small percentage of Georgia kaolin production (Figure 13), and most of South Carolina's production (374 kt, USGS 2002), is processed by dry air-float methods. Dry processing is less costly than wet processing but is not capable of improving kaolin quality other than by limited removal of grit material. The typical dry-process plant hauls the kaolin from the mines by highway truck and sorts it at the plant into various different crude grades in several separate bins. The different grades of clay are blended as they are loaded into a slicer, which breaks the lumps down to feed a dryer. The dried clay is then transported on a column of rapidly moving air into a roller mill or other dry mill where the clay is pulverized to a powder form. The air column sweeps the powdered clay from the mill through a whizzer or cyclone classifier where coarse sand-size particles can be removed as gangue or returned to the mill for further size reduction. Airfloat processed Georgia and South Carolina kaolins are used for ceramic sanitaryware, dinnerware, and decorative tile; as a pigment extender in floor coverings, paints, insecticide, and herbicide carriers; and as aluminous raw material for fiberglass and portland cement manufacture.

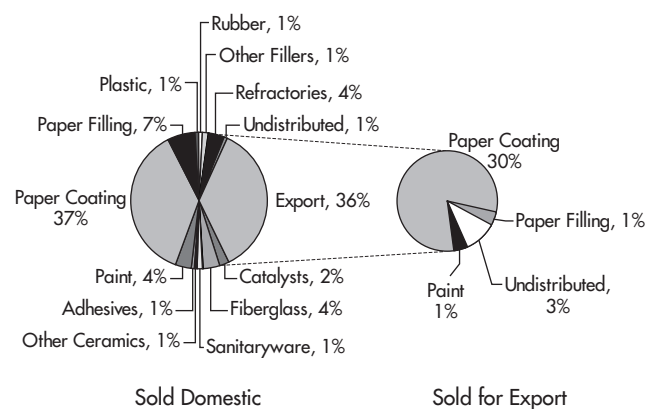
EXPLORATION

Strategy

The most effective exploration for new deposits of commercial grade kaolin is begun by considering how the mineral was originally concentrated, altered, or deposited. The history of a kaolin deposit's formation is a useful indicator of the topography, elevation, structural attitude, degree of alteration, and stratigraphic sequence in which favorable deposits of kaolin are most likely to be discovered.

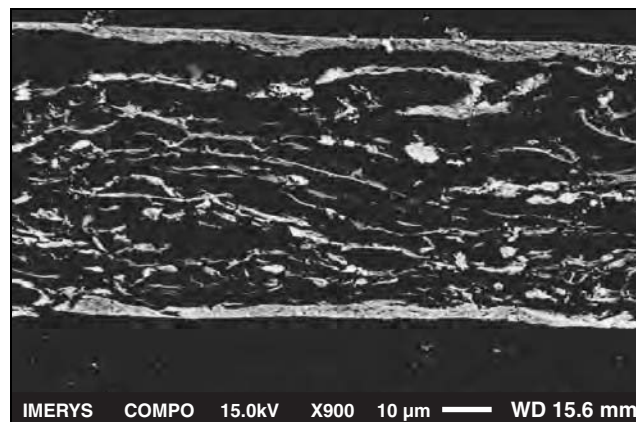
As examples, the Devon and Cornwall-type hydrothermally altered primary kaolins are typically discovered as alteration deposits along high-angle shear zones or joints in the parent granite and therefore are commonly found in near-vertical funnel-shaped concentrations. Exploration for this type of kaolin takes into consideration the preferred orientation of joint systems that were used by hydrothermal kaolinizing fluids, which cut the types of granitic rocks that tend to be altered to commercial grade kaolin. Knowing that kaolinization occurs in the district to a depth of several hundred meters, a drilling program needs to be prepared to drill to at least that depth.

By contrast, Sparta-type primary kaolin from middle Georgia formed by surficial weathering of the muscovite-biotite granite and therefore occurs as a near-surface pallid saprolite blanket beneath upland divides where the weathering zone has been seasonally wet-



Source: USGS 2002.

Figure 16. Georgia kaolin production for 2002 compiled by the USGS. Total kaolin volume sold by Georgia producers in 2002 was 6,830 kt with a value of \$893 million.



Courtesy of IMERYS.

Figure 17. Electron photomicrograph showing a cross-section of coated paper. The very bright lines at the top and base of the paper are kaolin coatings. The bright regions between the coating and darker-colored wood fibers are mineral filler.

ted and dried. By this model, Sparta-type primary kaolins are not expected to occur beneath stream valleys which have been continually water saturated. A drilling strategy for this type of primary kaolin concentrates on shallow exploration and stops coring when the saprolite begins to contain unaltered feldspars from the parent rock.

As a further example, the very productive central Georgia kaolins and eastern Amazon region Brazilian kaolins were deposited in low-energy water bodies associated with a fluvial deltaic sedimentary environment. These kaolin deposits therefore occur as clay lenses scattered in fining-upward sedimentary sequences. The common presence in Georgia of a thick overlying smectitic marine clay unit suggests that exploration needs to be concentrated along elevations where the marine clay cover has been breached by later erosion, allowing fresh groundwater to access the kaolin lenses and to oxidize sulfide minerals and organic matter.

Necessity for Continuous New Exploration

Because most kaolin mining operations require a very large capital investment for processing plant construction and for periodic

Table 6. Typical drill spacing plan for kaolin exploration and mine development

Intent of drilling campaign	Drill hole grid spacing	
	m	ft
Initial exploratory work	120	400
Preliminary proving of reserves	60	200
Preparation for stripping and mining	30	100
Mine quality control	15	50

Table 7. Kaolin pigment grade structure for application in paper coatings. Particle size is reported at the range midpoint as equivalent spherical diameter (esd) using a gravitational settling particle-size analysis method.

Grade	Particle Size, esd
Ultrafine	98 wt %, <2 µm
Fine #1	95 wt %, <2 µm
#1	90 wt %, <2 µm
#2	85 wt %, <2 µm
#3	65 wt %, <2 µm

upgrades, there is a continual need for at least several decades of ore reserves.

Many types of kaolin deposits can be worked to produce quite variable recovery of finished clay products from large tonnages of crude kaolin. As examples, the Devon–Cornwall primary kaolin pits are said to yield 8% to 20% finished product from wet crude ore. At the other extreme, the Rio Jari fine particle size, sedimentary kaolin deposit in northeastern Brazil is reputed to provide product recovery of about 70% finished product from a wet crude ore. Whatever the anticipated recovery for the kaolin district being mined, the exploration manager must continually discover an increasingly large tonnage of proven ore reserves in order to maintain a future clay reserve to support investment in costly new plant and equipment.

Exploration Methods

In areas where core drilling equipment is available, new kaolin deposits are discovered by widely spaced “wildcat” drilling in areas near previously known commercial deposits and at elevations or areas of favorable geology. This initial discovery drilling may be done at drill-hole spacing of 240 m (800 ft) or greater. Once commercial quality kaolin is encountered by this type of drilling, it is customary to have a surveyed grid laid out for carefully spaced drilling to develop an actual mining plan. Typically, this type of sequential development drilling is done by variations of the spacing plan shown in Table 6. In the Georgia kaolin district, typical core drilling equipment is truck-mounted units with integral mud pump equipped with a double-tube core barrel and hard-metal alloy tipped bits. Core may be NX (nominal 2½ in. diameter), which provides sufficient samples for extensive laboratory testing.

Typically, in this type of kaolin exploration, the overburden and nonkaolinitic zones are drilled through by “fishtail” bit without coring. When kaolin cuttings are observed in the drill fluids, the core barrel is inserted into the borehole, and continuous core samples are taken until the clay zone has been completely penetrated. The clay core is forced from the inner barrel by hydraulic pressure from the mud pump. Kaolin core is carefully marked to identify the property drilled, the grid location of the hole, and top and bottom

depths of the interval sampled. The core is then packed in wooden or cardboard boxes, or bagged by depth interval, and transported to the core testing laboratory.

In the core testing laboratory the kaolin is trimmed to remove contamination, analyzed for crude clay quality, and then tested for potential product quality by replicating on the lab bench scale the beneficiation performed in the processing plant. Typically, laboratory tests are done for grit (+325 mesh) residue content, brightness, color, particle size, low- and high-shear viscosity, and for other physical and chemical properties needed by the customer. Testing results are posted on carefully scaled grid maps, which are used as the basis for all mine planning, initial quality control, and reserve calculations.

MINING METHODS

Primary kaolin deposits, with their typical large percentages of coarse grit material, commonly have a soft, mealy texture. This type of primary kaolin is often mined by a “water cannon” or monitor, by which the clay is washed from the bank or highwall by a high-pressure stream of water. The resulting clay slurry flows to the lowest portion of the pit where most coarse grit particles are allowed to settle out from the kaolin slurry, which is pumped through a pipeline to the refinery.

The more-concentrated sedimentary kaolin deposits, which have much lower grit content due to the fluvial process of sedimentary winnowing, are usually mined by dry excavation methods. The open pit mines are laid out from about 1 to 15 hectares (acres) in size, depending on economics, ore zone thickness, and production demand for the exposed kaolin. Overburden is removed by backhoe and large capacity off-road haul trucks, two-motor pan scrapers, or dragline. Pit highwall slopes are usually worked at a 1:1 ratio, or 45 degree angle, and may be as deep as 45 m (150 ft) or even more if necessary. Average overburden to clay ratio may be as high as 4:1 to 8:1, or even higher if the kaolin is of a particularly needed grade.

Many of the deeper kaolin mines may need to contend with large volumes of groundwater, from either perched or artesian water zones. Mine water levels may be controlled by dewatering from a ditch encircling the perimeter of the pit. Excessive ground and surface water is pumped from a sump located in the ditch to an impoundment area where the water is clarified prior to being discharged into nearby streams. Alternatively, dewatering wells can be used to lower the artesian water level in particularly wet and deep kaolin mines.

After excavation, the kaolin is transported from mine to processing plant by two basic methods: as dispersed slurry by pipeline or as solid lump clay by highway haul trucks. The slurry transport system is much less costly after the pipeline cost is amortized, and also saves on fuel costs and potential damage to public roads. Slurry transport of the kaolin has the additional advantage of allowing degritting operations at the mining area, where the grit can be disposed of with overburden.

TRENDS

Production Statistics

The USGS and the China Clay Producers Association (CCPA) compile statistics on worldwide kaolin production. The CCPA statistics (a available from <http://www.kaolin.com>) focus on paper grades produced in Georgia by the four major wet-processed kaolin producers: Engelhard, IMERYS, J.M. Huber, and Thiele Kaolin Company. The CCPA categorizes several grades based on product particle size, brightness, or additional processing. Standard kaolin grades typically have GE brightness between 84 and

89 and specified particle-size ranges (Table 7). High-brightness, paper-coating kaolin typically has GE brightness of >89. Highly processed grades include delaminated, calcined, aggregated, and engineered.

Particle shape and particle-size distribution are properties that are now engineered into many pigments to add functional value in specific market segments or to specific customer needs. These products comprise the engineered grade category. Particle engineering has reduced the importance of the coating kaolin grade structure based on particle size (Table 7) and raised the importance of the pigment's functional performance in the customer's application, much like a specialty chemical (Bundy 1993). The kaolin industry's move to engineered pigments and functional fillers, similar to other engineered industrial minerals, prevents simple commoditization of kaolin into a few grades that fit all consumer needs.

Market Trends

Several factors strongly influence the volumes of kaolin produced to meet global market demands:

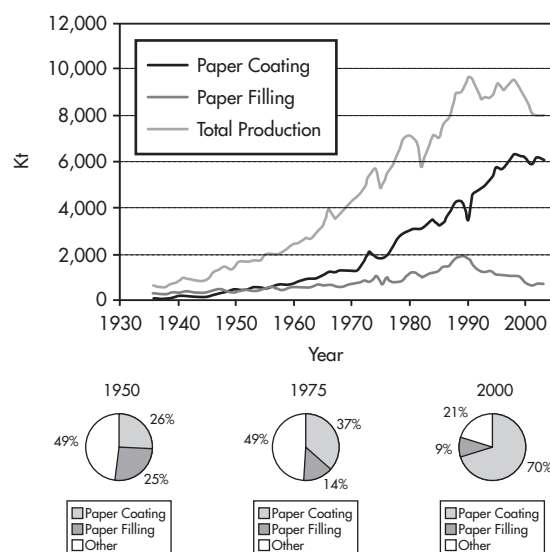
- The paper market drives the demand for world production of beneficiated kaolin products (Figure 18). In 2000, about 79% of Georgian production, 90% of Brazilian production, and 75% of Cornish production was for the paper market.
- The growth in kaolin production is mostly related to its use since the 1930s as a pigment to improve the appearance and printability of coated paper and coated paper board (Figures 10 and 18).
- Since the 1940s most paper-coating kaolin has come from sedimentary kaolin ores (Figure 10).
- Kaolin demand for paper filling has fallen since the 1980s. This is seen in the U.S. market, where precipitated calcium carbonate (PCC) has replaced kaolin as the filler of choice in uncoated woodfree (freesheet) paper grades. This choice is paper-mill specific and driven by (1) PCC's high brightness and light-scattering properties relative to regular brightness of hydrous kaolin, (2) the availability of carbon dioxide from the paper mill's lime kiln, and (3) the relative logistics cost of delivered kaolin and lime.
- The kaolin growth rate for paper coating diminished in the late 1990s as European-type coated papers that contain high levels of calcium carbonate gained market share. This change in the growth rate caused the oversupply of kaolin pigments and resulted in some manufacturing shutdowns in the United States and the United Kingdom (Figure 10). The number of wet-processed kaolin producers in Georgia dropped to four from six active companies in the early 1990s. Brazil has continued to grow because of the favorable quality and cost of products produced in the Amazon region.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Health and Safety

Kaolin producers must comply with health and safety regulations. Health regulations enforced by state and federal government bodies cover aspects of worker safety in the mines and process operations. In the United States mine and associated milling and laboratory workplace safety and health is regulated by the U.S. Mine Safety and Health Administration (MSHA). Kaolin operations in the European Union and Brazil also comply with similar strict workplace safety requirements. For example, Brazil requires manufacturers to have on-site medical staff at production operations.

The health and safety of employees working for customers and for the end users are also a concern for kaolin producers.



Courtesy of USGS.

Figure 18. Georgia kaolin production for paper filling and paper coating, 1900–2002

Kaolin is recognized as a chemically inert material that can be safely used and handled in many applications. Most wet-processed kaolin products comply with U.S. Food and Drug Administration (FDA) or equivalent regulations for use in food contact applications with paper and paperboard. FDA compliance covers the minerals as well as the chemicals used during processing and for slurry preservation, including biocides. Some kaolin products also are designed to meet pharmaceutical or United States Pharmacopeia (USP) regulations where the product may be ingested, as in the case of anti-diarrhea medications. USP regulations determine permissible levels of metals and other compounds in the processed kaolin. Kaolin dust can pose a pulmonary hazard at high levels over extended periods of exposure, and some kaolin products may contain low levels of crystalline silica, such as natural quartz particles. The product material safety data sheets (MSDS) should be consulted when handling any product.

Pollution Control

Kaolin producers invest significant resources on environmental compliance to meet local and federal environmental regulations. Although the mining process disrupts land, mines are reclaimed to their original topography or improved by development of wetlands or ponds. To prevent soil erosion and to recondition the restored soils, mine lands are replanted with grasses. Reclaimed kaolin mine lands in Georgia and Brazil are frequently replanted with trees. In Cornwall, one mined-out pit became the site of the Eden Project, a series of domes that contain flora from different climates and continents.

Emissions from kaolin process operations are strictly controlled. Coarse mineral tailings and slimes from kaolin beneficiation are emptied into impounds that are acidified to flocculate and remove solids. In compliance with water permits, the clarified water discharge from these impounds is chemically neutralized prior to discharge into streams. Air emissions are also strictly controlled by permits that limit the levels of dust, sulfur dioxide, and nitrous oxides discharged into the atmosphere. Environmental compliance is engineered into kaolin process operations, and most

operations make every effort to maximize kaolin recovery to prevent unwanted losses that fill impounds.

Sustainable development is a relatively new term that encompasses the past practices by kaolin producers to carry on long-term stewardship of the land, to maintain a healthy and safe environment for workers and neighbors, and to minimize raw material and energy consumption. The close dependence between local communities and kaolin producers requires continued discourse to resolve issues and maintain productive relationships. Innovation in terms of processing and product development are necessary to maintain the viability of the business relative to competition and increasing costs, as well as to extend reserves to resources once not considered economically useful.

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Palygorskite and Sepiolite (Hormites)*

Haydn H. Murray and Huitang Zhou

INTRODUCTION

The hormite clay minerals palygorskite and sepiolite are elongate clays that have many important industrial applications. Important deposits of these clays occur in the United States, China, Senegal, Spain, India, and Ukraine. The majority of the deposits are Miocene in age. Mining is by open-pit methods, and the processing is dry, although there is some wet processing for special applications.

Palygorskite and sepiolite are hydrated magnesium, iron, and aluminum silicates. In the United States, the term *attapulgit* is used in place of palygorskite; however, the International Nomenclature Committee determined that palygorskite is the preferred name (Bailey et al. 1971).

In 1862, Savchenkov used the name “palygorskite” to describe a mineral from the Palygorsk locality in the Ural Mountains (Hay 1975). J. deLapparent proposed the name “attapulgit” for clays from Attapulgis, Georgia, in the United States, and from Mormoiron in France, because he thought them to be different than palygorskite, but Bailey et al. (1971) proved them to be the same.

Both palygorskite and sepiolite are referred to as sorptive clays because of their large surface area and high sorptive capacity. The term *fuller's earth* adds additional complications to the nomenclature. Fuller's earth is more or less a catchall term for clays and other fine-grained earthy materials suitable for bleaching and sorbent uses. It has no compositional or mineralogical meaning. Fuller's earth was first applied to earthy materials used in cleansing and fulling wool, thereby removing lanolin and dirt—thus the name fuller's earth (Robertson 1986). The term “fuller's earth” is used quite often for palygorskite and sepiolite, some smectites, and other sorptive materials. For more detailed information, refer to the chapter on fuller's earth elsewhere in this volume.

Because of the elongate shape of palygorskite and sepiolite, the industrial applications are many and diverse. The elongate shape of the particles prevents flocculation, so these clays are used as suspending agents in systems with high electrolyte concentrations.

MINERALOGY, OCCURRENCE, AND ORIGIN

Mineralogy

Both palygorskite and sepiolite are 2:1 layer silicates, which means that the octahedral layer is bound above and below by a silica tetrahedral sheet. The tetrahedral sheets are linked infinitely in two dimensions. These two minerals are structurally different from other clay minerals in that the octahedral sheets extend in only one dimension and the tetrahedral sheets are divided into ribbons by a periodic inversion of rows of tetrahedrons. Figure 1 shows the structure of palygorskite (attapulgit) and Figure 2 shows the structure of sepiolite; the channels between the ribbon strips are larger in sepiolite than in palygorskite. In palygorskite the dimensions of the channels are approximately 4 Å by 6 Å and in sepiolite the dimensions are about 4 Å by 9.5 Å. Figure 3 shows a scanning electron micrograph (SEM) of palygorskite. The general chemical formula for palygorskite is $\text{Mg}_5(\text{Si}_8\text{O}_{20})(\text{OH})_2(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$ and for sepiolite is $\text{Mg}_8(\text{Si}_{12}\text{O}_{30})(\text{OH})_4(\text{OH}_2)_4 \cdot \text{N H}_2\text{O}$.

These two clay minerals contain two types of water—one coordinated to the octahedral cations and the other loosely bonded in the channels. The latter water is referred to as zeolitic water. The channels may also contain exchangeable cations. The elongate morphology and the presence of the channels are the most important physical attributes, which are described later in this chapter.

Palygorskite is more common than sepiolite. Usually, minor quantities of sepiolite are associated with the palygorskite. The major exception is the large sepiolite deposit near Madrid in Spain. Minor minerals in these deposits are smectite, quartz, dolomite, calcite, and occasionally clinoptilolite.

Bradley (1940) determined the structure of palygorskite and Brauner and Preisinger (1956) determined the structure of sepiolite. Merkl (1989) in his study of the palygorskite deposits in south Georgia and north Florida observed two distinct morphological forms: short-length palygorskite and long-length palygorskite. The short form is 2 μm or less, and the long-length form is greater than 10 μm. He determined that the short-length form had a low magnesium content, whereas the long-length form had a high magnesium content.

Origin and Occurrence

The important deposits of palygorskite and sepiolite occur in southeastern United States, China, Senegal, Spain, and Ukraine (Figure 4). All these major deposits are Eocene or Miocene in age. The origin of these deposits is somewhat uncertain, but in

* At the 13th International Clay Conference held in August, 2005, in Tokyo, the International Nomenclature Committee recommended that use of the term “hormites” be discontinued and all future references be replaced with palygorskite and sepiolite. Therefore, this chapter, originally titled “Hormites,” has been renamed “Palygorskite and Sepiolite” and references to hormites throughout the chapter have been replaced with palygorskite and sepiolite.

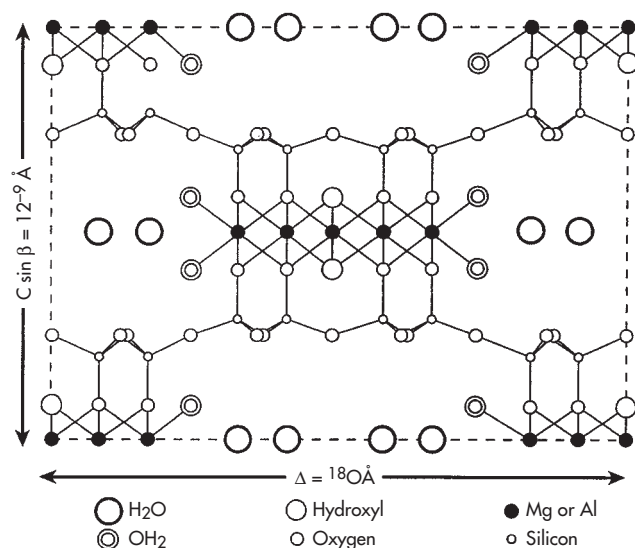


Figure 1. Structure of palygorskite

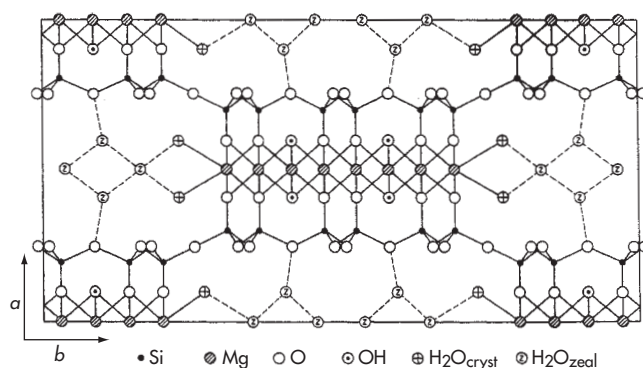


Figure 2. Structure of sepiolite

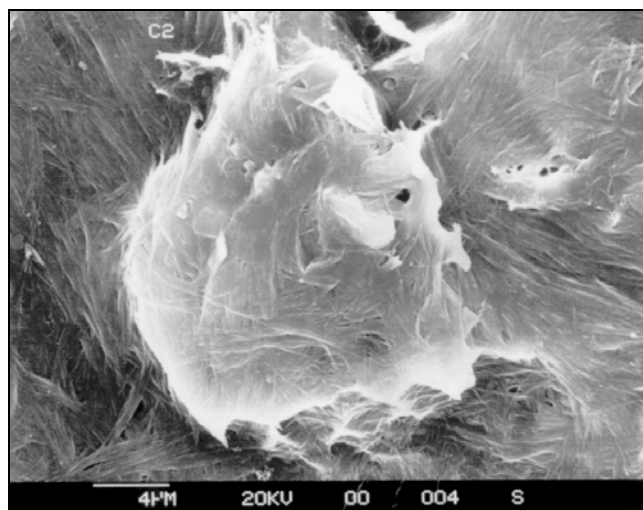


Figure 3. SEM of palygorskite

general most formed in shallow marine lagoons or tidal flats and in supersaline lakes. The magnesium needed to form the palygorskite, sepiolite, and dolomite was apparently introduced by the reaction of detrital material with magnesium-rich brines and salts resulting from the evaporation of the entrapped sea water (Patterson 1974). The palygorskite and sepiolite precipitated in these hypersaline restricted lagoons or lakes. The dolomite formed under conditions in which the amount of aluminum and silicon was less available from the clastic materials that entered the basin (Weaver and Beck 1972).

United States

The palygorskite-rich deposits in south Georgia and north Florida dominate the world's production. The deposits extend from Quincy, Florida, on the south to the Meigs, Georgia, area on the north (Figure 5), about 80 km. The deposition of the palygorskite took place in a shallow water trough that connected the Gulf of Mexico with the Southeast Georgia Embayment on the Atlantic Ocean (Merkl 1989). The seawater in this trough was characterized by fluctuating salinities, and at times the lagoons were closed off from normal circulation. There was sufficient magnesium present to precipitate palygorskite. The mineralogical content changes from dominantly palygorskite in the Quincy–Attapulga District to a mixture of smectite and palygorskite in the northern area around Ochlocknee and Meigs. Millot (1970) believes that smectite is transformed to palygorskite and sepiolite in a saline, alkaline water environment. These Georgia–Florida deposits are early to middle Miocene in age.

The palygorskite-type fuller's earth occurs in two distinct stratigraphic intervals. The younger Meigs Member of early middle Miocene age unconformably overlies the Dogtown Clay Member of late Lower Miocene age (Figure 6). Both of these members are part of the Hawthorne Group. The Meigs Member contains about equal proportions of smectite and short-length palygorskite along with quartz and a small amount of sepiolite, Opal-A, and sporadic amounts of clinoptilolite. In some sections of the deposit, diatoms comprise up to 50% or more of the fabric. The Dogtown Member has longer length palygorskite and minor amounts of quartz, smectite, and dolomite along with trace amounts of pyrite (Merkl 1989). The deposits in the Dogtown Clay Member in the southern district range from 2 m to slightly more than 3 m in thickness. The deposits in the Meigs Member in the northern district near Ochlocknee and Meigs range from 9 to 14 m in thickness.

Sepiolite is mined in small quantities near La Barge Wells, Nevada, about 160 km north west of Las Vegas in the Amargosa Valley. The sepiolite occurs in thin beds less than 1 m thick interbedded with deposits of saponite. These deposits are Pleistocene in age (Papke 1969).

China

Palygorskite is mined and processed in an area located near the provincial boundary of Anhui and Jiangsu near Guanshan and Xuyi, respectively (Figure 7). At the Guanshan deposit, the palygorskite occurs directly beneath a thick basalt. The palygorskite ranges between 3 and 6 m in thickness (Zhou and Murray 2003). The palygorskite in the Guanshan deposit was precipitated in a lacustrine environment as the alteration product of a basaltic ash (Zhou 1996). The deposits are in the upper member of the Huaguoshan Formation, which is Middle Miocene in age (Figure 7). Within the last 20 years, more than 20 high-quality palygorskite deposits have been discovered in the area shown in Figure 7. The Geological Survey of China estimated that there are more than 200 Mt of palygorskite reserves in this area. The mineralogy of these deposits is dominantly



Figure 4. Location of major palygorskite and sepiolite deposits

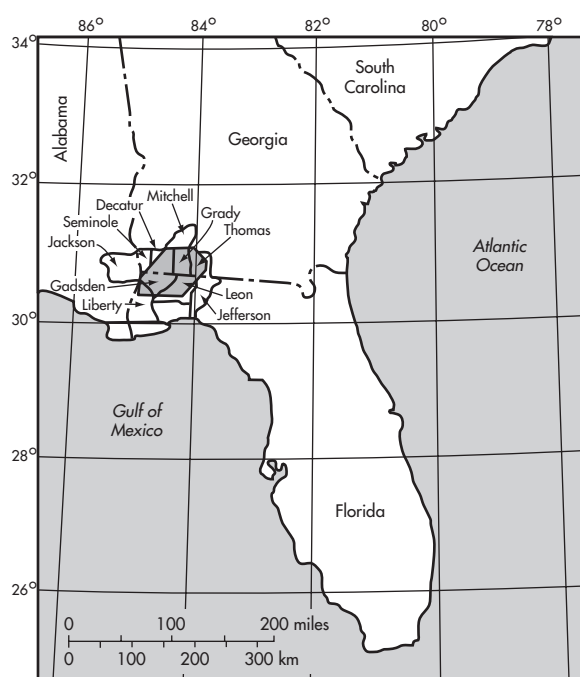


Figure 5. Location of the south Georgia–north Florida fuller's earth deposits

palygorskite with minor amounts of smectite, quartz, and dolomite. In the Guanshan deposit, the smectite content increases significantly below the palygorskite layer.

Senegal

Palygorskite is mined near the town of Theis, Senegal, which is approximately 100 km east of Dakar. In this area, the palygorskite directly overlies an aluminum phosphate deposit that is also mined.

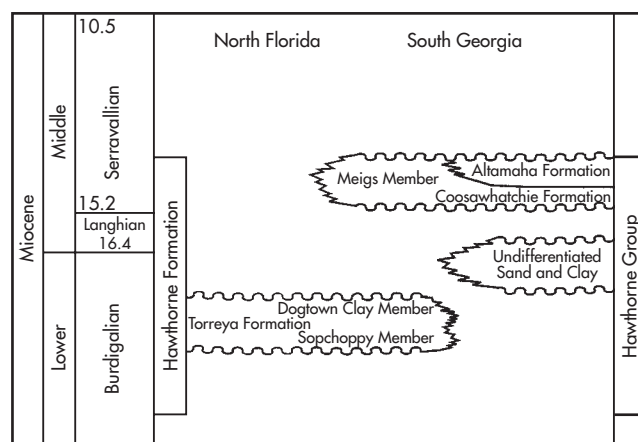


Figure 6. Stratigraphic relationship of the Meigs Clay and Dogtown Clay members

The age of the palygorskite is Early Eocene, and the beds range from 2 to 6 m in thickness (Wirth 1968). The palygorskite is transported by truck to Dakar, and the majority is shipped to Europe. It is estimated that about 400 kt are processed and shipped annually. The palygorskite is used for industrial absorbents, pet litter, and drilling mud mainly in the North Sea. The deposits are palygorskite along with minor amounts of sepiolite, quartz, and dolomite. The palygorskite beds extend south–southwest from Theis to the southern border of Senegal, a distance of about 100 km. The overburden is very thin, usually less than 2 m.

Spain

The world's major commercial sepiolite deposit is located at Vicalvaro near Madrid. The sepiolite was precipitated in Tertiary lakes in an evaporitic sequence (Huertas, Lima res, and Martin-Vivaldi 1971). The thickness ranges from 1 to 5 m. The major uses for this

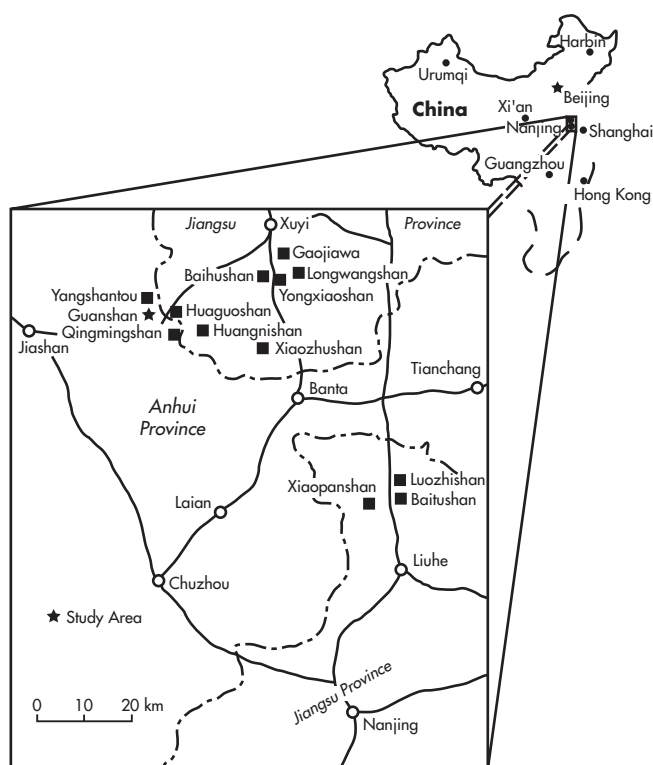


Figure 7. Location of palygorskite deposits in China

sepiolite are pet litter, agricultural carriers, and drilling mud. Approximately 500,000 t are produced annually from the deposits at Vicalvaro. Other locations in Spain producing palygorskite and sepiolite are Toledo, Torreon el Ruhe, Lebija, Almeria, and Maderuelo (Griffiths 1991). Galan (1996) reviewed the properties and applications of these clays and showed the relationship between the structure, composition, and physical properties and their industrial applications. Galan et al. (1976) described a deposit of palygorskite in the province of Caceres. In addition to the applications previously mentioned, palygorskite and sepiolite are used in plastics, mastics, catalysts, bleaching earth, ceramics, and binders for animal feed.

Ukraine

Ovcharenko et al. (1964) described large deposits of palygorskite of Lower Miocene age. Near Kiev, Ukraine, in the Cherkassey District, palygorskite is mined primarily for use in drilling muds. The palygorskite in Ukraine occurs in the central portion of the Ukrainian crystalline massif in the regions near Cherkassey and Kiev. The palygorskite-rich bed occurs in the middle section of a bentonite deposit and is Lower Miocene in age (Ovcharenko and Kuvovsky 1984). The thickness of the palygorskite layer is approximately 2 m. Smectite, hydromica, and quartz are the other mineral constituents in the palygorskite-rich layer.

Other Locations

Palygorskite occurs in Western Australia in a surface deposit at Lake Marromyne. In Turkey, sepiolite is produced near Eskisehir in Anatolia. In Somalia, a deposit of sepiolite is used mainly to produce decorative carvings that are sold to tourists. In Guatemala, there is a deposit of palygorskite about 40 km from the Gulf of Mexico and 30 km south of the Belize border.

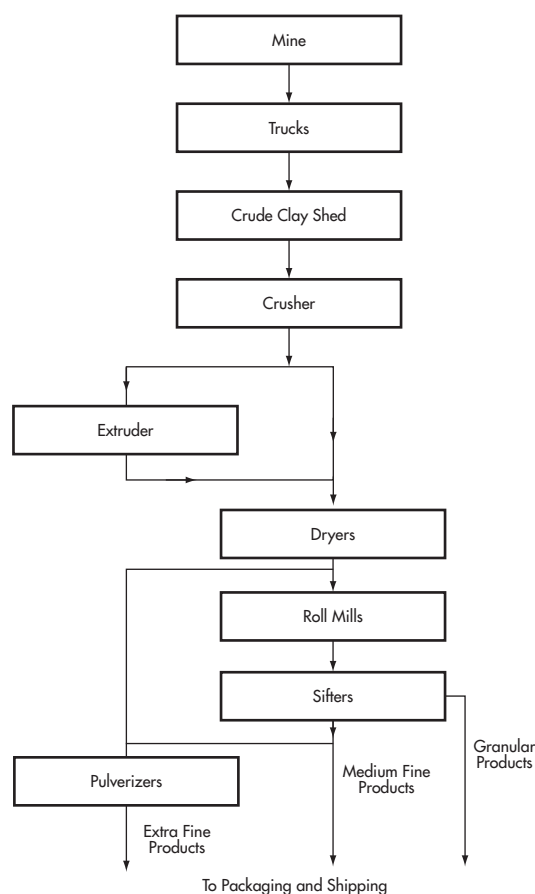


Figure 8. Process flow sheet for palygorskite and sepiolite production

MINING AND PROCESSING

Palygorskite and sepiolite are surface mined. The overburden is stripped with motorized scrapers, draglines, shovels, or bulldozers. The clay is mined using shovels, backhoes, small draglines, or front-end loaders, and is then loaded in trucks that transport the clay to the processing plant. The processing is generally quite simple, involving crushing, drying, classification, and pulverizing. Figure 8 shows a general process flow sheet. Special processes to enhance certain properties are sometimes used, including extrusion to separate the elongate particles; adding 1% or 2% MgO to improve the viscosity for use in drilling muds or thickeners; high heat drying to remove the zeolitic water from the channels in the structure, which produces LVM (low-volatile material) that improves the sorbent properties; and ultrafine pulverization to improve suspension properties and increase the surface area for use in certain pharmaceutical and paint applications. Some palygorskites are acid activated to enhance their bleaching activity for use in clarifying edible and nonedible oils. This acid activation process can be dry, or wet if a superior bleaching earth is required.

Pet litter and agricultural absorbents are granular products that are produced by drying, roll crushing, and screening to a specific granular size. The granular products generally are 15/30, 30/60, and 60/90. This means that the granule passes through the first number and is retained on the second number. A 15/30 product means that all the granules range between 15 and 30 mesh.

PHYSICAL PROPERTIES AND APPLICATIONS

Particle size, shape, distribution, surface area, chemistry, and charge are important physical properties that relate to the application of palygorskite and sepiolite. The properties of these clays that relate to their applications are

- 2:1 layer and inverted structure
- Octahedral substitutions (Mg, Fe, Al)
- Moderate charge on the lattice
- Moderate base exchange capacity (30 to 50 meq/100 g)
- Elongate shape
- Specific gravity 2.0–2.3 g/cm³
- Mohs hardness 2.0–2.5
- High surface area (150 to 320 m²/g)
- High absorption capacity
- High viscosity
- API (American Petroleum Institute) yield—100 to 115 bbl/t

The most important physical property of these clays is their elongate shape, because in many applications it is the controlling property. Considerable substitution of aluminum by magnesium and iron in the octahedral layer gives the particles a moderately high surface charge. This surface charge and the high surface area give the clays a moderate exchange capacity normally ranging from 30 to 50 meq/100 g. The large surface area of more than 100 m²/g, the charge on the lattice, and the periodic inverted silica tetrahedra, which creates parallel channels in the lattice, give palygorskite and sepiolite a high sorptive capacity. These properties, along with the elongate habit of the minerals, make them very useful in many industrial applications. The high viscosity of liquids into which these clays are added is a physical rather than a chemical viscosity, which makes for a very stable suspension viscosity.

The more important industrial applications of palygorskite and sepiolite follow:

- | | |
|-------------------------------|----------------------------|
| • Adhesives | • Laundry washing powders |
| • Agricultural carriers | • Metal drawing lubricants |
| • Animal feed bondants | • Paint and coatings |
| • Anticaking agent | • Paper |
| • Catalyst supports | • Pet litter |
| • Decolorizing oils | • Pharmaceuticals |
| • Drilling fluids | • Polishes |
| • Environmental liners | • Reinforcing fillers |
| • Foundry sand binders | • Suspension fertilizers |
| • Granular carriers | • Tape joint compounds |
| • Industrial floor absorbents | • Wax emulsions |

One of the more important and larger uses is in drilling fluids, where both the viscosity and the gel strength of the mud are not affected by variations in electrolyte content as are drilling muds in which bentonite is used. Palygorskite and sepiolite drilling muds can be used with salt water or when formation brines become a serious problem. The specifications for their use (API Specification 13A) in drilling mud follow. These measurements are made in water containing 40 g of salt (NaCl) per 100 cc of water.

- Viscosity—30 centipoise minimum at 600 rpm
- Yield point/plastic viscosity ratio—3 maximum
- Filtrate volume—15 cm³ maximum
- Residue—75 μ m—4.0 wt % maximum

Table 1. Annual 2004 world production of palygorskite and sepiolite, st

United States	1,200,000
Spain	900,000
Senegal	150,000
China	70,000
India	60,000
Others	100,000
Total	2,480,000

The clays are not flocculated because of their elongate particle shape, and thus they are used as suspending agents and thickeners in paint, medicines, pharmaceuticals, and cosmetics. Ultrafine pulverization to 95% less than 10 μ m substantially improves the suspension properties. Another large use is as floor-sweep compounds that absorb oil and grease spills on factory and service station floors and in other areas where oil and grease spills are a safety problem. Granular clay particles are the most effective type of floor absorbent.

Palygorskite and sepiolite are used extensively in agricultural applications as absorbents and carriers for chemicals and pesticides. High heat drying at a temperature high enough to remove the zeolitic water in the structural channels improves the sorbent properties. The chemical or pesticide is mixed with the clay granules and then placed in the ground with the seed. Tests for absorbent granules are done using the General Services Administration's Federal Specification P-A-1056A. The pesticide or chemical fertilizer is slowly released to provide the necessary protection or fertilizer for the growing plant. Finely pulverized clays are also used to absorb chemicals, which can then be dusted or sprayed on the plant or on the surface of the ground.

Another very large use for palygorskites and sepiolites is pet litter. Granular particles of the clay are an effective litter for absorbing animal waste, particularly for domestic cats. The clay granules absorb the waste and greatly minimize the odors.

Haden (1963) described the properties and applications of palygorskite and pointed out both the colloidal and non-colloidal characteristics that make it an important industrial clay. In the past, palygorskite was used as a catalyst in no carbon required (NCR) paper, but today this is a very minor application. An important future application of palygorskite and sepiolite will be in blends with sodium bentonite in landfill and toxic waste liners or barriers (Keith 2000). The estimated annual world production figure in 2004 totaled more than 2,400,000 st. Table 1 gives a breakdown of this estimate.

FUTURE CONSIDERATIONS AND ENVIRONMENTAL ISSUES

All palygorskite and sepiolite are surface mined and, in most countries, the mining company is required by law to reclaim the land. Common practice is to open a cut, mine the clay, and then spoil the overburden from the next cut into the mined-out area. The spoil is leveled or sloped to meet the standards prescribed by the government, and grasses and/or trees are planted. Sometimes the topsoil is put back on top of the spoil and used for agriculture.

In each of the producing areas described in this chapter, the reserves are substantial, so there is no immediate concern about production in the foreseeable future. Current world production is more than 2 Mt. The markets for both palygorskite and sepiolite will continue to expand in the future. An annual growth rate of 2% to 5% is anticipated.

In the processing plants, the major environmental issue is air quality because of dust. Air quality is maintained by using dust collectors on dryers, pulverizers, baggers, and belt-transfer points. These elongate clays have not been shown to be serious health hazards. Dust, however, if inhaled in considerable amounts day after day, can cause lung problems. Therefore, using dust collectors, face masks, and other devices protects the workers from inhaling too much dust. Most clay dust contains quartz, which is a crystalline silica. Crystalline silica is a suspected carcinogen. Most all of the quartz, however, is 20 µm or larger, which is not in the respirable range of 2 to 10 µm. The small amount of quartz in the respirable range is occluded, which means that the quartz is covered by clay particles, so the crystalline silica does not contact the walls of the lungs. Palygorskite and sepiolite contain no deleterious trace elements or chemical compounds that are hazardous to human health.

Several studies have been made to determine if the elongate clay particles are a possible carcinogen, but to date all the results indicate it is not a carcinogen.

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Refractory Clays

Colin C. Harvey, William L. Headrick Jr., and James G. Hemrick

INTRODUCTION

Naturally occurring rocks and clays have served as refractories since they were first used for ovens in China around 30,000 BC. The earliest fired clay refractories appeared later, about 4000 BC. These materials met most industrial needs until the 19th century and the onset of the industrial revolution. This technological transition created a need for better refractories and refractory technology to meet the demands of the growing industries, especially steel manufacturing. As a response to this need, high-purity silica brick and magnesite brick were introduced in the mid-1800s, and carbon and carbon-bonded brick were introduced in the late 1800s. In the United States, the American Ceramic Society was founded in 1899, in part to meet industry demands for improved refractories. Further developments included the introduction of synthetic raw materials in the late 1800s and dolomite bricks in the early 1900s, although their use was limited until the mid-1900s. Synthetic raw materials have since enabled the production of refractories with higher purity and performance, but with higher costs than those produced from mineral raw materials. Today's refractories are produced from minerals, from synthetic raw materials, and from combinations of the two.

Refractory clays are used mainly in making firebricks and blocks of many shapes, insulating bricks, saggars, refractory mortars and mixes, monolithic and castable materials, ramming and air gun mixes, and other products. In Europe and elsewhere, a product called *chamotte* (Anon. 1972a, 1972b) is made by calcining high-grade fire clays and other kaolinitic clays. A similar material produced in the United States is called calcined clay or calcined kaolin. A related material called mullite refractory is made by calcining bauxitic clay or clayey bauxite. Chamotte and calcined clay must be further fabricated into finished refractory products. Considerable tonnages of fire clay have also been previously used in the United States in the manufacture of light-colored face brick, tile, stoneware, and other products.

PRODUCT SPECIFICATIONS

The specifications for refractory clays are as numerous as the different uses. Because resistance to heat is the most essential property, many specifications are based on the heat duty required. Resistance to shrinkage, warping, cracking, and abrasion is also very important in many products, and expressions of the requirements for these properties appear in some specifications. Many of the end products must fulfill rigid dimensional specifications.

Restrictions on raw clay commonly include specifications for plasticity, impurities, and content of alkalis, alkaline earths, and other constituents that reduce fusion points.

GEOLOGY AND MINERALOGY

The mineralogy, occurrence, and origin of refractory kaolin and refractory ball clay are discussed in the companion chapters on kaolins and ball clays in this volume. Consequently, the following discussions concern these topics only as they apply to fire clay.

The degree of ordering of the kaolinite, the principal mineral in fire clay, varies considerably. Most of the kaolinite in the harder and purer varieties of fire clay (also termed *flint clay*) is very well ordered and even more perfectly crystalline than the kaolinite in many kaolins. The kaolinite in the hard fire clay also tends to occur in coarser particles, and in the harder varieties the grains are interlocking. The kaolinite in the plastic varieties of fire clay, however, is ordinarily characterized by imperfectly crystalline structures. The more disordered form of this kaolinite has been widely referred to as fire clay mineral to distinguish it from the more perfectly crystallized forms.

Some of the better grades of refractory clays contain minerals that are richer in aluminum than kaolinite, and, therefore, higher alumina products can be made from them. Some refractory kaolin is a mixture of kaolinite and gibbsite, $\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$. The better grades of fire clay, which are exceptionally rich in aluminum, consist of kaolinite and diaspore, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot \text{AlO}(\text{OH})$, and minor quantities of boehmite, $\text{AlO}(\text{OH})$.

OCCURRENCE AND ORIGIN

The physical characteristics of fire clay vary considerably; the clays range from soft and plastic to flintlike (Ryan 1978). Fire clay, therefore, is divisible into plastic, semiplastic, semiflint, and flint types. Flint clay has unique properties for a clay: it lacks plasticity, it breaks with a conchoidal parting into shardlike particles, and most of it is as brittle as limestone. Typical diaspore-bearing flint clay is brittle and has an oolitic, pisolitic, or nodular texture. Such clay is referred to as burley, birdseye, or nodular clay.

Most fire clay occurs in sedimentary rocks, and deposits range in age from Pennsylvanian to Tertiary. Fire clay is particularly common in rocks of Pennsylvanian age, and deposits of this age occur as underclays (seat earths) immediately below or closely associated with coal beds. Fire clays of Cretaceous and Tertiary age often

occur in lenticular bodies. Some deposits of these ages are associated with lignite and are probably underclays, and others have apparently been transported and deposited in local basins in a near-shore, swamp, or floodplain environment.

Opinions differ considerably on the origin of the extensive fire clays occurring below coal beds. Some geologists (Patterson and Hosterman 1963) believe that most underclay deposits formed mainly by the alteration of aluminous sediments in a swampy environment. Some mineralogists, however, believe that these clays were transported and some sort of a sedimentary winnowing process caused the rather pure accumulations of kaolinite in fire clay. Some clays of Cretaceous and Tertiary age were transported and formed by a process similar to those thought to have formed the transported kaolin deposits.

DISTRIBUTION OF DEPOSITS

United States

Fire clay of Pennsylvanian age is widely scattered throughout the Appalachian region and parts of the Mississippi Valley (Anon. 1967). The very-high-quality diaspore-bearing clay and other grades of fire clay occur in the Clearfield District, Pennsylvania, and in the Ozark region in Missouri (Keller 1952). High-grade kaolinitic flint clay and semiflint clays are mined in the Olive Hill District, Kentucky (Patterson and Hosterman 1963); Oak Hill District, Ohio (Stout 1923); and Somerset District, Pennsylvania (Hosterman et al. 1968). Major districts producing fire clay suitable for low- and moderate-heat-duty refractory products include the Allegheny Valley and Beaver Valley districts, Pennsylvania; Cordova District, Alabama; East Liverpool District, Ohio and West Virginia; and the Tuscarawas Valley and Hocking Valley districts, Ohio (Hosterman et al. 1968); and a region that includes parts of Monroe, Audrain, Callaway, and Montgomery counties, Missouri (McQueen 1943).

The largest and best quality fire clay deposits in the Rocky Mountain region are in Fremont, Pueblo, Custer, Huerfano, Jefferson, and Las Animas counties in Colorado. These deposits are in the Purgatoire Formation and Dakota Sandstone of Cretaceous age (Waagé 1953). Fire clay in these deposits occurs as isolated tabular lenses ranging in thickness from 1 to 6 m.

In addition to the fire clay mentioned in the foregoing discussions, other deposits are scattered throughout the western states (Van Sant 1959, 1964; Mark 1963; Anon. 1967). These deposits are of several types, and they include transported, residual, and hydrothermally formed clay. Districts in which these scattered deposits occur include several areas in King County and the Castle Rock area in Cowlitz County, Washington; the Molalla and Hobart Butte areas, Oregon; and the Alberhill area, California. Most of these deposits are of Cenozoic age. Refractory kaolin is produced primarily in the following districts: (1) Georgia–South Carolina kaolin belt; (2) Andersonville, Georgia (Anon. 1972b); (3) Eufaula, Alabama; (4) Arkansas bauxite region; (5) scattered districts in Texas; (6) Latah County, Idaho; and (7) Ione, California (Anon. 1972a). Refractory ball clay is produced primarily in the western parts of Kentucky and Tennessee, but some of the ball clay produced in Texas can be used in refractory products.

The total refractory clay resources in the United States suitable for low-heat-duty refractory products were estimated to be as much as 7 Gt in the 1960s (Hosterman et al. 1968). Since then, however, the decrease in production of many kiln-based industries has led to a steady decrease in demand. In addition, the reserves of high-quality refractory raw materials have been depleted. The clays that can now be mined and processed at competitive costs are suitable only for low-heat-duty products and total less than 1 Gt. The

reserves are primarily in the fire clay and refractory kaolin and ball clay districts outlined previously. A few remaining resources of high-grade diaspore clay are mainly under considerable overburden in Pennsylvania, and only small resources are present in Missouri. The bauxitic kaolin resources are primarily in the Arkansas bauxite region and the Eufaula, Alabama, and Andersonville, Georgia, districts. Some deposits also occur in other parts of Alabama and Georgia.

Other Countries

Refractory clays are produced in many countries; the information available on worldwide production is, however, sketchy and incomplete. This is partly because the distinction between fire clay and miscellaneous clay is not made in some countries, and clay used for refractory products is lumped with kaolin in others.

Those countries that produce more than 1 Mtpy of refractory (fire) clay include Germany, Japan, India, the People's Republic of China, and the United Kingdom. The production in France exceeded 1 Mtpy a few years ago, but has apparently dropped below this figure in recent years. Other countries producing 100,000 tpy to 1 Mtpy include Argentina, Australia, India, Italy, Mexico, Sweden, the United Arab Republic, Uruguay, and Yugoslavia. Refractory clay is exported from the People's Republic of China. Fire clay is also mined in the former Soviet Union and Czechoslovakia, Hungary, Poland, and other Eastern European countries.

As in the United States, fire clay in other countries is in several types of deposits. Kaolinitic fire clay associated with coal beds of Carboniferous age is mined in France, Germany, the United Kingdom, and elsewhere. Very high alumina diaspore bearing flint clays are sources of refractory materials in Israel, the People's Republic of China, Scotland, and South Africa. Refractory kaolin is mined in Australia, Japan, India, Hungary, Italy, Czechoslovakia, Poland, Sweden, Yugoslavia, Mexico, Argentina, Brazil, Chile, Peru, the Republic of South Africa, the United Arab Republic, Iran, and other countries; most such deposits are no older than Cretaceous.

EXPLORATION AND EVALUATION

The methods used in exploring and evaluating fire clay deposits are in general similar to those used for bentonite and kaolin, except that different drilling and testing procedures are required. Drilling fire clay deposits, particularly those of Pennsylvanian age, ordinarily requires diamond bits and core barrels of the type used for minerals in hard rock. This is because the clay itself and the rocks overlying the deposits are hard.

The most common test in evaluating fire clay is determining pyrometric cone equivalence (PCE). For refractory applications, the pyrometric cone measures the combined effects of temperature and time (Klinefelter and Hamlin 1957; Norton 1968). This technique is widely used and consists of series of cones manufactured from various proportions of standard raw materials that will distort at known temperatures. These cones, which consist of a series of standardized unfired ceramic compositions molded into the shape of triangular pyramids, are used to calibrate performance of both refractories and ceramic ware within furnaces. The sample of kaolin is molded into the standard cone shape and is heated along with several standard cones so that its end point can be determined in terms of an equivalent cone number. ASTM test method C24-56 gives the procedure of making this PCE test (Anon. 1972a, 1972b). Other commonly used tests for refractory clays include chemical analysis for soluble sulfate, because only very low levels can be tolerated in refractory products.

In addition to the PCE requirement, fired test pieces also may be tested for such properties as high-temperature stability, hot

strength, porosity, and spalling (Norton 1968; Anon.1972b). Chemical analyses are also required for some evaluations, and the contents of alkalis, alkaline earths, iron oxides, and a few less common elements are critical because they act as fluxes when clay refractories are heated.

PREPARATION FOR MARKETS

Fire clay and other refractory clays are mined by methods similar to those used for other types of clay. A much higher percentage of fire clay mining in the past, however, was underground. Underground mining was used where higher quality clays occurred at considerable depths or where overlying rocks were too hard to strip profitably. Little if any underground mining is now undertaken for refractory clays in the United States, but it is still widely practiced in developing countries throughout the world.

Firebrick and related products are prepared for markets by grinding the clay, shaping or forming the firebrick or other products, and firing (Figure 1). Commonly several varieties of fire clay and grog (crushed, previously fired clay) are blended to make a mix desired for a certain product, and blends are varied considerably to prepare different grades of firebrick. The harder clays are ordinarily the most refractory, and because they lack plasticity, small proportions of kaolin or plastic fire clay or both are added to aid in forming and bonding the brick until firing. Most firebrick is formed by hydraulic or other mechanical presses, but several types of products are intricately shaped and must be formed by hand.

Most firebrick is fired in tunnel kilns heated by gas or oil. A few plants, particularly those making specially shaped products or having a limited market, use downdraft kilns. Finished products are palletized and shipped by rail or truck. Overseas shipments require heavy crating with padded packaging. Calcined clay is ordinarily fired in rotary kilns and shipped in paper bags and in bulk carloads.

APPLICATIONS OF REFRACTORIES

Refractories are used to line furnaces, kilns, smelters, chemical reactor vessels, and gasifiers. By definition they are resistant to heat and chemical and mechanical attack. Refractories are designed to meet the needs of the many industries using them with different classes and grades of refractories produced to meet each industry's demand. Important properties of refractories are heat resistance; chemical inertness; resistance to mechanical and thermal stress and strain (especially thermal shock); resistance to corrosion and erosion by solids, entrained particulates, liquids and gases; resistance to impact; permeability; and many other properties whose importance varies according to the use of the refractory (Schacht 2004).

Refractory materials are used throughout the many industries of the world as in insulation or containment vessel linings in high-temperature and corrosive environments (Carneglia and Barna 1992). They must not only be capable of performing these tasks at elevated temperatures but also may be called on to bear mechanical and thermal loads. These materials are so essential that it would be difficult to identify an industrial process that does not use refractory materials in one aspect or another. Refractories are characterized by two aspects that qualify them as strategic materials: (1) their ability to contain heat, chemicals, and melts; and (2) the crosscutting nature of their utility. Figure 2 shows the ranges of usage temperatures for numerous industrial applications of refractories.

CURRENT FURNACE TECHNOLOGIES

Many different types of furnaces are used in United States industries, with different refractory types and issues prevalent for each type. Fifteen classifications of furnaces can be identified, with common issues for each type: blast furnaces; basic oxygen fur-

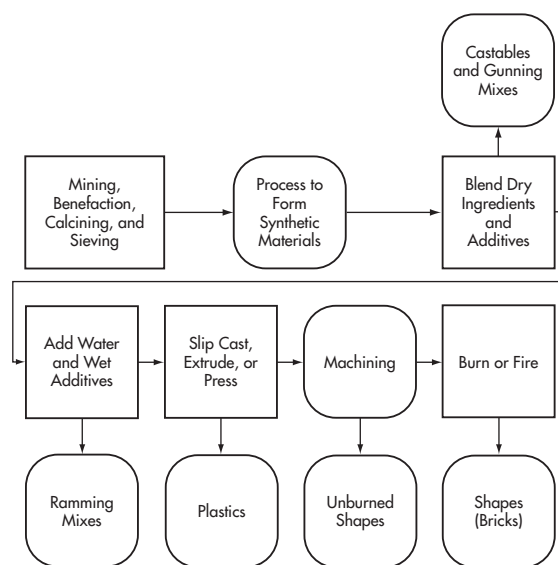


Figure 1. Steps in refractory production

naces; reverberatory furnaces; multiple hearth furnaces; transfer vessels (i.e., ladles, tundishes, troughs, runners); electrolytic smelters; kilns and calciners; electric arc furnaces; cupolas; heat treatment or annealing furnaces and drying ovens; stills and retorts; reactors, reformers, and refiners; steam boilers and incinerators; gasifiers; and heat exchangers. Table 1 lists typical industrial applications of these 15 furnace types. Table 2 lists refractory challenges and problems related to these furnace types, as reported by industry personnel.

REFRACTORY USAGE IN INDUSTRY

Although refractories are used in most, if not all, of the industries in the United States, the iron and steel industry consumes 70% of the refractories used, whereas the cement and lime industry consumes 7%, the ceramics industry 6%, the glass industry 3% to 4%, and the oil industry about 4%. According to U.S. Geological Survey (USGS) census figures, 400,000 t of refractory clay were shipped in 2003.

The most widely used raw materials for the production of refractories are listed in the sections that follow, along with some of their advantages and disadvantages. Many minerals make up each group of raw materials. Refractory raw materials are generally classified as acidic, neutral, or basic depending on the primary component.

Classification of Refractory Minerals

Refractory minerals containing aluminosilicates are acidic; those made of magnesia or calcia are basic; and others, primarily containing alumina, are neutral. These classifications are derived from historical slag practices in the metal industries. The following is a list of refractory minerals with their classifications.

- Zircon (ZrSiO_4): acidic; found in silica sands; used for glass contact refractories because of its resistance to molten glass
- Quartzite (SiO_2): acidic; used for roofs of furnaces where high strength and refractoriness are necessary (silica refractories are poor in thermal shock and alkali resistance)
- Fire clay ($[\text{x}]\text{Al}_2\text{O}_3 \cdot [1-\text{x}]\text{SiO}_2$): acidic; 30% to 45% alumina (Al_2O_3), includes andalusite (Al_2SiO_5), flint clay, pyrophyllite ($\text{AlSi}_2\text{O}_5\text{OH}$); the most widely used refractory raw material

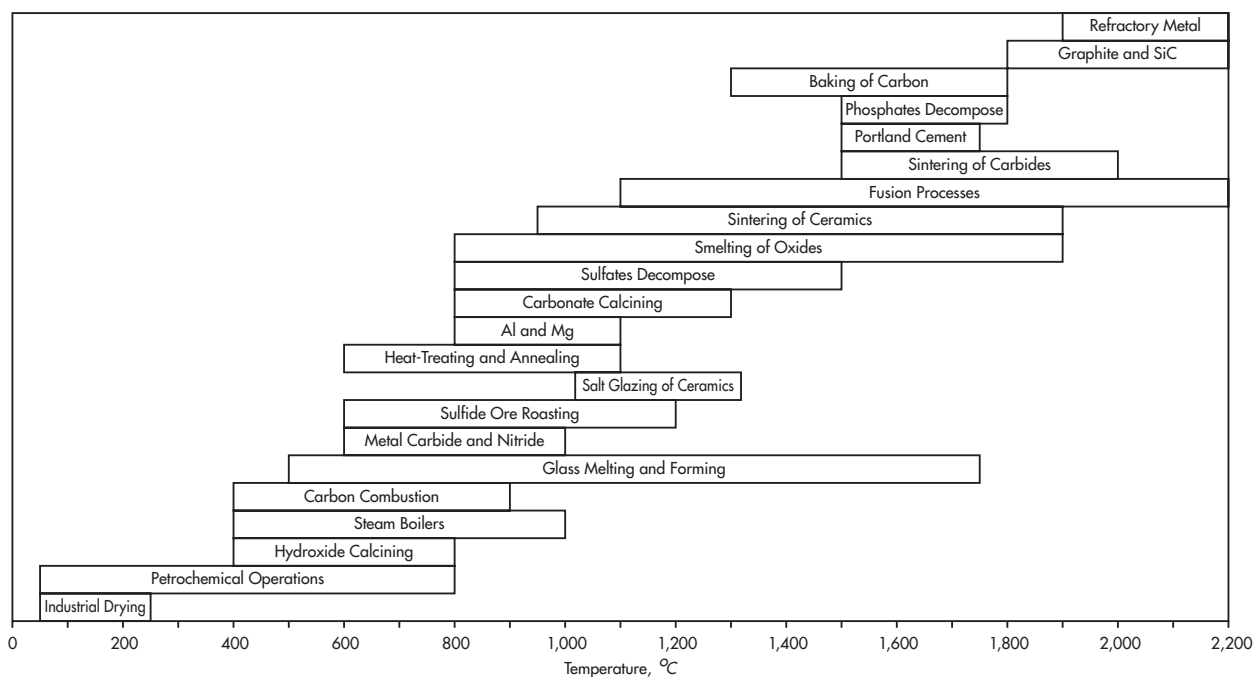


Figure 2. Temperature regimes for industrial applications of refractories

Table 1. Types of furnaces used in U.S. industry

Furnace Type	Industrial Furnace Applications								
	Aluminum	Cement and Lime	Chemical and Petrochemical	Forest Products	Glass	Heat-Treatment	Iron and Steel	Metal Casting	Other
Blast							X		X*
Basic oxygen	X						X		
Reverberatory					X		X	X	X†
Multiple hearth									X†
Ladles/tundishes/troughs/runners	X				X			X	X‡X
Electrolytic smelters	X								X§
Kilns and calciners	X	X	X	X	X		X		X**††
Electric arc							X		X‡‡
Cupolas						X	X		
Heat-treatment/annealing furnaces and drying ovens	X						X	X	X***§§
Still and retorts									X***
Reactors/reformers/refiners									
Steam boilers/incinerators	X	X	X	X		X			X†††
Gasifiers			X	X					
Heat exchangers	X	X	X	X	X	X	X	X	

* Lead.

† Copper.

‡ Molten metal handling.

§ Magnesium.

** Ceramics.

†† Mining.

‡‡ Oxide melting.

§§ Various metal products.

*** Organic and inorganic products.

††† Virtually all industries.

Table 2. Refractory challenges for furnaces used in U.S. industry

Furnace Type	Refractory Challenges							
	Abrasion	Caking Agglomeration	Contamination Fouling	Corrosion Wear	Erosion	Mechanical Degradation	Thermal Insulation	Thermomechanical Degradation/ Shock
Blast	X			X	X	X		X
Basic oxygen			X	X	X	X	X	X
Reverberatory			X	X	X		X	X
Multiple hearth	X			X			X	
Ladles/tundishes/troughs/runners			X	X		X	X	X
Electrolytic smelters			X	X		X	X	
Kilns and calciners	X	X		X	X	X	X	X
Electric arc				X	X		X	X
Cupolas								
Heat-treatment/annealing furnaces and drying ovens								X
Still and retorts	X			X			X	
Reactors/reformers/refiners	X			X			X	
Steam boilers and incinerators	X			X	X	X	X	X
Gasifiers	X			X	X	X	X	X
Heat exchangers	X							X

- Sillimanite and kyanite (Al_2SiO_5): acidic; used at higher temperatures than those at which fire clay can be used for tile and casting mixes
- Bauxite ($[\text{x}]\text{Al}_2\text{O}_3 \cdot [1-\text{x}]\text{H}_2\text{O}$): neutral; most widely used for alumina production; made up of gibbsite ($\text{Al}(\text{OH})_3$), boehmite ($\text{AlO}(\text{OH})$), and diaspore ($\text{AlO}(\text{OH})$); used at higher temperatures than those at which sillimanite-based refractories can be used
- Chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$): neutral; used as a buffer between acidic and basic refractories
- Magnesite (MgCO_3): basic; generally used in ferrous metal industries
- Dolomite ($\text{CaMg}(\text{CO}_3)_2$): basic; generally used in ferrous metal industries; more susceptible to hydration than magnesite
- Graphite (C): naturally occurring form of carbon; nonwetting and resistant to chemical attack, but oxidizes

Synthetic Raw Materials Used for Refractory Production

Synthetic raw materials have enabled the production of improved refractories with higher purities, but these cost more than refractories produced from mineral raw materials. The most widely used synthetic materials for the production of refractories are as follows, including generalities of their advantages and disadvantages.

- Alumina (Al_2O_3): neutral; produced from bauxite, aluminum salts, and aluminum metal; one of the most used and studied refractory materials; other materials are generally compared to alumina
- Mullite ($\text{Al}_4\text{Si}_1.5\text{O}_{9.75}$): neutral; produced from kyanite ($\text{Al}_2\text{O}_3 \cdot \text{SiO}_2$), kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), or various combinations of alumina- and silica-containing raw materials; theoretically, 72% Al_2O_3 , but commercially available grades range from 47% to 85% Al_2O_3

- Spinel (MgAl_2O_4): neutral; produced from alumina (Al_2O_3) and magnesia (MgO); synthesized using a wide range of raw materials and techniques; theoretically, 72% Al_2O_3 , but commercially available grades range from 65% to 90% Al_2O_3 ; more corrosion resistant than alumina in many instances without the hydration problems of dolomite ($\text{CaO} \cdot \text{MgO}$) or magnesia (MgO)
- Calcium aluminate cement ($[\text{x}]\text{CaO} \cdot [1-\text{x}]\text{Al}_2\text{O}_3$): neutral to basic; produced from lime (CaO) and alumina blended in many ratios depending on the desired alumina ratio; hydratable binder used for most refractory castables; other binder systems include colloidal silica (SiO_2), sodium silicate ($\text{Na}_2\text{O} \cdot \text{SiO}_2$), and phosphoric acid (H_3PO_4), among others
- Silicon carbide (SiC): produced from silica sand and coke; very hard material used in load-bearing and abrasion-resistance applications; very high thermal conductivity
- Boron carbide (B_4C): rarely used for refractories except in instances where higher abrasion resistance is needed than with refractory grade silicon carbide
- Silicon nitride (Si_3N_4): similar in properties and use to silicon carbide but generally more resistant to oxidation and thermal shock
- Boron nitride (BN): often used as a lubricant, a seal, and an antiwetting agent; two crystal forms similar to carbon; hexagonal flakes like graphite and cubic like diamond

Production Techniques and Finished Refractory Materials

The American Society for Testing and Materials (ASTM) classifies refractories according to forming technique and chemistry. The production technique is tied to the forming technique and chemistry of the refractory. General production follows the steps shown in

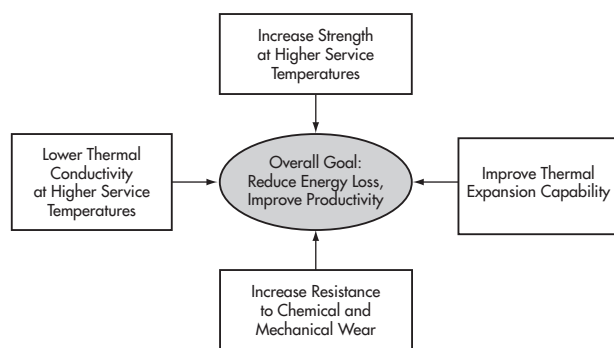


Figure 3. Improving refractory materials for improved energy efficiency

Figure 3. Those materials that do not pass quality control at any point in the process are crushed and sieved to form synthetic raw materials.

The following classifications are for shaped refractories (all ASTM standard classifications are available at <http://www.astm.org>):

- C27-98, Standard Classification of Fireclay and High-Alumina Refractory Brick
 - C155-97, Standard Classification of Insulating Firebrick
 - C1547-02, Standard Classification for Fusion-Cast Refractory Blocks and Shapes
 - C416-97, Standard Classification of Silica Refractory Brick
 - C455-97, Standard Classification of Chrome Brick, Chrome-Magnesia Brick, Magnesite-Chrome Brick, and Magnesite Brick
 - C467-97, Standard Classification of Mullite Refractories
 - C545-97, Standard Classification of Zircon Refractories
- The following classifications are for unshaped refractories:
- C673-97, Standard Classification of Fireclay and High-Alumina Plastic Refractories and Ramming Mixes
 - C401-91, Standard Classification of Alumina and Alumina-Silicate Castable Refractories

GOVERNMENT, ENVIRONMENT, AND HEALTH CONSIDERATIONS

Crystalline silica, asbestos, hexavalent chrome, formaldehyde, and the introduced regulations on maximum allowable control technology (MACT) are the greatest government, environmental, and health concerns facing the refractories industry today. The following discusses these concerns and what refractory companies are doing to alleviate them.

Crystalline silica exposure is the single greatest government and health-related issue facing refractory producers because it is found in abundance in almost all refractory raw materials. Therefore, refractory companies are working to reduce dust exposure to reduce the threat of crystalline silica-related health concerns (Crolius 2005).

Asbestos use has declined to near zero because of prevalent health concerns. Many refractory companies are eliminating vermiculite and other asbestos-containing raw materials from their products because of their small asbestos content.

Hexavalent chrome also continues to be a problem for refractory producers. During use, hexavalent chrome may be produced from chrome-containing refractories. Therefore, chrome

use in refractories has drastically fallen because of health concerns, and companies continue to try to eliminate chrome in their products.

Formaldehyde is a small but looming problem, because it is used in many refractory binder systems. The extent of the formaldehyde problem may change in the coming years as its effect on health is better understood or if current regulations are changed.

MACT is the Environmental Protection Agency's plan to limit air pollutants, thus improving the environment. New facilities will need to be constructed and existing facilities may have to retrofit to meet these guidelines.

Of these considerations, crystalline silica is the greatest concern to the refractories industry because most refractories today contain crystalline silica. It is important that refractory material suppliers, producers, and end users work together to alleviate these concerns.

RESEARCH AND DEVELOPMENT

Recent Research

Substantial changes that have occurred in refractories technology over the past 25 years have resulted in crosscutting impacts (issues common to many applications) on a number of the manufacturing industries (Freitag and Richerson 1998). Some of these have included reduction of energy consumption in heat-treating furnaces by (1) the use of fibrous and high-strength porous insulation; (2) the use of resin-bonded MgO-C-metal linings in basic oxygen furnaces in the steel industry, which have greatly extended the number of heats between needed relinings; (3) the use of SiC-based refractories in steel blast furnaces, which has led to increased furnace life; (4) the advent of oxyfuel melting leading to renewed interest in alternative refractory materials in the glass industry, which will allow for processing at higher temperatures and greater corrosion resistance to high alkali and water-rich environments; and (5) the development of many ceramic compositions that have received limited evaluation but have not reached maturity or production status. All these events are representative of industrial process improvements that can be accomplished through advances in refractory materials, yet additional improvements are still possible, which could lead to substantial energy savings throughout the various industries.

Future Research

Evaluation of refractory usage and the barriers and needs of energy-intensive process industries shows several common themes concerning improving refractory materials to improve energy efficiency. These themes relate to reducing energy loss and increasing productivity by developing higher-strength refractories capable of operating at higher temperatures, developing refractories with lower thermal conductivity to reduce wall losses at higher service temperatures, improving the thermal expansion capabilities of current refractories, and developing refractories with greater resistance to chemical and mechanical wear (such as corrosion, erosion, and abrasion). This is conceptualized in Figure 3.

Many issues appear common to multiple industries, as shown by an analysis of current refractory use, current barriers, possible improvements in process energy efficiency, and R&D needs. The following research focus areas and technical R&D topics have been identified as issues common to many applications of refractories.

- *Degradation mechanisms of refractories in different environments.* Further work is needed to determine the mechanisms responsible for the chemical and mechanical degradation of refractories in the various environments in which they are called to operate.

- *Thermal control.* Advances in thermomechanical properties of refractory materials allow furnaces to operate with longer campaigns and with higher levels of insulation for reducing heat losses.
- *Thermomechanical properties at elevated temperature.* Determination of key properties of refractories at elevated temperatures, including elastic modulus, strength, creep behavior, physical and thermal stability resistance, dimensional changes (thermal expansion and changes due to chemical alteration), and thermal conductivity, is needed.

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Diamonds

W. Dan Hausel

INTRODUCTION

Diamond is an extraordinary mineral with extreme hardness and inherent beauty that is sought for personal adornment and industrial use. Because the genesis of this unique mineral requires extreme temperature and pressure, natural diamond is rare—so rare that some diamonds are the most valuable commodity on earth, based on weight.

Diamonds are mined on several continents. The value of the raw production has resulted in a multi-billion-dollar industry. Natural diamond production annually averages more than 110 million carats, valued at more than \$7 billion for the raw stones. Diamond values dramatically increase following the fashioning of the stones, and the value again dramatically increases with their dressing in jewelry, such that diamond jewelry typically sells for 10 to 100 times the value of the raw stone. Industrial diamonds, which are of considerably lower value, include synthetic industrial diamonds. Synthetic industrial diamond production has an average annual value of about \$1 billion.

MINERALOGY

Diamond consists simply of carbon. In nature, native carbon may occur as one of the following polymorphs: diamond, graphite, or lonsdaleite (Erllich and Hausel 2002). The physical differences among these polymorphs reflect the different bonds between the carbon atoms in the crystal structure. In diamond, the coordination of the carbon atoms is tetrahedral with each atom held to four others by strong covalent bonds, resulting in a mineral with extreme hardness.

In contrast, graphite has six-member hexagonal carbon rings that resonate between single- and double-shared electron bonds. These graphite sheets are very strong, but the hexagonal rings are stacked and do not share electrons between adjacent sheets, only a residual electrical charge—thus, no chemical bonds occur between the sheets, resulting in graphite being soft and the sheets easily separated.

The hexagonal modification of diamond, known as lonsdaleite, has a closer -packed arrangement of atoms than diamond or graphite, resulting in a rare mineral of extreme hardness (Lonsdale 1971). Lonsdaleite was initially synthesized at temperatures greater than 1,000°C (1,830°F) under static pressures exceeding 130 kbar (Bundy and Kasper 1967). DuPont de Nemours and Co. obtained the same transformation by intense shock compression and thermal

quenching. Lonsdaleite has since been identified in meteorites and in rare unconventional host rocks, the most notable being the Popigay Depression in Siberia (Erllich and Hausel 2002). The extreme hardness of lonsdaleite makes it ideal for industrial grinding, but its rarity makes it unattractive for commercial use.

Crystal Habit

Diamonds are isometric with cubic, octahedral, hexoctahedral, dodecahedral, trisoctahedral, and related habits. Twinning along the octahedral {111} plane is common, and many crystals are often flattened parallel to this plane, producing a habit that appears as flattened, triangular-shaped diamond known as a *macle*.

Cube

Cubes are a relatively uncommon habit for diamond, and when found are primarily frosted industrial stones. Many have been found in placers in Brazil, and a significant percentage of diamonds in the Snap Lake kimberlites of Canada have cubic habit (Pokhilenko et al. 2003). Crystal faces of a cube often exhibit square-shaped pyramidal depressions rotated 45° diagonally to the edge of the crystal face. The cube may also include scattered trigons mixed with pyramidal and other depressions of hexagonal morphology visible with a microscope.

Octahedron

The octahedron is an eight-sided crystal that has the appearance of 2 four-sided pyramids attached at a common base. Each pyramid contains four equilateral triangles known as octahedral faces. In nature, an octahedral face will often have positive or negative trigons—small equilateral triangles that are visible under a microscope. These are growths or etches on the crystal surface that represent disequilibrium during transport to the earth's surface from the initial stable conditions at depth within the mantle.

Partial resorption of the octahedron will result in different crystal habits, including a rounded dodecahedron (12-sided) with rhombic faces. Further resorption may result in ridges on the rhombic faces, yielding a 24-sided crystal known as a *trishexahedron*. Many diamonds from Argyle, Australia; Murfreesboro, Arkansas; and the Colorado–Wyoming State Line District exhibit resorbed crystal habits. Four-sided tetrahedral diamonds are sometimes encountered that are distorted octahedrons (Orlov 1977; Bruton 1979).

Diamonds commonly enclose mineral inclusions along cleavage planes. These tiny inclusions provide important data on the origin of diamond and can be used to determine the age of the stone or to identify the unique chemistry associated with the genesis of diamond.

Bort

Bort is poor-grade diamond used as an industrial abrasive. It forms rounded grains with a rough exterior and has a radiating crystal habit. The term is also applied to diamonds of inferior quality and to small diamond fragments.

Carbonado

Carbonado is a black to grayish, opaque, fine-grained aggregate of microscopic diamond, graphite, and amorphous carbon with or without accessory minerals. The material is hard, occurs mainly as irregular porous concretions and dendritic aggregates of minute octahedra, and sometimes forms regular, globular concretions. Carbonado is characterized by large aggregates (averaging 8 to 12 mm in diameter) that commonly weigh as much as 20 carats. Specimens of several hundred carats are not uncommon. The density for carbonado is less than that for diamond and varies from 3.13 to 3.46 gm/cm³.

Although carbonado had been found in placers in Brazil and Russia, it was not until the 1990s that it was found in situ. Twenty-six grains of carbonado ranging in size from 0.1 to 1 mm were recovered from a 330-lb sample taken from a vachite (a specific type of basalt from the Avacha volcano of eastern Kamchatka) (Smishlyaev 1999; Erlich and Hausel 2002).

Physical Properties of Diamond

Diamond exhibits perfect octahedral cleavage with conchoidal fracture. The mineral is brittle and will easily break with a mild strike of a hammer. Even so, it is the hardest of all naturally occurring minerals and is assigned a hardness of 10 on the Mohs scale and nearly 8,000 kg/mm² on the Knoop scale. Corundum, the next hardest naturally occurring mineral, has a Mohs hardness of 9. Even so, corundum does not even compare to diamond and only has a Knoop scale hardness of 1,370 kg/mm². Because of diamond's extreme hardness and excellent transparency, diamond is extensively used in jewelry and has a variety of industrial uses.

Diamond's hardness varies in different crystallographic directions. This allows for the mineral to be polished with less difficulty in specific directions using diamond powder. For example, it is less difficult to grind the octahedral corners of the diamond, whereas grinding parallel to the octahedral face is nearly impossible.

With perfect cleavage in four directions parallel to the octahedral faces, an octahedron can be fashioned from an irregular diamond by cleaving (Orlov 1977). The specific gravity of diamond (3.516 to 3.525) is high enough that the gem will concentrate in placers with "black sand." This density is surprisingly high, given that it is composed of such a light element. Compared to graphite, diamond is twice as dense because of the close packing of atoms.

Color

Diamonds occur in a variety of colors, including white to colorless and shades of yellow, red, pink, orange, green, blue, brown, gray, and black. Those that are strongly colored are termed *fancies*. Colored diamonds have included some spectacular stones. For example, at the 1989 Christie's Auction in New York, a 3.14-carat Argyle pink sold for \$1.5 million. More recently, a 0.95-carat fancy purplish red Argyle diamond sold for nearly \$1 million. The world's largest faceted diamond, a yellow-brown fancy known as the 545.7-carat

Golden Jubilee (Harlow 1998), is considered priceless. Possibly the most famous diamond in the world, the 45-carat Hope, is a blue fancy.

In most other gemstones, color is the result of minor transition element impurities; however, this is not the case for diamond. Color in many diamonds is related to nitrogen and boron impurities or is the result of structural defects. Diamonds with dispersed nitrogen may produce yellow (canary) gemstones. If the diamond contains some boron, it may be blue, such as the Hope diamond. The Hope was found in India; however, many natural blue diamonds have come from the Premier mine in South Africa. Blue diamonds with traces of boron are referred to as type IIb diamonds and are semiconductors. Natural irradiation may also result in blue coloration in some diamonds (Harlow 1998).

The most common color for diamond is brown. Before the development of the Argyle mine in Australia in 1986, brown diamonds were considered industrial stones. But because of Australian marketing strategies, brown diamonds are now highly prized gems. The lighter brown stones are labeled champagne and the darker brown referred to as cognac. Yellow is the second most common color, and such stones are referred to as Cape diamonds in reference to the Cape Province of South Africa. When the yellow color is intense, the stone is referred to as canary.

Pink, red, and purple diamonds are rare. The color in these is concentrated in tiny lamellae (referred to as pink graining) in an otherwise colorless diamond. The color lamellae are thought to be the result of deformation of the diamond structure.

Even though there are many green diamonds, few are faceted, primarily because most have a thin green surface layer covering clear diamond that is removed during faceting. Faceted green diamonds are so rare that only one is relatively well known (the 41-carat Dresden Green), and is thought to have either originated in India or Brazil. The color in most green diamonds is the result of natural irradiation. Other green diamonds may result from hydrogen impurities. Another variety, known as a green transmitter, produces strong fluorescence that tends to mask the yellow color of the stone. Other colors include rare orange and violet diamonds (Harlow 1998).

One of the better-known black diamonds is the 67.5-carat Orlov. Black diamonds are colored by numerous graphite inclusions, which also make the diamond an electrical conductor. These are difficult to polish because of abundant soft graphite, so black gem diamonds are uncommon. Opalescent, or fancy milky white diamond is the result of numerous mineral inclusions and possibly nitrogen defects in the crystal (Harlow 1998).

Dispersion, Transparency, Conductivity, Wet Ability

Diamond has a high coefficient of dispersion (0.044), the coefficient is the difference in refractive index of two visible light wavelengths at the opposite ends of the spectrum (one blue-violet and the other red), resulting in the distinct fire seen in faceted diamond caused by its high dispersion. Diamond is completely transparent to a broad segment of the electromagnetic spectrum, making it useful in a variety of industrial, electrical, and scientific applications. It is also transparent to radio and microwaves. Colorless diamonds are also transparent to visible light wavelengths extending into the ultraviolet (UV), and a few rare diamonds (type II) are transparent over much of the UV spectrum (Harlow 1998).

Diamond has a luster described as greasy to adamantine that is related to its high refractive index (IR = 2.4195) and density. Such high density greatly diminishes the speed of light. For example, the speed of light in a vacuum is 186,000 miles/sec (300,000 km/sec), but in diamond, it is only 77,000 miles/sec (Harlow 1998).

Many diamonds are luminescent: approximately one third of all diamonds luminesce blue when placed in UV light. In most cases, luminescence will stop when the UV light is turned off (known as fluorescence). Diamonds fluoresce in both long- and short-wave UV light. The fluorescence is usually greater in long-wave light, and diamond may appear blue, green, yellow, or occasionally red. Fluorescence is generally weak, however, and it may not be readily apparent to the naked eye. In some cases, light emission is still visible for a brief interval after the UV light source is turned off (known as phosphorescence). Some diamonds may also show brilliant phosphorescence when rubbed or exposed to the electric charge in a vacuum tube, or when exposed to UV light (Dana and Ford 1951).

At room temperature, diamond is four times as thermally conductive as copper, even though it is not electrically conductive. Because of the ability to conduct heat, diamond has a tendency to feel cool to the lips when touched, since the gemstone conducts heat away from the lips. This is why diamonds have been referred to as *ice*. Gem testers (about the size of a pen) are designed to identify the unique thermal conductivity of diamond and distinguish it from other gems and imitations.

Diamonds are hydrophobic (nonwetable). Even though diamond is 3.5 times heavier than water, it can be induced to float on water. Because it is hydrophobic, diamond will attract grease, thus providing an efficient method for extracting diamond from ore concentrates (i.e., grease table).

Diamonds are unaffected by heat except at high temperatures. When heated in oxygen, diamond will burn to carbon dioxide (CO₂). Without oxygen, diamond will transform to graphite at much higher temperatures (1,900°C [3,450°F]). Diamonds are unaffected by acids.

ORIGIN AND OCCURRENCE

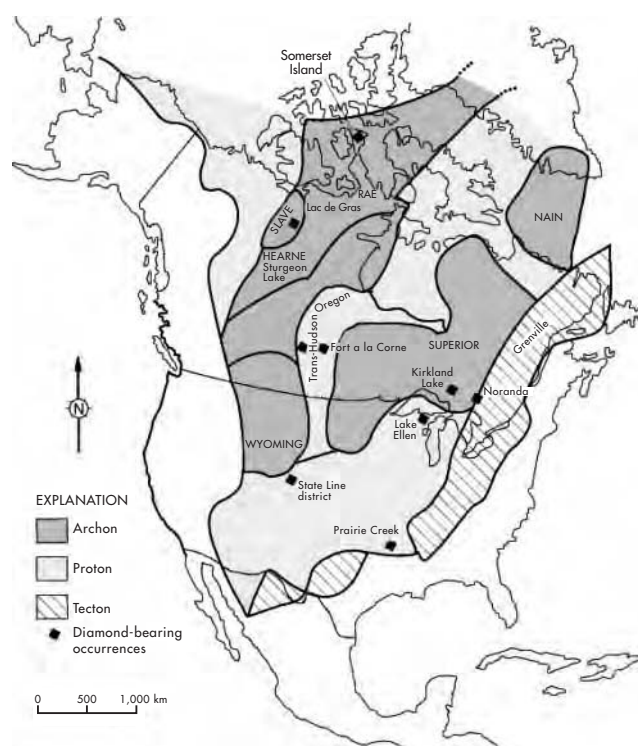
There are literally thousands of known kimberlites and many hundreds of lamproites and lamprophyres, but only a handful contain commercial amounts of diamond. One estimate made many years ago suggested that less than 1% of all kimberlites are commercially mineralized (Lampietti and Sutherland 1978). Although many hundreds of new discoveries have been made since that paper was published, this statistic remains essentially valid.

Diamondiferous kimberlites and lamproites are essentially restricted to cratons and cratonized terrains. These include stable Archean cratonic cores (known as Archons) as well as cratonized Proterozoic margins (referred to as Protons) (Figure 1). Some unconventional diamondiferous host rocks have also been identified in cratons and outside cratonic terrains within tectonically active regions along the margins of cratons. Because high ore grades have been detected in some of these, unconventional commercial host rocks are anticipated to be found in the future (Erlach and Hausel 2002). Current diamond exploration programs are designed to search for conventional host rocks (i.e., kimberlite and lamproite) or for placers presumably derived from these.

Most diamonds are considered xenocrysts that separated from disaggregated mantle peridotite and eclogite during transportation to the earth's surface in kimberlitic, lamproitic, and some lamprophyric magmas. Kimberlites, lamproites, and lamprophyres tend to occur in clusters of a few to more than 100 occurrences. Structural control is thought to be important in the emplacement of these, and several structural orientations are often recognized within each district.

Kimberlite

The majority of diamond mines are developed in kimberlite such as the Wesselton, DeBeers, Kimberley, Dutoitspan, and Ekati, or in



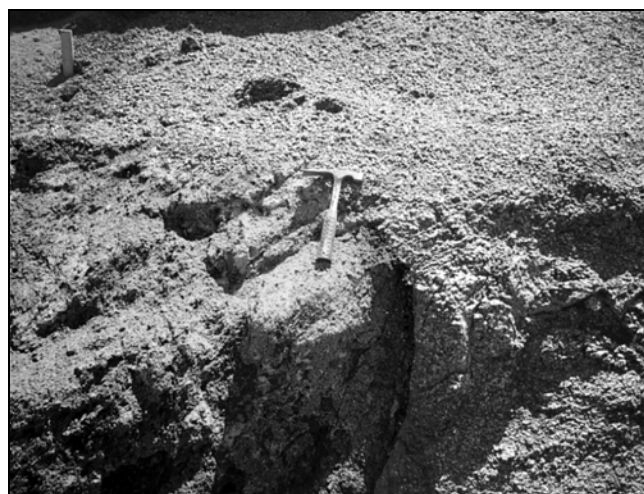
Adapted from Levinson, Gurney, and Kirkley 1992.

Figure 1. The North American craton showing regions of favorability for conventional diamondiferous host rocks. Major Archean provinces are in all capital letters.

placers, particularly beach placers along the west coast of Africa. Lampietti and Sutherland (1978) reported that only about 10% of the known kimberlites were mineralized with diamond. This statistic may no longer be valid in that as many as 50% of kimberlites found in Canada and Wyoming in recent years, and possibly as many as 90% in Colorado, have yielded diamond. Even so, only a very small portion is commercially mineralized. When economic, kimberlites may contain hundreds of millions to billions of dollars worth of stones; thus kimberlites should be a priority target in any exploration program.

Kimberlites are essentially carbonated alkali peridotites that exsolve CO₂ during ascent to the surface from the earth's upper mantle, resulting in diatremes with considerable brecciation and dissolution-rounded xenoliths and cognate nodules. The diatremes appear as subvertical to vertical pipes that taper down at depth, forming steeply inclined cylindrical bodies. The average angle of inclination of the walls of various pipes in the Kimberley region of South Africa (Wesselton, DeBeers, Kimberley, and Dutoitspan) is 82° to 85°. Ideally, the pipes have rounded to ellipsoidal horizontal cross-sections filled with kimberlitic tuff or tuff-breccia. Many continue from the surface to depths of 2 to 2.4 km, where they pinch down to narrow root zones emanating from a feeder dike.

The Kimberley pipe, which was mined out by 1915 (about 20 years after discovery), contracted sharply at depth. At the lowest level of mining (1,056 m), it was no longer pipe shaped but rather had the appearance of three intersecting dikes (Kennedy and Nordlie 1968). Combined with the estimated 1,600 m of erosion since the time of emplacement, the depth to the original point of expansion was probably 2.4 km.



Courtesy of W.D. Hausel.

Figure 2. Exposed contact of a Schaffer diamondiferous kimberlite, Wyoming, showing the knife sharp contact between the kimberlite (left) and granite (right), explained by adiabatic cooling of the kimberlite magma during eruption

Kimberlitic magmas are interpreted to originate from depths as great as 200 km and travel to the earth's surface in a matter of hours (O'Hara, Richardson, and Wilson 1971). The magma is thought to rise rapidly, possibly 10 to 30 km/hr in order to transport high-density ultramafic xenoliths. Within the last few kilometers of the surface, emplacement rates are thought to increase dramatically to several hundred kilometers per hour. Such velocities could bring diamonds from the mantle to the surface in less than a day. McGretchin (1968) estimated that the speed of the fluidized material near the surface increased to as much as 400 m/sec, or about the speed of sound (Mach 1 or 331 m/sec). Some estimates have even suggested kimberlite emplacement at the earth's surface may have achieved velocities exceeding Mach 3 (Hughes 1982).

The temperature of the magma at the point of eruption is relatively cool (Figure 2). Watson (1967) indicated a magma temperature of less than 600°C (1,110°F) on the basis of the coking effects on coal intruded by kimberlite. A low temperature of emplacement is also supported by the absence of any visible thermal effects on country rock adjacent to most kimberlite contacts. Davidson (1967) suggested the temperature of emplacement may have been as low as 200°C based on the retention of argon. Hughes (1982) pointed out that the near-surface temperatures of the gas-charged kimberlite melt may be as low as 0°C (32°F) because of the adiabatic expansion of CO₂ gas as kimberlite erupts at the surface.

Kimberlites typically transport xenoliths and xenocrysts to the surface. Many of these are derived from mantle depths and some form a distinct suite of minerals that are referred to as kimberlitic indicator minerals. The traditional indicator minerals used to explore for kimberlite include pyrope garnet, chromian diopside, chromian enstatite, picroilmenite, chromite, and diamond.

Lamproite

Serious interest in lamproite intensified following the discovery of a world-class diamond deposit in olivine lamproite in 1979 in the Kimberley region at Argyle, Western Australia. The discovery led to the recognition of other diamondiferous lamproites in Australia,

Brazil, China, Gabon, Zambia, Ivory Coast, India, Russia, and the United States.

Scott-Smith (1996) subdivides lamproites into two general groups: phlogopite-leucite lamproites (~60% SiO₂ [silicon dioxide]) and olivine lamproites (>20% MgO [magnesium oxide], 35% to 45% SiO₂, and 7% K₂O [potassium oxide]) with abundant serpentine pseudomorphs after olivine. Instead of pipes with steep walls that slowly diminish in diameter with increasing depth, lamproites are characterized by "champagne-glass" vents filled by tuffaceous rocks, often with massive volcanic rocks in the core.

In some cases, lamproites appear to have formed in the diamond stability field (Nixon 1995). A qualitative correlation between diamond and olivine in lamproite is confirmed in both the Ellendale, Australia, and Kapamba, Zambia, provinces in which diamond grades are consistently higher in olivine lamproites than leucite lamproites. When found, diamonds occur primarily in pyroclastic rocks; the magmatic phases are notoriously diamond poor, owing to the high temperatures sustained in the flows during eruption, which are antipathetic to diamond preservation; that is, the diamonds will burn (Scott-Smith 1986).

Where vents flare out, a potential for substantial tonnages exists in larger craters. At Argyle, Western Australia, past reserve estimates of 94 Mt of ore at an average grade of 750 carats/100 t led to its classification as a world-class deposit. Some of the richer portions of this deposit yielded grades as high as 2,000 carats/100 t. Large numbers of the Argyle diamonds, however, are graphitized and partially resorbed; more than 60% are irregular in shape and include macles, polycrystalline forms, and rounded dodecahedrons. The largest Argyle diamond weighed 42.6 carats; the overall size of diamonds is quite small (average <0.1 carat). Nearly 80% are brown, and the remaining stones are dominantly yellow or colorless. Rare but economically important pink to red diamonds bring Argyle fame (Shigley, Chapman, and Ellison 2001).

Many lamproitic diamonds are relatively small and include common fancy yellow to brown stones. For example, macro diamonds (>1 mm) from the Ellendale field in Western Australia are dominantly yellow dodecahedra, and many micro diamonds are colorless or pale-brown, frosted, step-layered octahedral (Shigley, Chapman, and Ellison 2001).

Placers

Because of a relatively high specific gravity (3.5) and extreme hardness, diamonds are often found in secondary stream or marine placers with other minerals of relatively high specific gravity such as magnetite, spinel, ilmenite, rutile, garnet, and gold. Some of the more productive deposits include stream and marine placers where a large percentage of diamonds are gem quality, owing to fracturing and disaggregation of imperfect industrial diamonds during stream transport. Considerable numbers of diamonds have been mined from stream sediments along the Orange River basin in southern Africa and continuing in beach sands downcurrent from the mouth of the Orange River along the Atlantic coast. Historically, there have been many reports of gold prospectors finding diamonds while searching for placer gold. Examples include California, Colorado, Georgia, North Carolina, and Wyoming in the United States, and New South Wales in Australia (Hausel 1998).

Placer diamond deposits formed throughout geological history as is evident by diamonds in ancient Proterozoic paleoplacers in the Witwatersrand metaconglomerates of South Africa and the Snowy Range Group in Wyoming, United States, as well as modern placers along the Atlantic coast of Africa and Smoke Creek near the Argyle mine, Australia.

DISTRIBUTION AND PRODUCTION

Diamond Production

Diamonds are mined from at least 20 countries, and the leading producers of natural diamond are Australia, Botswana, Canada, South Africa, Russia, and Zaire. The World Diamond Council estimated that natural diamond production in 1999 was more than 111 million carats, valued at US\$7.4 billion. In 2000, diamond production was estimated at more than 110 million carats, valued at US\$7.9 billion. In 2001, the U.S. Geological Survey (USGS) estimated that 119 million carats were mined, with an estimated value of US\$7.3 billion, and in 2003, diamond production estimates stood at 132 million carats (Olson 2003). The *Northern Miner* (Anon. 2005) reported that rough diamond sales in 2003 for the Diamond Trading Company (DeBeers marketing arm) were \$5.52 billion.

Canada ranked sixth in diamond production during the same period, but in the second quarter of 2004, it surpassed South Africa to become the third largest diamond producer (based on value). This is one of the great exploration success stories of the twentieth century because before 1998, Canada did not have a diamond industry (Krajick 2001).

Industrial diamonds have considerably less value than gem diamond, and much of industrial production is now synthetic. In 2001, nearly 70% of the total natural and synthetic industrial diamond production came from Ireland, Russia, and the United States: 92% was synthetic (Olson 2001). According to the USGS, world production of natural industrial diamond totaled 48 million carats in 2001 and 48.9 million carats in 2002. More than one third of the world's natural diamond production was classified as industrial. This represented only a very small percentage (~1%), however, of the total monetary value of natural diamond production. Australia led the market in recovery of natural industrial diamonds and has averaged 22.1 million carats per year; however, declining reserves at the Argyle mine resulted in Australian industrial diamond production of only 13.1 million carats in 2001 and in 2002 (Olson 2003).

The World Diamond Council reported that the United States was the largest producer of synthetic industrial diamonds, with 125 million carats manufactured in 1999. The USGS reported that domestic synthetic industrial diamond production for 2002 was 310 million carats. The total industrial output worldwide was estimated to be in excess of 800 million carats in 2001, valued at more than US\$600 million (Olson 2001). Domestic synthetic diamonds were produced by two companies: GE Superabrasives in Ohio and Mypodiamond Inc. in New Jersey.

Natural diamond production was dominated by southern African countries with a significant contribution by Russia and Australia. Nearly all of the Australian diamond production was from the Argyle mine, which accounted for more than 20% of world's diamonds. The relatively low quality of the Argyle diamonds, however, rendered the production to be less valuable than some smaller operations elsewhere.

Diamond Distribution

Although there are hundreds of known diamond occurrences around the world, commercial diamond deposits are rare. In the richest, diamond occurs in concentrations of much less than 1 ppm (Lampietti and Sutherland 1978). The few commercial diamond deposits are hosted by kimberlite, lamproite, and placers derived from these host rocks. These are all associated with Archean cratons and cratonized Proterozoic belts. The discovery of several unconventional host rocks in recent years, though, some with very high ore grades, suggests that other rock types and geological environments will become diamond targets in the future (Hausel 1996; Erlich and Hausel

Table 1. Diamond production of major mines in 2001

Country	Carats, ×1000	Amount, kt	US\$/carat	Value, US\$ million
Canada				
Ekati	3,685	3,685	144	531
Botswana				
Jwaneng	12,339	8,920	110	1,357
Orapa	13,056	15,779	50	653
Letlhakane	1,021	3,625	180	184
South Africa				
Venetia	4,977	4,602	85	423
Namaqualand	808	6,083	180	145
Finsch	2,465	4,768	70	173
Premier	1,637	3,102	75	123
Kimberley	550	3,766	110	61
Baken	65	5,835	400	26
Koffiefontein	145	2,299	225	33
Russia				
Udachnaya	11,500	9,000	85	978
Jubilee	5,500	9,100	65	358
Australia				
Argyle	26,000	15,100	11	286
Merlin	70	270	110	8
Namibia				
Namdeb Onshore	1,385	21,867	220	305

Adapted from *Mining Journal* 2002.

The world's natural diamonds are produced from a small group of deposits, which typically have operating lives of 20 to 30 years. A notable exception is the Premier mine (South Africa), which potentially could operate for more than 100 years (Levinson, Gurney, and Kirkley 1992) (see Table 1).

Africa

The Orange River basin with its many tributaries covers a region with more than 3,000 known barren and diamondiferous kimberlite pipes that include some of the richest pipes in the world. The principal diamond-producing countries in Africa are Angola, Botswana, the Central African Republic, the Democratic Republic of Congo (formerly Zaire), Ghana, Guinea, Namibia, Sierra Leone, South Africa, and Zimbabwe. In total, Africa accounts for nearly 50% of the world's diamond production.

Angola. Angola produces 2 million carats of high-quality diamonds annually derived primarily from alluvial sources. Nearly all diamond production is derived from alluvial sources in the Andrada and Lucapara areas of northeastern Luanda Norte and the Cuango River. Only minor amounts are mined from colluvial and eluvial deposits overlying kimberlite at the Camafuca–Camazomba intrusive along the Chicapa River near Calonda. Other kimberlites have been identified in Angola (Janse 1995).

Atlantic Coast. Erosion of diamond pipes and dikes in the Orange River basin resulted in the concentration of millions of diamonds in the basin and along the Atlantic Ocean shoreline. Stream sediments in the basin and beach sands along the west coast of Africa extending from Port Nolloth, Namaqualand, to Luderitz, Namibia, contain placer diamonds. The powerful energy generated by the wave action along this coast has destroyed or broken large numbers of poor-quality stones while gemstones remain intact.

Botswana. DeBeers discovered three world-class kimberlite pipes (Orapa, Letlhakane, and Jwaneng) in Botswana between 1967 and 1973. The Orapa pipe was found in 1967 and production began in 1972. It is the second largest producer of diamonds in the world and yielded more than 13 million carats in 2001 (Table 1). The Jwaneng pipe was discovered in 1973 under the sands of the Kalahari Desert, and mining began on the property in 1982. It has been the third most productive diamond mine by weight and first by value. Two smaller pipes known as the Letlhakane 1 and 2 were discovered in 1968.

Botswana's diamond reserves are immense. Total production in 2001 was a record 26.3 million carats, compared to 21.26 million carats in 1999 and 19.8 million carats in 1998. Output from the mines was 13 million, 1 million, and 12 million carats from Orapa, Letlhakane, and Jwaneng, respectively (Table 1). A fourth mine, Tswapong, produced 10,100 carats in 1999. An application for a fifth mine at Gope in the Central Kgale Game Reserve was reviewed in 1999, and Debswana Diamond Company Ltd. (formed by the Botswana government and South Africa's DeBeers in equal partnership) applied for a license beginning in 2001 to mine diamonds from four small kimberlite pipes known as the B/K pipes near the Orapa mine.

Central African Republic. Diamonds from the Central African Republic are mined from alluvium. Diamondiferous alluvium has been found near Briatouche in the central area of the country; Carnot-Berberati in the southwest; and the Mouka Ouadda plateau in the northeastern portion of the Central African Republic. To date, the source rocks for the diamonds have not been identified. Production amounts to about 500,000 carats per year (Janse 1995).

Democratic Republic of Congo. Formerly known as Zaire, the Democratic Republic of Congo accounts for about 18% of the world production and, in recent years, has been the second largest producer by weight, next to Australia. Only 6% of the Congo diamonds, however, are gem quality with another 40% near-gem, resulting in the Congo being the fourth-ranked producer based on value. According to the American Museum of Natural History Web site (undated), the Mbuji-Mayi mine in the Congo has been a prolific source for diamonds with recent annual production of about 5 million carats.

Ghana. Most diamonds in Ghana (formerly known as the Gold Coast) have been mined from two placers known as the Akwatia and Birim concessions located north west of the capital city of Accra. Annual production peaked at 2,283,000 carats in 1975 and has since declined. About 10% of country's output is classified as gem quality, and most of the remaining stones are micro-diamonds (<2 mm) (Janse 1996). Recoverable resources are estimated to range between 20 and 50 million carats and Ghana's estimated annual production could well exceed 1.3 million carats (Miller 1995). The Akwatia deposits are nearly depleted, but large new resources have been identified at the Birim River deposits. One altered meta-lamproite was found that is thought to represent a primary source for diamonds.

Guinea. Most Guinean diamonds are mined from exceptionally rich gravel placers. Some of the gravel was traced to the Banankoro kimberlite swarms in eastern Guinea, which consists of small uneconomic dikes and pipes. Rich placers mined downstream from the kimberlite swarms were part of the Aredor placer mine (closed in 1993), and produced a number of large diamonds including several that weighed more than 100 carats; the largest was the Guinean Star, weighing 255.6 carats (Janse 1995).

Ivory Coast. Also known as Côte d'Ivoire, Ivory Coast produces a small number of diamonds annually from alluvial deposits and dikes in the Seguela area in the western portion of the country. Alluvial deposits in the Toritya field in central Ivory Coast also pro-

duce a limited number. The source of many diamonds for the Seguela placers is the Toubabouko olivine lamproite dike. Another dike, the Bobi lamproite, has yielded about 400,000 carats from the rock and overlying eluvial deposits (Mitchell and Bergman 1991; Janse 1996).

Lesotho. Several kimberlites were found in Lesotho (formerly Basutoland) but production is limited. Two pipes, the Kao and the Letseng-la-Terai kimberlites, are apparently low grade. The Letseng pipe, however, operated as a commercial mine from 1977 to 1982 and produced some large stones, including a pale-brown 601-carat diamond (Janse 1995).

Liberia. Almost all Liberian diamond production (45% of which is gem quality) comes from small alluvial diggings around Gbapa.

Mali. Alluvial diamonds and kimberlite pipes occur near Kenieba in western Mali, but no commercial diamond deposits have been identified (Janse 1996).

Namibia. Formerly known as South West Africa, Namibia is a source for small high-quality diamonds from placers and alluvium. Essentially all of Namibia's production is derived from alluvial, and coastal and submarine terrace deposits in the Namaqualand coastal region, which includes the coastal region from Luderitz to Bogenfels.

Submerged terrace deposits are mined to depths of 100 m along the coast. These are thought to extend 100 km from shore along the continental shelf (Janse 1995). The Elizabeth Bay deposit along the coast 30 km south of Luderitz began production in 1991 and has yielded many very high-quality small diamonds. The deposit was reported to host 38 Mt of ore averaging 0.066 carats/t. The Auchas mine, located on the north bank of the Orange River 45 km inland, was reported to contain 12.3 Mt averaging 0.036 carats/t. Kimberlites in Namibia occur in five different fields; all have proven to be barren (Janse 1995).

Sierra Leone. Diamonds in Sierra Leone are found in stream and river placers, and in terraces, off-shore terraces, and also in a few kimberlites. Many placers have been depleted, although large high-grade zones are still mined. Kimberlite dikes and two small pipes were found on the Tongo deposit. The dikes were relatively rich, but their narrow width made them unfavorable for mining. The small Koidu pipe (0.4 ha) has an ore grade reported at 1.0 carat/t and is reported to host a very high occurrence (60%) of gem-quality stones. Sierra Leone is known for its relatively large, high-quality placer gemstones, and has produced some very attractive stones including the Woyie River diamond, which weighs 770 carats.

South Africa. Diamonds were initially reported in South Africa in the 1860s, and between 1870 and 1871, a great diamond rush occurred along the Orange River, resulting in discovery of several deposits (Wagner 1914). South Africa is the fifth largest producer of diamonds (by value) with annual production of 8 to 10 million carats. In 2001, the South African mines produced 10.65 million carats. The region has produced more than 500 million carats since the 1860s. A high percentage of these have been gem and near-gem, and South African mines have produced some of the largest diamonds found in history.

The diamonds occur in kimberlite pipes and dikes and in associated alluvial placers. The largest pipe in South Africa is the 54-ha Premier. The Premier mine has been the source of some of the world's largest diamonds, including the Cullinan, Premier Rose, Niarchos, Centenary, and Golden Jubilee. The largest diamond ever found, the fist-size (3,106 carats) Cullinan, was recovered from the Premier.

The Finsch mine covers 17.9 ha and lies 160 km northwest of Kimberley. It is one of De Beers' seven South African operations.

Discovered in 1961, the deposit was initially developed by open pit. Since 1991, underground mine operations continued beneath the abandoned pit. Production from the mine in 2001 was 2.46 million carats from 4.8 Mt of ore (51.7 carats/100 t).

Diamond-bearing gravels were discovered as early as 1903, close to the Limpopo River, 35 km northeast of the present location of the Venetia mine in South Africa. In 1969, DeBeers launched a reconnaissance sampling program to locate the source of the alluvial deposits, and kimberlite pipes were discovered upstream in 1980. Mine construction began in 1990, and the Venetia mine opened in 1992, with full production in 1993. This mine represents one of DeBeers' single largest investments in South Africa. Situated 80 km from Messina in the Northern Province, the property required a capital investment of \$400 million. The mine produced 4.98 million carats from 4.6 Mt of ore in 2001 (108 carats/100 t).

There are 12 kimberlites in the Venetia cluster. Of the 11 pipes and 1 dike, only two kimberlites, K1 and K2, are currently being mined. Some of the pipes were formed by multiple intrusive events, resulting in a variety of kimberlite facies. The kimberlites are clustered over approximately 3 km, and the total surface area of kimberlite is 28 ha. Venetia is being mined by conventional open pit. Surface mining is expected to continue for 20 years with the targeted pit depth of 400 m.

Swaziland. One small commercial operation is reported in Swaziland. Janse (1995) describes an alluvial deposit referred to as the Hlane occurring downstream from the small (2.8 ha) Dokolwayo kimberlite pipe. The placer has produced about 50,000 carats/year since 1983.

Tanzania. Diamonds were initially found in alluvial deposits and later in eluvium on the Mabuki kimberlite 60 km south of Lake Victoria in northern Tanzania. In 1940 another diamondiferous kimberlite of significance was found 140 km south of Lake Victoria by an independent Canadian prospector, John Williamson, who apparently rode a bicycle in his search for diamonds. This pipe, the largest economic kimberlite ever found, is known as the Mwadui pipe. The Mwadui is 1,500 m in diameter, covering 146 ha of surface area. The pipe produced some fine pink stones and averaged more than 500,000 carats annually in the 1960s, with declining production in recent years. DeBeers later discovered hundreds of other kimberlites in this region; none have been productive (Janse 1996).

Zimbabwe. Formerly known as Rhodesia, Zimbabwe has produced minor amounts of diamonds from alluvium. The first kimberlite found in southern Zimbabwe—named the Colossus pipe—was discovered near Lochard in 1907. The pipe was reported to be 1 km in diameter (Wagner 1971). Janse (1995), however, indicated the kimberlite to be considerably smaller (900 by 150 m) and not viable. Other kimberlites were found but all proved to be unprofitable with the exception of the River Ranch kimberlite, discovered in 1975. A mine was officially opened there in 1995, but production was minimal and operations ceased in 1998 (Janse 1995).

Australia

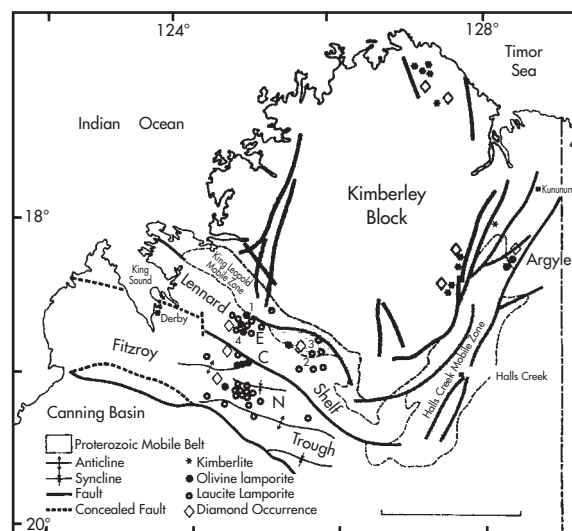
New South Wales. Alluvial diamonds were initially reported in New South Wales (NSW) in 1861, and were later found in Queensland (1887), in South Australia (1894), and in Tasmania (1899). From 1884 to 1922, 167,548 diamonds (with stones weighing as much as 8 carats) were recovered from alluvium in the Copeton field, NSW.

The diamonds were found in gravel buried by Tertiary basalt in an active tectonic environment similar to that of the Urals in Russia, the west coast of the United States, and some Archean greenstone terrains in Canada (Erlich and Hausel 2002; Ayer and Wyman 2003; Kaminsky, Sablukov, and Sablukova 2003). It is



Courtesy of W.D. Hausel.

Figure 3. The Argyle mine



Source: Skinner et al. 1985; reprinted with permission of the Geological Society of South Africa.

Figure 4. The Kimberley block, Western Australia, showing locations of kimberlites, lamproites, diamonds, the Ellendale field (E), Calwinyardah field (C), and Noonkanbah field (N)

thought that the diamonds were derived from phreatomagmatic volcanoclastics and tuffs associated with lamprophyre pipes (Atkinson and Smith 1995). Diamonds in such geological terrains provide signatures, suggesting derivation from a relatively shallow mantle (<80 km) (Ayer and Wyman 2003).

Northern Territories. Decades after the diamond discoveries in NSW, Ashton Exploration discovered diamonds in 1976 near Mt. Percy, West Kimberley, by following a trail of kimberlitic indicator minerals. The mineral trail led to diamondiferous lamproite in the Ellendale field (Tertiary). In August 1979, diamonds were found in Smoke Creek, more than 350 km to the northeast. In October 1979, the 1.2-billion-year-old (Ga) Argyle lamproite was discovered (Atkinson and Smith 1995) (Figure 3). Both lamproite fields are located within Proterozoic mobile belts cratonized about 1.8 Ga and were tectonically active until the Devonian or later (Jacques et al. 1982, 1983; Atkinson, Smith, and Boxer 1984) (Figure 4).

Currently, about 450 lamproites, kimberlites, and lamprophyres have been identified in Australia, of which more than 180 are diamondiferous. Some of the recently discovered kimberlites yielded minor to significant diamond grades (Berryman et al. 1999).

Production began in the mid-1980s at the Argyle mine, and Australia became a leading diamond producer. At full production, the mine yielded more than 30% of the world's annual production. Further development of the open pit continued into 2001, and the current operator (Rio Tinto) reported plans to expand operations underground.

Diamonds were recovered from the Normandy Bow River placer mine in the lower reaches of Limestone Creek, 20 km northeast of the Argyle. This deposit was discovered in the early 1980s and mined by Poseidon/Freeport and Normandy from 1988 until late 1995 (Biggs and Garlick 1987). The plant was inactive at the end of late 1995, after nearly 7 million carats were produced from 24 Mt of gravel.

Kimberley Diamond Company acquired the Ellendale leases previously held by Argyle Diamond Mines. Initial bulk sampling results from Ellendale 4 and 9 revealed higher ore grades near the surface. The company reported the Ellendale 4 resource at more than 2 million carats to a depth of 140 m (23 Mt at 0.088 carats/t), which included a higher-grade zone (444,000 t at 0.261 carats/t) to a depth of 3 m. The near-surface enrichment zone was part of the mining target for 2002. Primary diamond resources of Ellendale 4 and 9 were estimated at more than 2.6 million carats.

For the first 3 years of operation, 2.2 Mt of ore was expected to be mined from the top 3 m of enriched material on both Ellendale 4 and 9. The ore was estimated to average 0.15 carat/t. The company also reported the discovery of 11 previously unknown lamproite pipes in the area (Shigley, Chapman, and Ellison 2001).

The Merlin mine, which was developed on a group of 12 diamondiferous kimberlites in northern Australia, yielded the country's largest diamond, the 104.73-carat Jungiila Bunajina ("star meteorite dreaming stone") white diamond. Merlin is located 80 km south of Borroloola. After 6 years of production, the mine closed in 2002 because of marginal ore.

Australia's total diamond production in 2001 was 26.2 million carats, a decrease of 0.4 million carats from the previous year. The Argyle mine (26.1 million carats) accounted for nearly all of the Australian production. At one point, Argyle mined nearly 40% of the world's annual diamonds: by the end of 2000, the mine had produced an extraordinary 558 million carats (Shigley, Chapman, and Ellison 2001). The Merlin mine in the Northern Territory produced 55,000 carats, making it the second largest Australian producer in 2001.

Brazil

A diamond rush occurred in Brazil in 1725, and by the end of 1729, several diamond placers had been found in eastern Brazil in the region of Diamantina ("diamond city"). Placers were also found along the Sao Francisco, Parana, Goyas, and other streams in southeastern Brazil.

In 1844, rich diamond placers were found in another region of Brazil—the state of Bahia to the north. During the first 120 years of mining, about 10 million carats were recovered, including some stones weighing more than 100 carats.

The primary source of the diamonds has not been found, and it was initially assumed that a rock referred to as itacolomite (micaeous sandstone) was the source. This assumption was based on the presence of middle Proterozoic diamondiferous conglomerates that have supported some small mining operations in the Diamantina Area.

The large number of diamonds found in placers suggests that major primary diamond deposits will be found in Brazil some day. Since 1967, a systematic exploration program identified more than 300 kimberlite, lamproite, kamafugite, and melilitite intrusives, none of which contain economic amounts of diamond (Bizzi et al. 1994; Meyer et al. 1994). A total of about 55 million carats have been recovered from Brazil, with annual production averaging about 1.2 million carats.

China

Diamond deposits in Liaoning Province in China are associated with kimberlite. More than 100 kimberlites are found in this region, including the Jingangshi Kimberlite, which contains commercial amounts of diamond (Sunagawa 1990). At another locality, the Changma mine in Shandong Province near Mengyin, about 500 km southeast of Beijing, is China's largest diamond producer. This deposit was initially mined as an open pit over the past several decades and converted to underground mining in 2002, with an expected life of another 30 years. The Changma deposit consists of two kimberlite diatremes and a dike that all merge at 40 m below the surface. The kimberlite has been drilled to depths of 600 m. Production from the mine during the past 30 years included 1.6 million carats recovered from ore that averaged 1.27 carats/t; the largest diamond was a 119-carat stone. The property has an indicated resource of 1.4 Mt of ore at a grade of 0.92 carats/t with an inferred resource of 1.5 Mt of 0.63 carats/t. The Changma property includes nine diamondiferous kimberlites with a total measured and indicated resource of 9.7 Mt at an average grade of 0.055 carats/t (Beales 2004).

India

Diamonds were reported in the Golconda region of India from medieval time to the nineteenth century. Golconda was actually the marketplace, and the source of the diamonds were placers in the Penner, Karnool, Godvari, and Makhnadi rivers in the Krishna Valley, and possibly in the Panna diamond field to the north in south-central India (Mathur 1982). Many of the better diamonds ended up in the royal treasuries of sultans and shahs of India and Persia. Total production is estimated at about 12 million carats (Milashev 1989).

The majority of the diamonds was found in placer deposits (Sakuntala and Brahman 1984), although diamonds were also found in the Majhagawan lamproite as early as 1827. After kimberlite was described in South Africa in 1877, intensive exploration in the ancient diamond-producing areas of India resulted in the discovery of what was thought to be kimberlite in areas adjacent to many placers (e.g., Majhagawan and Hinota near the Panna placer district, and the Wajakurnur and other intrusives in the Anantpur District). Years later, petrographic studies of some Indian kimberlites confirmed that many were actually olivine lamproite (e.g., Majhagawan and Chelima) (Scott-Smith 1989; Middlemost and Paul 1984; Rock et al. 1992). Diamonds recovered from the pipes are mostly transparent and flawless, with dominantly octahedral and dodecahedral habits. About 40% are gem quality (ore grade ~0.01 carats/t).

Mitchell and Bergman (1991) indicated that there are several other lamproites, kimberlites, and peridotites in this region, and Rock and others (1992) also reported several olivine lamprophyres and minettes of potential economic interest in eastern India. Known kimberlites in India are primarily Proterozoic in age and include diamondiferous kimberlites in the Wajrakarur field in the Andhra Pradesh of the southern kimberlite province and kimberlites in the Raipur field in southeastern Madhya Pradesh in the central province (Middlemost and Paul 1984).

Many of the Indian deposits were depleted by the nineteenth century and new deposits were discovered in the mid-twentieth century, including placers in the Junkel region and Koel Valley, and in the Simla region near the Himalayas (which were originally described in Sanskrit texts). Total historical production is estimated to be between 14 and 21 million carats. Currently, about 20,000 carats are produced each year.

North America

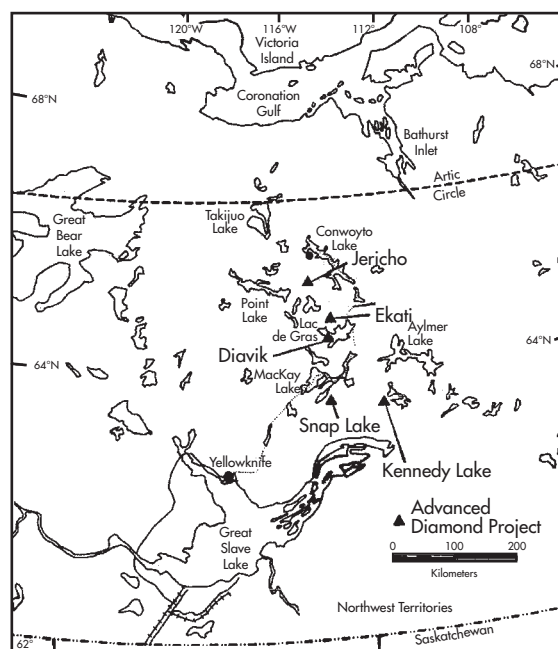
There is little doubt that Canada, which has become a major diamond producer, will remain in the forefront of diamond production and exploration for decades to come. Recent exploration in Canada has resulted in the discovery of more than 500 kimberlites (including some unconventional host rocks), of which nearly half are diamondiferous (Kjarsgaard and Levinson 2002). Some of the unconventional host rocks include lamprophyre (including minette) and actinolite schist at Wawa, Canada, that is interpreted to represent metamorphosed komatiite.

The North American craton is the largest in the world. The cratonic basement rocks of Canada continue south into the United States and underlie large parts of Montana–Wyoming and the Great Lakes region. Exploration in the United States, however, has been relatively minimal. Even so, more than 100 kimberlites, lamproites, and lamprophyres have been identified in the southern extension of the North American craton in Colorado, Wyoming, and Montana. Approximately half of the kimberlites found in Colorado and Wyoming are diamondiferous; only one in Montana has yielded diamonds to date. One mine was developed along the edge of the Wyoming craton in 1995–1996. The Kelsey Lake mine in the Colorado–Wyoming State Line District south of Laramie, Wyoming, contained low-grade ore (about 0.05 carats/t) and yielded some high-quality diamonds weighing as much as 28.3 carats (Coopersmith, Mitchell, and Hausel 2003). Mine operations ended because of legal problems.

The presence of several hundred kimberlitic indicator mineral anomalies, several diamonds, and some geophysical and remote sensing anomalies support the concept that the Wyoming craton has been intruded by a major swarm of kimberlitic and related intrusives, most of which remain undiscovered. Because a large part of the Wyoming craton remains unexplored for diamonds, additional discoveries are expected. In the Great Lakes region, a group of about 30 kimberlites are reported in the Michigan–Illinois Area (eight of which contain trace amounts of diamond) (Hausel 1998).

One of the great exploration success stories of the twentieth century was the discovery of diamonds in the Northwest Territories of Canada, which sparked the largest claim-staking rush in history (Krajick 2001). A group of diamondiferous kimberlites were found nearly 300 km northeast of Yellowknife under a group of shallow lakes in the Lac de Gras region. Within a few years following the discovery, BHP commissioned Canada's first diamond mine in late 1998 (Figure 5). This mine, known as Ekati, is a world-class mine. The mine property includes a group of 121 kimberlite intrusives, and to date, commercial mineralization has been identified and reserves established for the Fox, Leslie, Misery, Koala, Koala North, Panda, Beartooth, Sable, and Pigeon kimberlites on the Ekati property; the other kimberlites are being evaluated for reserves. The mine is anticipated to have a minimum life of at least 25 years.

In 2001, Ekati produced 3.7 million carats, totaling about 6% of the world's diamond value. In 2003, production increased to 6.96 million carats (Anon. 2004). The open-pit operation on the Panda kimberlite reached its maximum economic depth in 2003, 5 years after mining was initiated. The declining production from the Panda open pit, however, was replaced by production from the nearby Misery and Koala open pits. Evaluation showed that the



Source: Goepel McDermid Securities 1999; reprinted with permission from Robert W. Klassen.

Figure 5. Important diamond localities in Canada

Panda kimberlite mine life could be extended using underground mining techniques; thus, the remaining kimberlite is being developed using sublevel retreat mining. Underground mining was previously initiated at the adjacent Koala North pipe in 2002. The Panda underground mine is expected to produce 4.7 million carats over an operating period of 6 years, with production scheduled to begin in 2005, followed by full production in 2006. The Ekati production for the first quarter of 2004 totaled 1.27 million carats of diamonds, which was a 40% decline from the previous quarter. For the first 9 months of fiscal year 2004, the Ekati mine produced more than 5.3 million carats.

Ore reserves at the Ekati mine are substantial. On June 30, 2003, the Ekati mine reported 47.7 Mt of ore reserves graded at 0.8 carats/t (36.6 million carats of recoverable diamonds) based on a 2-mm cut-off size. Measured, indicated, and inferred kimberlite resources stood at 127.9 Mt of ore containing an estimated 171.2 million carats (Robertson 2004). As exploration continues on the property, these reserves will increase.

A few other commercial properties have been identified in the Northwest Territories, and several other properties are being explored or evaluated for reserves. These include Snap Lake, Diavik, and Jericho.

Production at the Diavik mine began in 2003. The Diavik pipes located in the Lac de Gras region east of Ekati are being mined by Diavik Diamond Mines based at Yellowknife (Figure 5). Diavik Diamond Mines is a subsidiary of London-based Rio Tinto, and the mine is a joint venture between Rio Tinto (60%) and Toronto-based Aber Diamond Mines (40%). Rio Tinto assumed operating responsibility from their subsidiary, Kennecott Canada Exploration. The deposit is estimated to contain 138 million carats of diamond and includes four kimberlites (A154S, A154N, A418, and A21). The A154S kimberlite is one of the richest kimberlites in the world and contains a reserve of 11.7 million carats at an average grade of 5.2 carats/t. The property is anticipated to yield 6 to

8 million carats/year when in full production and has reserves that will sustain the operation for 16 to 22 years. The property lies on a 20-km² island known as East Island, 300 km northeast of Yellowknife. The Diavik kimberlites (55 million years old [Ma]) intruded the Precambrian basement complex (2.5 to 2.7 Ga).

The Snap Lake mine is located in a kimberlite dike about 100 km south-southeast of Ekati and 220 km northeast of Yellowknife. Snap Lake will be DeBeers' first mine developed outside of southern Africa and is anticipated to begin production in 2006, or possibly as late as 2008. The kimberlite will be mined entirely underground. The kimberlite is estimated to contain 38.8 million carats with an average ore grade of 1.46 carats/t.

Toronto-based Tahera Diamond Corporation is the operator of the Jericho project, located about 170 km north of Ekati near Echo Bay's Lupin gold mine. This property includes six diamondiferous kimberlites within the Nunavut Territory. When placed into production, the property will produce about 6 million carats over a mine life of 8 years. Reserves of 2.6 Mt of ore averaging 1.2 carats/t have been established. The mine is expected to begin development in 2004 and production is scheduled for 2005 (Anon. 2004).

Another project of DeBeers Canada—the Victor Project—lies in the James Bay Lowlands. Victor is one of 18 kimberlite pipes discovered on the property, 16 of which are diamondiferous. The Victor kimberlite has a surface area of 15 ha and consists of two pipes, known as the Victor Main pipe and Victor Southwest pipe, that coalesce at the surface. The Victor kimberlite is a complex pipe consisting of pyroclastic crater and hypabyssal facies kimberlite and has highly variable diamond grades. If a decision is made to put the property in production, the open-pit mine will have a life of 12 years and total project life of 17 years. The proposed mine would be supported by a processing plant designed to process 2.5 Mtpy.

DeBeers is also involved in the Kennady (Gahcho Kue) Lake project, about 100 km east of Snap Lake near Ft. Defiance and southeast of Ekati. Kennady Lake is under exploration by a joint venture between Mountain Lake Resources and DeBeers. The property includes the 5034, Hearne, and Tuzo kimberlites. Initial sampling of the 5034 and Hearne pipes yielded an average ore grade of 1.67 carats/t. If this project receives a go-ahead, it is expected that permitting will require 2 to 3 years followed by another 3 years of mine development (Anon. 2004).

Since the 1990s, many other deposits have been found in Canada in the Northwest Territories, Nunavut, Alberta, Ontario, Quebec, and Saskatchewan (Olson 2001).

According to *Engineering and Mining Journal* (Anon. 2004), Canada is currently supplying about 15% of the world's diamonds and is expected to show dramatic increases in the future. In 2002, the Canadian diamond industry produced nearly 5 million carats. In 2003, production increased to 11.2 million carats, and it is estimated that essentially 50% of the world diamond exploration funding is focused on Canada.

Russia

The official discovery of kimberlite in Russia occurred in 1954 at what later became known as the Mir pipe (Erlich and Hausel 2002). In 1957, development began on placers associated with the Mir pipe and was followed by open-pit operations in the kimberlite. Years later, operations ceased at a depth of 340 m. The average ore grade was high in the upper mine levels (4.0 carats/t) but decreased near the bottom of the pit (1.50 to 2.0 carats/t). The Mir had high gem to industrial diamond content and was the source of several large gems, including the Star of Yakutia (232 carats) and the Diamond of 26th Party Congress (342.57 carats). Annual output from the mine was 6.0 million carats (Miller 1995).

The Udachnaya pipe was found in 1955, and mining began on the associated placers in 1957, followed by open-pit operations in the pipe. Udachnaya has been the most productive diamond mine in Russia with more than 14.4 million carats mined, of which 80% were gems. By 1956, over 500 kimberlites had been discovered in the former U.S.S.R. During the next 30 years, Russia became the third largest producer in the world; nearly all its production came from mines within the northern Siberian platform.

In 1960, the Aikhal pipe was discovered in Yakutia, where mining began in 1962 and ceased sometime between 1981 and 1988, presumably because of overproduction from other sources. Production resumed after 1988, and by 1995 the pit reached a final depth of 240 m. Annual production at the peak of mining was 600,000 carats at an average grade of 1.0 carat/t (Erlich and Hausel 2002).

Another commercial pipe, known as the Sytykanskaya, was discovered in 1955. Open-pit mining began in 1979, and 600,000 carats/year were produced (average grade of 0.60 carat/t). Another commercial diamond mine, the Internatsional'naya pipe, was found in 1969. Mining began in 1971 and the open pit was developed to a depth of 280 m by 1980. Open-pit operations ceased, but plans were made to resume mining underground.

The 23rd Party Congress pipe was discovered in 1959, and mining on this very rich pipe began in 1966. The ore averaged 6.0 carats/t and the open pit reached a depth of 124 m after 15 years of operation. The Jubilee (Yubileinaya) pipe was discovered in 1975. Following the removal of 70 to 100 m of basalt overburden, open-pit mining began. The Jubilee was anticipated to replace production from the declining Udachnaya pipe.

During the 1970s, other diamondiferous kimberlites were discovered within the Russian platform. At about the same time, several kimberlitic pipes were discovered northeast of the city of Arkhangel'sk, which included the Lomonosov diamond deposit. Currently, Russia is the fourth largest producer of diamonds in the world (by weight). The American Museum of Natural History Nature of Diamonds exhibit in New York City reported that the country has produced a total of 332 million carats and currently has an annual production of 10 to 12.5 million carats.

Venezuela

In 1890 and 1901, secondary placer deposits were discovered in Venezuela and Guyana, and near the end of the 1960s, a placer deposit was found on Caroní River in southeastern Venezuela. To mid-1969, 1.3 million carats had been mined; the largest stone weighed 12 carats. In September 1971, near the town of Salvación in the state of Bolívar, another significant placer was discovered. Within a short period, monthly diamond production from the Salvación region reached 50,000 carats, but the source of the diamonds remains unknown.

Other Cratons

Several diamondiferous pipes have been reported in other cratons such as in the Greenland region, and also in Kazakhstan. Kazakhstan also has the added attraction of having some very unusual and very rich unconventional metamorphic diamond deposits—but most of the diamonds are small, low-value industrial micro-diamonds (Erlich and Hausel 2002).

EXPLORATION

Cost figures for annual diamond exploration amounts to tens of millions of dollars. Capitalization costs for the development of the Ekati diamond mine in the Northwest Territories alone were more than US\$800 million. Regional circumstances will dictate which

exploration method will need to be used; however, when an exploration program begins, priority is given to areas of favorability for finding "traditional" diamondiferous host rocks. For example, commercial diamondiferous kimberlites are considered to be restricted to cratonic regions that have been relatively stable for about 1.5 Ga. Janse (1984, 1994) suggested that cratons be separated into areas of favorability known as Archons, Protons, and Tectons. This method for outlining regions of favorability provides an excellent first option priority list.

Archons (Archean basement stabilized more than 2.5 Ga ago) are considered to have high potential for discovery of commercial diamond deposits hosted by kimberlite and possibly lamproite and lamprophyre. Protons (Early to Middle Proterozoic [2.5 to 1.6 Ga] basement terrains) have moderate potential for commercial diamond deposits in kimberlite and high potential for similar deposits in lamproite and possibly lamprophyre. Tectons (Late Proterozoic [1.6 Ga to 600 Ma] basement terrains) are considered to have low potential for commercial diamondiferous host rock. Unconventional diamond deposits (such as high-pressure metamorphic complexes, astroblemes, subduction-related complexes, and divolcaniclastics) may occur in tectonically active terrains, but the methods for exploration for these are not well defined.

Following selection of a favorable terrain, topographic and geological maps, aerial and satellite imagery, and aerial geophysical data are examined. Unusual circular depressions, circular drainage patterns, noteworthy structural trends, and vegetation anomalies are noted. Geophysics is used to search for distinct ("bull's eye") conductors and magnetic anomalies. Geochemical data are examined for chromium (Cr), nickel (Ni), magnesium (Mg), and niobium (Nb) anomalies.

Stream-Sediment Sampling

One of the primary methods used in diamond exploration is a stream-sediment sampling program designed to search for "kimberlitic indicator minerals" (pyrope garnet, chromian diopside, chromian enstatite, picroilmenite, chromian spinel, and of course diamond). Diamond targets are small and can range from diatremes of several hectares to narrow dikes and sills. Diamond-bearing kimberlites and lamproites typically contain abundant soft serpentine with resistant mantle-derived xenocrysts and xenoliths. The serpentine matrix tends to decompose, releasing distinct, mantle-derived, kimberlitic indicator minerals into the surrounding environment. The indicator minerals may be carried downstream for hundreds of meters or several kilometers, depending on the climatic and geomorphic history of the region. Diamonds, however, are thought to be carried considerable distances—in some cases, hundreds of kilometers. The indicator minerals can provide a trail leading back to the source.

In the planning stages of stream-sediment sampling, proposed sample sites are initially marked in prominent drainages on a topographic map using a sample spacing designed to take advantage of the region. In arid regions, sample spacing should take advantage of relatively short transport distances of the indicator minerals. In subarctic to arctic areas (i.e., Canada, Sweden, Russia, etc.), sample density may be considerably lower, owing to the greater transport distance and the logistical difficulties of collecting samples. Anomalous areas are then resampled at a greater sample density.

The usual kimberlitic indicator minerals are rare to nonexistent in lamproite; thus other minerals (zircon, phlogopite, K-rich feldspar, armalcolite, priderite) may be considered that unfortunately have low specific gravity and poor resistance to abrasion, and are potentially difficult to identify. The better indicators for diamondiferous lamproite are diamond and magnesiochromite.

To take advantage of the dispersion of kimberlitic indicator minerals, the size of samples are determined based on the environment. For example, much larger samples are taken where there is a general lack of active streams compared to regions with active drainages. In areas with juvenile streams, samples are often panned on site to recover a few pounds of sample concentrate. Recovered indicator minerals are tested for chemistry using an electron microprobe to identify those that have higher probability of originating from the diamond stability field. The data are plotted on maps to facilitate evaluation.

Geomorphology

Kimberlite and olivine lamproite are often pervasively serpentinized, making outcrops the exception rather than the rule. In many cases, geomorphic expressions of pipes are subtle to unrecognizable. The Kimberley pipe in South Africa was expressed as a slight mound, but nearby pipes (i.e., Wessleton pipe) were expressed as subtle depressions. Others produced subtle modifications of drainage patterns (Mannard 1968). In the subarctic, where glaciation has scoured the landscape, some kimberlites produce noticeable depressions filled by lakes. In the semiarid region of Wyoming and Colorado, a few kimberlites are expressed as slight depressions, but most blend into the surrounding topography and may or may not have a subtle vegetation anomaly.

In the Ellendale field, in Western Australia, serpentinized diamondiferous olivine lamproites lie hidden under a thin layer of soil in a field of well-exposed leucite lamproite volcanoes. The Argyle lamproite and diamondiferous lamproites in the Murfreesboro Area of Arkansas were also hidden by a thin soil cover.

Lineaments

Many kimberlites and lamproites are structurally controlled (Hausel, McCallum, and Woodzick 1979; Hausel, Glahn, and Woodzick 1981; Macnae 1979, 1995; Nixon 1981; Atkinson 1989; Erlich and Hausel 2002). Controlling lineaments and fractures may be indicated by alignment of a cluster of intrusives or by the elongation of a pipe. In Lesotho, South Africa, Dempster and Richard (1973) reported a close association of kimberlite with lineaments: 96% of kimberlites were found along west–northwest trends, and many pipes were located where the west–northwest trends intersected west–southwest fractures.

Lamproites in the Leucite Hills, Wyoming, are found on the flank of the Rock Springs uplift, where distinct east–west fractures lie perpendicular to the axis of the uplift (Hausel, Gregory, and Sutherland 1995). In the West Kimberley Province of Western Australia, some lamproites are spatially associated with the Sandy Creek shear zone, a Proterozoic fault. In the Ellendale field, several lamproites lie near cross faults perpendicular to the Oscar Range trend, even though the intrusions do not appear to be directly related to any known fault. The Argyle lamproite to the east has an elongated morphology suggestive of fault control and intrudes a splay on the Glenhill fault (Jaques, Lewis, and Smith 1986).

Remote Sensing

Kingston (1984) reported that remote-sensing techniques are widely used to search for kimberlite; these include conventional and false color aerial photography, Landsat multispectral scanner satellite data, and airborne multispectral scanning. Multispectral scanning data are used to identify spectral anomalies related to magnesium-rich clays (i.e., montmorillonite), carbonate, and other material with low silica content. Image enhancement techniques (contrast enhancements, ratios, principal components, and clustering) produce images that are optimum for discrimination of kimberlite and

olivine lamproite soils. These and other photo images can be used to search for vegetation and structural anomalies. Airborne multispectral scanning provides higher resolution than Landsat and can also be used to measure reflectance qualities of clay in soil.

Many pipes and dikes possess distinct structural qualities or vegetation anomalies that may allow detection on aerial photographs. Mannard (1968) reported that kimberlites in southern and central Africa were identified on aerial photographs on the basis of vegetation anomalies, circular depressions or mounds, and tonal differences. Low-level aerial photographs (both conventional and false color or infrared) have been used to locate kimberlite in the former U.S.S.R. (Barygin 1962) and in the United States (Hausel, McCallum, and Woodzick 1979; Hausel et al. 2000, 2003).

Geophysical Surveys

Geophysical exploration has been successful in the search for hidden kimberlite and lamproite (Litinskii 1963a, 1963b; Gerrits 1967; Burley and Greenwood 1972; Hausel, McCallum, and Woodzick 1979; Hausel, Glahn, and Woodzick 1981; Paterson and MacFadyen 1984; Woodzick 1980), particularly in districts where kimberlites have previously been discovered. Contrasting geophysical properties are often favorable for distinguishing kimberlite, lamproite, and minette from country rock.

INPUT airborne surveys are effective in identifying both serpentinized and weathered kimberlite, owing to the combination of electromagnetics and magnetics used in the survey. Rock exposures of kimberlite may yield magnetic signatures but are poorly conductive, whereas deeply weathered kimberlites are conductive but poorly magnetic.

Because of the relatively small size of the diamond host rock, close flight-line spacing is necessary. In an airborne INPUT survey over the State Line District, Wyoming, a flight-line spacing of 200 m effectively detected several kimberlites and identified distinct magnetic anomalies interpreted as blind diatremes (Paterson and MacFadyen 1984). An aeromagnetic (200- to 400-m line spacing) survey flown over parts of northeastern Kansas identified several anomalies, some of which were drilled, resulting in the discovery of previously unknown kimberlites (i.e., Baldwin Creek, Tuttle, and Antioch kimberlites) (Berendsen and Weiss 2001). Flight-line spacings of 50 to 100 m were used for INPUT, magnetic, and radiometric surveys in the Ellendale field in Australia (Atkinson 1989; Janke 1983; Jaques, Lewis, and Smith 1986). The olivine lamproites yielded distinct dipolar magnetic anomalies.

In Yakutia Province, Russia, ground magnetic surveys were used where differences between the magnetic susceptibility of kimberlite and the carbonate sedimentary country rock were high. Airborne surveys also successfully detected anomalies as great as 5,000 gammas (Litinskii 1963b). In Mali, West Africa, the magnetic contrast between kimberlite and schist and sandstone country rock resulted in 2,400-gamma anomalies over kimberlite (Gerrits 1967). In Lesotho, anomalies over kimberlite were comparable with those in Yakutia Province (Burley and Greenwood 1972).

Fipke and colleagues (1995) indicated that barren peridotite phases in Arkansas yielded magnetic highs, but the diamondiferous phases were not detected. In northeastern Kansas, Brookins (1970) reported large positive (550 to 5,000 gamma) and negative (0 to -2,800 gamma) anomalies over some kimberlites emplaced in regional sedimentary rocks. The sedimentary rocks had relatively low magnetic susceptibility, making magnetic surveys an effective method for exploration.

Most kimberlites in the Colorado–Wyoming State Line District yielded small complex dipolar anomalies in the range of 25 to 150 gammas, with some isolated anomalies of 250 and 1,000 gam-

mas (Hausel, McCallum, and Woodzick 1979). Blue ground (weathered) kimberlite tends to mask magnetic anomalies. In the Iron Mountain District, where much of the kimberlite is relatively homogeneous, massive hypabyssal-facies kimberlite, only weak to indistinct magnetic anomalies were detected (Hausel et al. 2000).

Magnetite is replaced by hematite during weathering, masking near-surface magnetic affinity. Clay produced during weathering promotes water retention, thus weathered blue ground over kimberlite may produce vegetation anomalies that are susceptible to detection by electrical methods. For example, resistivity surveys in the Colorado–Wyoming State Line District detected apparent resistivity of 25 to 75 ohm-m over weathered kimberlite, compared with 150 to 2,250 ohm-m in the country rock granite (Hausel, McCallum, and Woodzick 1979).

Resistivity of weathered lamproite may be lower than that of country rock, owing to the conductive nature of smectitic clay relative to illite, kaolinite, and other clay minerals (Gerrits 1967; Janke 1983). The Argyle olivine lamproite, however, yielded moderate to strong resistivity anomalies (40 to 100 ohm-m) compared to the surrounding country rock (200 ohm-m) (Drew 1986).

Biogeochemical and Geochemical Surveys

Kimberlite and lamproite are potassic alkalic ultrabasic igneous rocks with elevated barium (Ba), cobalt (Co), Cr, cesium (Cs), phosphorus (P), lead (Pb), rubidium (Rb), strontium (Sr), tantalum (Ta), thorium (Th), uranium (U), vanadium (V), and light rare earth elements (LREE). The elevated Cr, Nb, Ni, and Ta may show up in nearby soils (Jaques 1998), but dispersion of these metals in soils is not extensive. Stream-sediment geochemistry generally is not useful because of efficient dispersion of most metals in streams. In the Colorado–Wyoming State Line District, Cominco American outlined several known kimberlite intrusives on the basis of Cr, Nb, and Ni soil geochemical anomalies. Dispersion patterns were restricted, however, and of little use in exploration in this terrain.

Gregory and Tooms (1969) found that Mg, Ni, and Nb anomalies did not extend farther than 0.6 km from the Prairie Creek lamproite, Arkansas. Haebig and Jackson (1986) noted that soil geochemical anomalies (Co, Cr, Nb, Ni) were detected in sand and soil immediately above lamproite vents in West Kimberley, Australia. Such anomalies could prove useful in the search for hidden olivine lamproites. Gregory (1984) used lithochemistry to distinguish olivine lamproite from leucite lamproite on the basis of Mg, Ni, Cr, and Co ratios.

Bergman (1987) suggested that olivine lamproites are generally enriched in compatible elements relative to leucite lamproites as a result of the abundance of xenocryst olivine in the former. Barren lamproites contain elevated alkali and lithophile contents (K, sodium [Na], Th, U, yttrium [Y], and zirconium [Zr]) relative to diamondiferous (olivine) lamproites. Diamondiferous lamproites possess twice the Co, Cr, Mg, Nb, and Ni and half the aluminum (Al), K, and Na as barren lamproites (Mitchell and Bergman 1991), and lamproites have anomalous titanium (Ti), K, Ba, Zr, and Nb compared to most other rocks. These components may favor the growth of specific flora or may stress local vegetation (Jaques 1998). The Big Spring vent, West Kimberley, Australia, is characterized by anomalous faint pink tones that reflect the growth pattern of grass on the vent (Jaques, Lewis, and Smith 1986).

Many kimberlites in the Colorado–Wyoming State Line District will not support growth of woody vegetation, resulting in open parks over kimberlite in otherwise forested areas. These same kimberlites may support a lush stand of grass delineating the limit of the intrusive. Distinct grassy vegetation anomalies over kimberlites in the Iron Mountain District, Wyoming, were used successfully to map

many intrusives (Hausel et al. 2000). The anomalies are especially distinct after a few days of rain in the late spring.

Some Siberian kimberlites support denser stands of larch (*Larix dahurica*) and abundant undergrowth of shrub willow (*Salix*) and alder (*Alnus*) compared to surrounding Cambrian carbonates. In central India, trees over the Hinota pipe are healthier, taller, and denser than those in the surrounding quartz arenite. This may be attributed to greater availability of K, P, micronutrients, and water.

Vegetation over the Sturgeon Lake kimberlite in Saskatchewan was tested for 48 elements; the kimberlite showed a consistent spatial relationship with Ni, Sr, Rb, Cr, manganese (Mn), and Nb, and to a lesser extent with Mg, P, and Ba; relatively high Ni concentrations occurred in dogwood twigs. In hazelnut twigs, Cr levels were greater than 15 ppm near the kimberlite but only 5 to 8 ppm elsewhere, and Nb was higher in hazelnut twigs. Sr and particularly Rb were relatively enriched in some plant species on kimberlite. The Sr was probably derived from the carbonates associated with the kimberlite, whereas the Rb was derived from phlogopite. Ni, Rb, and Sr distribution and Cr enrichment associated with Mn depletion in the twigs could be used to identify nearby kimberlite.

MINING AND MILLING

Economic diamond deposits depend on the average price of stones, the amount of waste material removed, mining methods, company politics, socioeconomics of the area, and many other factors. For example, a diamond deposit may be mined at a comparatively lower cost in a developing country because of the availability of an inexpensive labor force, although constructing an infrastructure in such an area could offset some of these benefits. In the United States, high labor and mining costs require higher-value ore for commercial operation; however, an infrastructure may already be available.

More than half of the world's natural diamonds are mined from kimberlite and lamproite and the rest are mined from placers. Economic cutoff grades are typically >0.10 carat/t (Jaques 1998), but the grade is highly dependent on mining costs and the value of the recovered diamonds. Thus the economic cutoff grade will vary depending on these factors. Average ore grades range from a high of 6.8 carats/t for Argyle to a low of about 0.15 carat/t for Prairie Creek, Arkansas. Some of the rich crater facies lamproite mined at Argyle yielded grades as high as 20 carats/t. Most economic deposits yield >30% gem-quality diamonds.

Commercial deposits include narrow dikes to pipes of 30 to 1,500 m across. Pipes range in surface area from 1 to 150 ha, averaging about 12 ha (Jaques 1998). Diamond mines possess resources in the neighborhood of more than 10 Mt to 350 Mt of ore, and the richest deposits contain reserves measured in the hundreds of millions of carats that are valued in the billions of dollars.

Open-pit diamond mines are typically designed to recover as little as 100,000 t to more than 10 Mt of ore per year. Annual diamond production may range from several thousand carats to a few million carats. For example, the Finsch mine, South Africa, produced about 5 million carats annually between 1981 and 1991, whereas annual diamond production for the extremely rich Argyle lamproite reached a record 39 million carats during the height of operation.

Diamond quality and size must also be considered in commercial operations. Lamproites appear to produce small diamonds with large percentages of colored stones. Many kimberlites yield a large range in diamonds, including some very large stones. For example, the average diamond from the Argyle lamproite is small (only <0.1 carat), and those from Ellendale lamproites are only 0.1 to

0.2 carat (Mitchell and Bergman 1991). The largest reported diamond from the Prairie Creek lamproite is 40.42 carats (Hausel 1998). Diamonds from some kimberlites, however, are extraordinary. The largest diamond ever recovered was the size of a human fist; it was mined from the Premier kimberlite, South Africa, and weighed 3,106 carats.

Bulk sampling is the initial step in evaluation of a commercial diamond deposit. If favorable, additional bulk samples are used to assist in establishing ore grade maps to aid in mine planning. Samples are taken on the surface and from drilling in order to achieve a three-dimensional view of ore grades. If the pipe is considered to be economic, planning is completed for an initial open-pit design and a mill placed near the pipe. Open-pit mining typically proceeds from a spiral road developed from the rim of the pit toward the center of the pipe. As mining proceeds, the country rock is cut back in steps to aid in supporting the high walls of the open pit. Mining in the pit may occur in an oval pattern or in a polygonal pattern (Bruton 1979).

As mining continues and the pipe narrows at depth, the open pit will shrink to smaller and smaller diameters. Mining operations may ultimately continue underground using bulk recovery by block caving. Fewer than 30% of diamond mines, however, are continued underground. And to do so, the diamond ore must be of relatively high value, because the cost of underground mining is considerably higher and the amount of ore recovered is considerably lower. Some kimberlites in Siberia and South Africa have been mined to depths of 1,080 m. Open pits may have mine lives of 2 to 50 years (Jaques 1998).

Following recovery of rock mined from open-pit operations, the ore is crushed and screened. Screening separates midsize from larger material rejects and from material too small to contain commercial diamonds. Decisions on the maximum screen size must weigh the cost of processing additional material with the loss of potentially priceless large diamonds.

The typical diamond mill has a basic flowsheet that begins with primary milling and continues to primary gravity concentration, secondary concentration, magnetic separation, and attrition milling. The final diamond extraction stage uses grease tables, electrostatic separation, or x-ray fluorescence extraction (Bruton 1979).

Placer mines are different. The size of a placer mine will vary from a small, one-person operation to a full-scale mine using bulldozers, scrapers, and dredges. Paystreaks are identified in streams or beaches; mining is then completed using small-scale or large-scale earth-moving equipment (Bruton 1979).

GEMOLOGY

The primary monetary value for diamond is as gemstones. Diamond prices vary considerably. There are approximately 5,000 diamond categories with prices that vary from \$0.5/carat up to several tens of thousands of dollars per carat (for large uncut or colored fancy diamonds) (Miller 1995). Many faceted diamonds are worth many times an equivalent weight in gold or platinum. Rough gemstone diamonds have values as high as 100 or more times that of industrial diamonds. After the diamonds are faceted, the value of the gem can increase another 10- to 100-fold, and the final placement of a stone in jewelry will again add another increase in the value of the stone. Thus, any mining operation should consider not only recovery of the gems but also the fashioning of the gems and marketing.

Diamonds are one of the more valuable commodities on earth, and arguably are the most valuable of all commodities based on weight. For example, some Argyle pink diamonds have sold for as much as \$1 million per carat (one carat weighs only 0.2 g [0.007 oz]). Thus, an equivalent weight in gold would be worth

only \$2.80 (at \$400/oz). The extreme value of diamond is due to its mystique, rarity, extreme hardness, high refractive index, and dispersion that can result in brilliant gems with distinctive “fire” when faceted and polished.

Four general types of natural commercial diamonds are recognized. These are *gem*, *bort* (poorly crystallized, gray, brown translucent to opaque), *ballas* (spherical aggregates formed of many small diamonds), and *carbonado* (opaque, black to gray, tough, and compact). Gem diamonds are further subdivided into *gem* and *near-gem* (low-quality gemstones).

The fashioning of diamond “rough” into a finished gem may require up to six steps that include marking, grooving, cleaving, sawing, girdling, and faceting (Hurlbut and Switzer 1979). Whether or not all of these steps are used depends on the size, shape, and quality of the rough stone.

The value of finished gem diamonds is judged by the “four Cs”: cut, clarity, carat weight, and color. The cut of a diamond can increase its value tremendously, and the better proportioned, polished, and faceted, the greater its value. When the girdle (base) and table of the diamond are proportioned correctly, the diamond will exhibit greater fire and brilliance.

Diamonds can be graded using the Gemological Institute of America’s color-grading system. This ranges from D (colorless) to X (light yellow). Each letter of the alphabet from D to X shows a slight increase in yellow tinge that is generally not apparent to the untrained eye (Hurlbut and Switzer 1979). Fancy diamonds are separated from colorless diamonds into groups based on color and intensity (Bruton 1978). Clarity is determined by the presence or absence of blemishes, flaws, and inclusions. One typical grading system ranges from Fl (flawless) to I₃ (imperfect) with intermediate grades of VVS₁ (very, very slightly imperfect), VVS₂, VS₁, VS₂, SI₁, SI₂, I₁, and I₂.

USE

The diamond industry is a multi-billion-dollar mega-industry. The unique physical and optical properties of diamond also make it indispensable and irreplaceable for many industrial uses in addition to personal adornment in jewelry.

Harlow (1998) and Olson (2001, 2003) describe many uses for industrial diamonds. Because of the mineral’s extreme hardness, industrial and synthetic diamonds are used extensively as abrasives in grinding, drilling, cutting, and polishing. Diamond also has chemical, electrical, optical, and thermal characteristics that make it the best material available for wear- and corrosion-resistant coatings, special lenses, heat sinks in electrical circuits, wire drawing, drilling, and many other advanced technologies. One significant future application will be in computer chips because of the diamond’s unmatched thermal conductivity and resistance to heat. A tremendous amount of heat can pass through diamond without causing damage.

Today’s speedy microprocessors run hot—up to 200°F—and microprocessors cannot run much faster without failing. Diamond microchips would be able to handle much higher temperatures that would liquefy ordinary silicon, allowing them to run at higher speeds. But manufacturers have not considered using the precious stone because it has never been possible to produce large diamond wafers affordably. The Florida-based Genesis and the Boston-based Apollo Diamond Company plan to use the diamond jewelry business to finance attempts to introduce diamonds into the semiconducting world.

At room temperature, diamond is the hardest known material with the highest thermal conductivity of any substance. Even though diamond is more expensive than competing abrasive materi-

als such as garnet, corundum, and carborundum, diamond has proven to be cost-effective in several industrial processes because it cuts faster and lasts longer than rival material. Synthetic industrial diamond is superior to natural industrial diamond in that it can be produced in unlimited quantities and tailored to meet specific applications. Consequently, manufactured diamond accounts for more than 90% of the industrial diamonds used in the United States.

According to the USGS, much of the synthetic industrial diamond produced domestically has been used as grit and powder (Olson 2002, 2003). The major uses were in machinery (27%), mineral services (18%), stone and ceramic products (17%), abrasives (16%), contract construction (13%), transportation equipment (6%), and miscellaneous uses (3%) (Olson 2002, 2003). Industrial diamonds are used in the production of computer chips; in construction; in the manufacture of machinery; for mineral and energy exploration and mining, stone cutting and polishing; and in transportation (infrastructure and vehicles). Stone cutting, along with highway construction and repair, are some of the largest users of industrial diamond.

Diamond has one significant limitation in industrial use: it reacts with iron at high temperature, causing the diamond to revert to graphite, which results in high rates of wear. In an iron-rich environment, diamond may be uneconomical to use in comparison to other conventional abrasives (i.e., aluminum oxide, silicon carbide, and boron nitride). Even though these are considerably softer than diamond, they are suitable as high-performance abrasives on ferrous work-pieces.

Diamond use has increased in both jewelry and industrial applications. One reason for the increase is the development of diamond synthesis technology, making it possible to produce diamond abrasives for specific applications. In the past, the only option was to use natural diamond, which had to be sorted by size and crushed, or by surface treatment such as rounding. Synthetic diamond abrasives, however, can now be produced under a controlled environment such that the shape of the crystal can be made irregular and sharp.

Diamond has many potential exotic applications. For example, the Venus probe was fitted with a transparent diamond window because diamond was the only material transparent to infrared light that could withstand the extreme cold and vacuum of space and the extreme high temperatures and atmospheric pressures of Venus’s atmosphere (up to 920°F, and pressures a hundred times that of Earth) (Ward 1979). Another exotic use gives new meaning to the family jewels. LifeGem in Illinois started manufacturing diamonds from cremated human ashes for jewelry for surviving relatives. The cost for a “family jewel” is reported to be more than \$2,000 for a 0.25-carat stone.

Diamond has applications in high-energy physics. Diamond windows are used in high-power lasers because of the high thermal conductivity, low absorption coefficient, and low value of temperature coefficient of refractive index. Diamond anvils are used in high-pressure research, where pressures greater than 4 megabars are needed. Such ultra-high-pressure research can simulate conditions in the core of the earth and on other planets.

Diamonds are also used in dental drills and surgical blades, and provide cutting edges that are many times sharper than the best steel blades. Since diamond has the greatest thermal conductivity of any material, pinhead-size gold-coated diamonds are used in high-capacity miniature transmitters that carry television and telephone signals.

Synthetics

Synthetic gem diamonds and simulants are becoming more common in the marketplace. These include cubic zirconia and moissanite.

Moissanite has twice the fire of natural diamond, is doubly refracting (unlike diamond and cubic zirconia, which are singly refractive), and has a hardness of 9.25—thus, both moissanite and cubic zirconia can easily be scratched by diamond. Double refraction is detectable in moissanite when viewing the front of the stone. The back facets will appear to be duplicated because of the double refraction—except when viewing down the optic axis where light is singly refractive. The optic axis is usually perpendicular to the table of moissanite; thus, one must observe the back facets through another facet to see evidence of double refraction.

Synthetic gem-quality diamonds can be produced in about 24 hours. Some stones weighing up to 3 carats have been produced for a few hundred dollars (uncut). Most are yellow, but some Russian stones are clear. In 1971, General Electric grew facet-quality synthetic diamonds that were nearly colorless (0.3 and 0.26 carats).

The colorless gemstones caused concern in the jewelry trade. Diamond simulants can be detected by a simple thermal conductivity test, but most jewelers were unprepared to distinguish faceted synthetic diamond from natural faceted diamond. Thus, DeBeers developed a diamond verification instrument known as Diamond-View, which uses UV fluorescence to distinguish colorless natural diamond from synthetic diamond. In addition, many synthetic diamonds examined by the Gemological Institute of America contain metallic inclusions in high enough abundance that they are able to attract a magnet. Nonfaceted synthetic diamonds exhibit a unique crystal habit of a cuboctahedron with a flat base. Synthetic diamonds also exhibit unusual dendritic and striated surface patterns. According to Shigley and others (1997), because of the technological challenges and high cost of production, it is unlikely that fashioned gem-quality diamonds larger than 25 points will affect the gemstone industry in commercial quantities.

FUTURE OF THE DIAMOND INDUSTRY

Diamonds have intrinsic value because of unique hardness, transparency, and thermal conductivity. Diamonds will be needed as long as there are industrialized nations. Without any foreseeable major economic disasters, the future of the diamond industry should remain strong.

As science and industry advance, additional applications for diamond are likely to be found in the electronics industry. Demand for diamonds for drilling in exploration for oil, gas, and minerals, and in the construction industries, is anticipated to increase. Some technological advances will demand both natural and synthetic diamond in the future.

For many years, the gem diamond industry was controlled by DeBeers—a monopoly so powerful that the diamond industry and DeBeers were thought by many to be the same. But the discovery of significant diamond resources outside of Africa has diminished DeBeers's control over the diamond market.

The first real threat to the monopoly occurred with the discovery of significant gem-quality diamond deposits in the former U.S.S.R. in the 1950s, but communistic bureaucracy could not compete with South Africa, and the Soviet diamonds did not greatly affect the market (Erlich and Hausel 2002). A major diamond discovery (Argyle) in Western Australia in the 1980s started the real first erosion of the monopoly. The Argyle deposit, however, though rich in diamonds, was dominated by industrial stones, and the gemstones recovered from the mine were small. Even so, the Australian company, Ashton Mining, decided to market their own production.

Some gemstones produced by Argyle included rare pink diamonds. Marketing strategies by the Australians were brilliant, resulting in the Argyle pinks becoming some of the more valuable gemstones on Earth. A large population of the Argyle diamonds

was also light-brown to brown and had been considered by the jewelry trade as industrial or near-gem. These were marketed as champagne and cognac diamonds, and the marketing strategy effectively resulted in these stones becoming highly sought gemstones. Even so, many of the Argyle diamonds were small and required the special cutting skills of gem cutters in India and Sri Lanka.

The next major diamond discoveries were made on the North American craton. This is the largest craton, with the largest Archon core, in the world. Based on the sheer size of the craton, and the many finds of detrital diamonds in glacial moraines, this craton should have been a high-priority target for diamond exploration groups. But for many years, the North American craton was ignored.

The discovery of economic diamond deposits in this craton was the result of unrelenting prospecting by a small group of geologists (Krajick 2001). The discovery set off the greatest rush in modern history and resulted in the development of a diamond industry in Canada.

Diamond production began in Canada following the capitalization of BHP's Ekati mine at more than \$800 million. A few other mines have now been developed, and in April 2004, the value of diamond production from Canada surpassed that of South Africa. This occurred in 6 years. In the future, many more discoveries of diamondiferous kimberlite can be expected in the North American craton. To date, as many as 500 kimberlites and some unconventional host rocks have been identified in Canada—early reports are that 50% contain diamonds—which could easily make the North American craton the primary source of diamonds in the near future.

The North American craton extends across the Canadian border into the United States, where several diamond deposits have been found. Even so, much of the terrain in the United States has not been prospected, or was only partially explored for diamonds. Many exploration targets remain inexplicably unexplored. To date, only two deposits have been mined for diamonds in the United States—one in the Colorado-Wyoming State Line District, and another near Murfreesboro, Arkansas.

Diamond exploration in the near future will continue to focus on Canada, where the geology and political climate are favorable. In addition to discoveries of diamonds in kimberlite and some lamproites, one might anticipate additional diamond discoveries in some unconventional host rocks such as minettes, alnoites, other lamprophyres, komatiites, and in particular, subduction-zone-related breccias.

One concern that has arisen is the potential production of relatively inexpensive synthetic gem-quality diamonds. Natural gem-quality diamonds, however, are also relatively inexpensive until they are faceted and mounted in jewelry. And it is human nature to want a natural gem rather than a synthetic stone or imitation. Gem-quality synthetic diamonds will probably not greatly affect the jewelry market.

CONCLUSION

With the current trend of investment, exploration, and progressive pro-mining atmosphere, it is anticipated that Canada will be a leading diamond producer for decades to come. The sheer size of the North American craton allows one to predict Canada to become the world's primary source for diamonds in the future. Unless there is a major change in attitude of the U.S. government and the population, little is expected to be produced in the United States, even though parts of the country are underlain by this craton. The importance of the North American craton in the future of the diamond industry has resulted in investments of hundreds of millions of dollars in exploration in North America.

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Diatomite

Richard O.Y. Breese and Frederick M. Bodycomb

INTRODUCTION

Terminology and Definitions

The term diatomite is applied both geologically and commercially to the nearly pure sedimentary accumulation of diatom frustules—the microscopic skeletons of unicellular aquatic algae belonging to the class of golden brown algae, Bacillariophyceae. The sediments are fine-grained, highly siliceous, and consist primarily of amorphous opaline silica with only minor amounts of organic residue, secondary minerals, and codeposited nondiatomaceous or crystalline clastic debris. In the geological sense, the name diatomite implies sedimentary accumulations that have reached appreciable thickness, and consequently, when thick enough, such accumulations may have possible commercial potential. Although the term diatomite is popularly and inappropriately applied to any sediment in which there is an abundance of diatom frustules, alternative terminology is more correctly employed to describe less pure diatomaceous sediments (for example, clay-bearing diatomite or diatom-bearing clay). Synonyms in current usage include diatomaceous earth and kieselgur. More antiquated and obsolete terminology includes tripoli powder, tripolite, and infusorial earth.

Unusual Considerations Specific to Diatomite

Worldwide, diatomites occur within Tertiary to Recent lacustrine and marine sedimentary facies. Although diatomite is widespread throughout the world, deposits that contain high-purity, commercially versatile ore are uncommon. Physical properties of the diatom and of processed diatomite that provide unique commercial value in a broad spectrum of market end uses include ornate fine structure, low bulk density, high porosity, and high surface area. Properties of equal importance are mild abrasiveness, high absorptive capacity, insulating ability, relative inertness, high silica content, and high brightness. End use markets are diverse and range from insulating brick and absorbents through quality-sensitive filter aids and premium quality functional fillers.

Notwithstanding both the economic attractiveness of the specialty markets and the commercial versatility of the high-purity deposits, deposits of lesser purity are mined in many parts of the world for less demanding uses. Mining costs are minimized through open-pit quarrying, but in Europe, Asia, Africa, and South America, underground mining methods are also employed. Blasting is not required because diatomite is so soft and easily broken with mechanized equipment.

Following gentle crushing, the ore is dried, milled, and processed into one of three broad categories of products: natural (milled, not calcined), straight calcined, and flux calcined grades. Each of these principal categories is further subdivided into additional grades through particle-size adjustment of the powders. Agglomeration of particles, alteration of fine structure, and color change are achieved through calcination. The addition of flux before calcination further accentuates these changes.

The first industrial use of diatomite can be traced back some 2,000 years to the Greeks and to the use of diatomaceous earth in lightweight building brick and in ceramic pottery. It was not until the mid-1800s, however, that the unique properties of diatomite were first recognized and the market end uses investigated and developed. One of the most important of the early uses followed the development of dynamite by Alfred Nobel in the mid-1860s. Diatomite came to be used as a component of the explosive to improve stability and safety. Other early uses included low-temperature insulating and refractory bricks and as a component in fireproofing and insulating construction panels. During the 1920s, processing technology underwent a very rapid evolution with the development of calcination, flux calcination, and air classification technologies. Through these technologies, many different size and grade classifications could be made for the rapidly diversifying market applications and end uses.

Today, the application of processed diatomite for filter aid is the largest of the quality-sensitive end uses. Specific filtration uses include, among others, the clarification of beer, wine, and other liquors; vegetable oil; syrup and sugar; pharmaceuticals; motor oil; and swimming pool water. As a functional filler and extender, processed diatomite is ideally suited for use in paint, rubber, and plastic formulations. Other filler applications include uses as an antiblocking agent in plastic film, as an anticaking agent for fertilizer, as a thermal insulating material, as a catalyst carrier, in polishes and abrasives, as pesticides and fertilizer carriers, and for chromatographic supports. Throughout much of the world, diatomite is still used as a component of insulating brick and as an absorbent. Emerging applications include using diatomite as a natural grade insecticide and in the separation of fluid chemicals.

PRODUCTION, TRADE, AND RESOURCES

Production and Consumption Statistics

Estimates of world production vary by source, but including all quality grades, production in 1992 totaled in excess of 1.5 Mt. With the

Table 1. World production of diatomite, kt[†]

Country	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003 ^e
Algeria	3 ^{e,‡}	3 ^r	4 [‡]	4 ^e	2	2	3	3 ^e	3	3	3
Argentina	3	6	5	9 ^{e,‡}	7 ^r	25	34 ^r	18 ^r	28 ^r	23 ^r	20
Australia ^e	11	11	11	11	11	20	20	20	20	20	20
Brazil ^e	16	17	14 [‡]	14 [‡]	14	14	13 ^r	13 ^r	13 ^r	13 ^r	13
Canada ^{e,§}	10	10	NR	NR	NR	NR	NR	NR	NR	NR	NR
Chile	6	10	11	12	12	15	14	13	23	30 ^r	30
China	NR	230 ^{e,r,**}	250 ^{e,**}	300 ^e	330 ^e	335 ^e	340 ^e	350 ^e	350 ^e	370 ^e	380
Colombia ^e	4	4	4	4	4	4	4	4	4	4	4
Commonwealth of Independent States ^e											80
Costa Rica	7 ^r	7 ^e	7 ^e	2 ^{r,‡}	2	16 ^r	18	35	26	26	25
Czech Republic	39	40	29	35	42 ^r	35	37	34	83 ^r	28 ^r	30
Denmark ^{e,††,‡}	96	285 ^r	186 ^r	185	185	185	185	234 ^r	231 ^r	231 ^r	232
France ^e	85	90	80	85	80	80	80	75	75	75	75
Germany ^e	52 [‡]	52	50	0	0	0	0	0	0	0	0
Iceland ^e	19	25	28	26 [‡]	26 ^r	26	28	28	30 ^r	31 ^r	30
Iran ^{e,‡‡}	<½ [‡]	<½	<½	<½	<½	1	4 [‡]	5	5	5	5
Italy ^e	25	25	25	25	25	25	25	25	25	25	25
Japan ^e	NR	184	175	194 [‡]	194	190	190	190	180 ^r	80 ^r	180
Kenya	1	1	<½	<½	<½	<½	1 ^r	<½ ^r	<½ ^r	1 ^r	1
Korea	67	83	81	70	54	37	30	34	28	21 ^r	21
Macedonia ^e	5	5	5	5	5	5	5 ^r	5	5	5	5
Mexico	46	52	50	52	59	67	65	96	69	62 ^r	60
Peru ^e	35	35	35	35	35	35	35	35	35	35	35
Poland	2	3	2	2	1	2	1	1	1	1	1
Portugal ^e	2	2 ^r	2	2	2	2	2	2	2	2	2
Romania ^e	10	35	50	57	24	35 ^r	12	9	10 ^r	20 ^r	20
South Africa	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Soviet Union, former ^{e,§§}	150	120	110	100	90	80	80	80	80	80	NR
Spain ^{e,***}	38	36	45 ^r	34 [‡]	36	36	36	35	35	35	35
Thailand	8	6	6	2	<½	0	2	<½	1 ^r	1 ^r	1
United Kingdom ^e	<½ [‡]	<½	NR	NR	NR	NR	NR	NR	NR	NR	NR
United States ^{†††}	649 ^r	646	722 ^e	729 ^e	773	725	747	677	644	624	620
Yugoslavia	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR	NR
Total	1,390^r	2,020^r	1,990^r	1,990^r	2,010^r	2,000^r	2,010^r	2,020^r	2,010^r	1,950^r	1,950

Courtesy of U.S. Geological Survey and U.S. Bureau of Mines.

Abbreviations: e = estimated, r = revised, NR = not reported.

* World totals, U.S. data, and estimated data are rounded to no more than three significant digits; may not equal totals shown.

† Table includes data through April 4, 2004.

‡ Reported figure.

§ Includes unknown quantity of fuller's earth.

** May not include building and insulation brick estimated at 150,000 t (in 1995) to 200,000 t (in 1999).

†† Data represent "extracted molar," calculated as reported cubic meters times 1.5. Contains about 30% clay.

‡‡ Data are for Iranian years beginning March 21 of that stated.

§§ The Soviet Union was dissolved in December 1991, but information is inadequate for formulation of reliable estimates for individual countries.

*** Includes tripoli.

††† Sold or used by producers.

addition of Chinese figures, world production in the following decade ranged from 2.02 Mt in 1994 and 1999 to 1.95 Mt in 2003 (Taylor 1994; Antonides 1997; Dolley 1999–2003). Production trends are shown in Table 1. The average price per ton (Table 2), on a weighted basis by end use volume, rose from US\$ 219 in 1990 to a high of \$271 in 2001, followed by a drop to \$258 in 2003 (Taylor

1994; Antonides 1997; Dolley 1999–2003). The United States remains the dominant world producer, followed by China, Japan, Denmark, the former Soviet Union, France, and Mexico. According to the USGS, filter aids comprised 62% to 73% of the diatomite products sold or consumed in the United States during the past decade. Sales or consumption of fillers represented 11% to 17%;

Table 2. Price per metric ton of diatomite (weighted average)

Year	Average Value, US\$	Year	Average Value, US\$	Year	Average Value, US\$
1990	219	1995	238	2000	256
1991	229	1996	242	2001	271
1992	237	1997	244	2002	255
1993	251	1998	248	2003	258
1994	248	1999	238		

Courtesy of U.S. Geological Survey.

Table 3. Chemical composition of natural diatomites (oven-dried basis)

Constituent, %	EaglePicher, Lovelock, Nevada	EaglePicher, Vale, Oregon*	Lompoc, California†	Denmark (Moler)	Albacete, Spain†	Jalisco, Mexico†	Chile	Jilin, China
Silica (SiO ₂)	89.75	87.92	89.70	67.80	88.60	91.20	89.68	90.07
Alumina (Al ₂ O ₃)	3.08	3.66	3.72	10.30	0.62	3.20	2.18	1.98
Iron oxide (Fe ₂ O ₃)	1.33	1.37	1.09	6.85	0.20	0.70	0.38	0.67
Titanium oxide (TiO ₂)	0.14	0.29	0.10	1.21	0.05	0.16	0.05	0.09
Phosphate (P ₂ O ₅)	0.04	0.05	0.10	0.21	na	0.05	0.04	0.06
Lime CaO ()	0.41	0.52	0.30	1.35	3.00	0.19	0.41	0.39
Magnesium MgO ()	0.11	0.15	0.55	1.64	0.81	0.42	0.31	0.28
Sodium (Na ₂ O)	0.19	0.56	0.31	0.46	0.50	0.13	0.97	0.22
Potassium (K ₂ O)	0.22	0.13	0.41	1.47	0.39	0.24	0.45	0.35
Ignition loss	4.70	5.15	3.70	7.91	5.20	3.60	5.90	6.30
Total	99.97	99.80	99.98	99.20	99.37	99.89	100.37	100.41

na = not available.

* Courtesy of EaglePicher Filtration & Minerals, Inc.

† Source: Kadey 1983.

insulation 2% to 4%; and other uses, including absorbents, additives, abrasives, and admixtures, 9% to 25%. The total value of diatomite products sold or used in the United States reached \$159 million for 2002 (Dolley 2002).

World Reserves

The world resource base of diatomite (inclusive of all qualities, and irrespective of end use suitability and proximity to infrastructure/markets) is vast, and there should be no worldwide shortage in the foreseeable future.

GEOLOGY

Mineralogy, Composition, and Chemical Properties

Diatomite is a fine-grained siliceous sedimentary rock or unlithified sediment of biogenic origin. It is chiefly composed of amorphous silica, present in the form of opaline diatom skeletons or frustules. Kamatani (1971) noted that the silica of recent frustules resembles amorphous silica gel, whereas the composition of fossil frustules resembles an opaline silica that has a lower solubility than the silica of its recent counterparts. Combined water held within the opaline structure of frustules varies among species and is reported to range as high as 9.6 wt % in some lacustrine forms to as low as 1.9 wt % in specific marine species (Tappan 1980; Lisitsyn 1967). In addition to silica, which is the major component, alumina, iron, alkali metals, alkaline earths, and other minor components are present (Table 3).

The silica content (as SiO₂) of diatomite samples, as determined on an organic-free basis, typically ranges from 80% to 90%, but silica contents as high as 97% have been encountered. As

determined through oxide analysis, iron, calcium, aluminum, titanium, sodium, potassium, and other elements are typically present in minor amounts of several percent or less (Table 3). Many elements are present in trace amounts (Table 4). Codeposited and secondary minerals of ten found in diatomites include clays, quartz, gypsum, mica, calcite, and feldspars. Less commonly, saltpre, pyrite, sulfur, manganese nodules, and vivianite and other phosphates are present. Chert and volcanic ash are often abundant constituents of the sediment. Common biogenic constituents include the tests of ostracods and bivalves, the siliceous remains of sponges, silicoflagellates, radiolaria, carbonized fossil leaves, and fossilized fish bones.

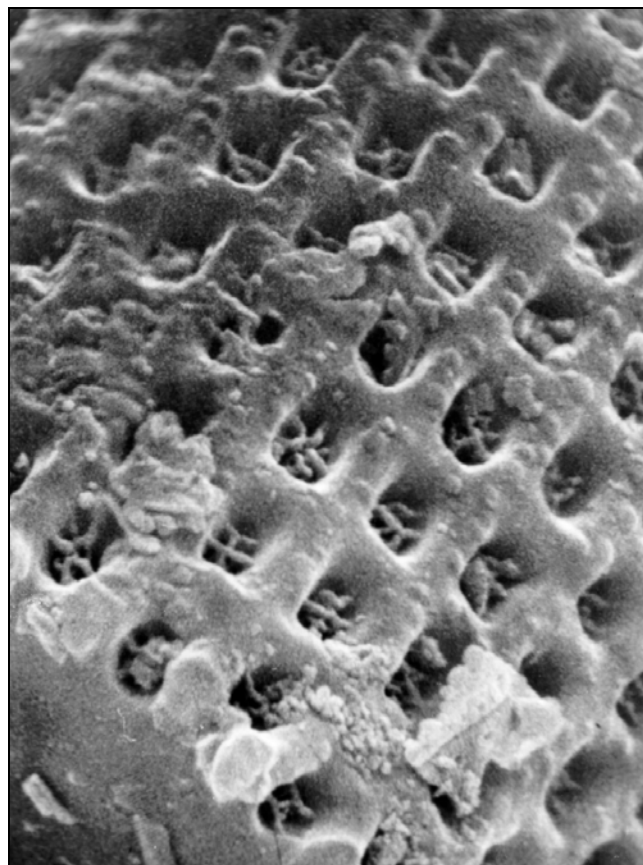
When chemical and mineral impurities are present in great abundance, alternative terminology is used to describe the sediment (e.g., sandy diatomite, clay-bearing diatomite, diatomaceous marl, and diatomaceous peat). These extraneous materials can affect the properties of the final product, including pH, the solubles present, density, and abrasiveness. In such cases, the ore's commercial suitability for some uses will be adversely affected, unless the contaminants can be removed or rendered insoluble through processing.

Thermal processing, or calcination, produces fundamental changes in the composition and nature of the opaline silica frustule. Within the trade, the term *calcination* has been loosely and incorrectly applied to the thermal processing of diatomite with or without the addition of a fluxing agent. Technically, the thermal treatment of diatomite is a sintering or agglomeration process achieved through incipient fusion. Calcination not only dehydrates the amorphous silica but initiates conversion of the opal to cristobalite. As much as 40% to 60% of the amorphous diatomaceous opal may be converted to cristobalite through flux calcination. As is discussed later, the

Table 4. Typical trace element analysis of EaglePicher Filtration & Minerals, Inc., Celatom FW-14 Product

Element	ppm	Element	ppm	Element	ppm	Element	ppm
Aluminum	>1,000	Fluorine	320	Neodymium	15	Sodium	>1,000
Antimony	3	Gadolinium	NR	Nickel	7	Strontium	84
Arsenic	5	Gallium	8	Niobium	<10	Sulfur	70
Barium	188	Germanium	<10	Osmium	NR	Tantalum	<1
Beryllium	2	Gold	<1	Palladium	<1	Tellurium	NR
Bismuth	<5	Hafnium	1	Phosphorus	320	Terbium	<1
Boron	40	Holmium	NR	Platinum	<1	Thallium	<2
Bromine	2	Indium	NR	Potassium	>1,000	Thorium	2
Cadmium	<1	Iodine	<1	Praseodymium	NR	Thulium	NR
Calcium	>1,000	Iridium	<1	Rhenium	NR	Tin	<1
Cerium	18	Iron	>1,000	Rhodium	<1	Titanium	>1,000
Cesium	8	Lanthanum	11	Rubidium	10	Tungsten	6
Chlorine	NR	Lead	<2	Ruthenium	<1	Uranium	3
Chromium	7	Lithium	6	Samarium	1	Vanadium	140
Cobalt	2	Lutetium	<1	Scandium	3	Ytterbium	<1
Copper	11	Magnesium	>1,000	Selenium	<3	Yttrium	10
Dysprosium	NR	Manganese	44	Silicon	>1,000	Zinc	32
Erbium	NR	Molybdenum	10	Silver	<1	Zirconium	58
Europium	0.5						

NR = not recorded.



Courtesy of EaglePicher Filtration & Minerals, Inc.

Figure 1. Scanning electron micrograph of an *Aulacosira* (previously *Melosira*) occurring in an EaglePicher Filtration & Minerals, Inc., deposit in Nevada

health issues related to the crystalline silica species present in diatomite products came under worldwide examination during the latter half of the 1980s, and health- and environment-related legislation was promulgated as a result. Other changes in physical properties that are induced through thermal processing are discussed in the sections that follow.

Morphology

The diatom is a member of a diverse group of single-celled, often colonial algae. The class is subdivided into two major groups: the Pennales forms have axial symmetry and the Centrales forms have radial symmetry. To date, more than 12,000 distinct species have been recognized (Tappan 1980).

Each cell possesses an internal, ornate siliceous skeleton consisting of two valves that fit together much like a pill box. The morphology of the frustules varies widely among species and serves as the basis for taxonomic classification. The surface of each valve is punctuated by a series of openings that comprise the complex fine structure of the frustule and impart a design that is distinctive to individual species (Figure 1). The size of the frustules ranges from 0.75 to 1,000 μm , large enough, as in the case of *Ellerbeckia teres* (previously *Melosira teres*) and some *Coscinodiscus* forms, to be visible with a hand lens. Most are in the range from 10 to 150 μm and require a microscope to be seen. The frustule of the living cell is covered by a jelly secreted by the algae and contains organelles typical of photosynthesizing plants.

Physical Properties

Low block density, typically ranging from 320 to 640 g/L, distinguishes diatomite from all other fine-grained sediments. High brightness, or whiteness, is an additional and distinctive attribute of nearly pure diatomites.

The fundamental chemical composition and intricate structure of the diatom frustule give diatomite unique commercial value and versatility in filtration and filler applications, unmatched by that of other natural forms of silica. Inherently, the fine particulate structure

of the diatom skeleton imparts low density and high surface area to milled powders. Ultimately, the fine structure also provides high porosity and permeability, along with the clarifying ability required in filtration applications. These same physical attributes impart high absorptive capability as well as low thermal conductivity. Although the skeletal structure is rigid and serves as an effective abrasive agent, the delicate particles tend to break and gently polish rather than scour. In filler and filtration applications that are sensitive to purity, diatomaceous silica remains relatively inert and lends only its physical properties. The melting point of diatomaceous silica ranges between 1,400° and 1,750°C.

Broad adjustment of physical properties is achieved through the thermal sintering process. Calcination reduces surface area by destroying the fine structure. Calcination and flux calcination progressively increase the specific gravity from 2.0 to 2.3; decrease the surface area of milled powders from ~10–30 m²/g to 0.5–5.0 m²/g; and increase the hardness of the silica from 4.5–5 to 5.5–6 (measured on the Mohs scale). The refractive index of natural powders ranges from 1.40 to 1.46 and increases to 1.49 through flux calcination.

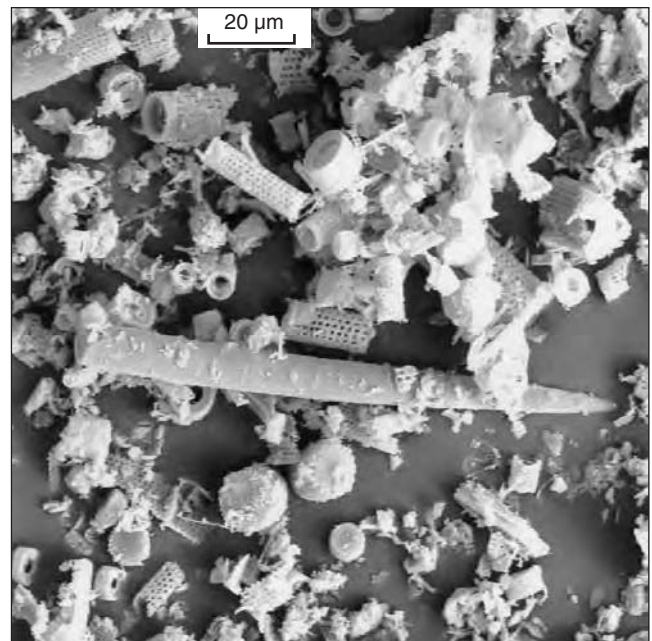
Origin

Diatoms thrive in diverse habitats including marine, brackish, and lacustrine/stream environments. In addition, diatoms live in moist soils and on the surfaces of rocks and vegetation (Bradbury 1988). Species are also reported in exotic and specialized environments such as caves, snow and ice, hot springs, and in relatively dry areas (Patrick and Reimer 1966; Bradbury 1988). Basic biological requirements include sufficient moisture; sufficient exposure to light; an adequate physiochemical environment; and the availability of nutrients, trace elements, and an abundant silica supply.

Within aquatic environments that provide the basic requirements, diverse communities of planktonic, attached, and benthic diatoms can flourish and contribute to the geologic sedimentary record. The species composition of a living diatom community and—eventually—the sedimentary fossil community, as well as the dominance of individual species within a population, can depend on environmental variables such as water chemistry, pH, nutrient abundance, turbidity, temperature, and water depth, among others. Although some species are quite tolerant of environmental variance, the presence or morphotype of others requires or depends on specific ecological conditions. Both long- and short-term changes in population composition, in response to environmental change through time, can be observed within individual deposits. Such changes can produce several distinct types of diatomite ore within individual deposits, and these distinctions are important to investigate because varying types of diatomite ore may exhibit different physical properties, and thus varying suitability for specific end use applications.

Ecological conditions vary widely among lakes, and consequently, corresponding diatom populations can exhibit wide variation. Far from being solely of academic interest, characteristic assemblages can, in some cases, be used to fingerprint or recognize individual deposits and sources of commercial products. Figures 2 through 5 show several distinctive assemblages. Moreover, recognition of assemblages and changes in diatom population can assist in identifying individual beds within a single deposit, yield a useful mapping/stratigraphic location tool in extensively covered or structurally complex deposits, and aid in delineating commercial-quality ore bodies.

Deposits of diatomite reflect stable environmental and depositional conditions, as well as an optimum preservation environment. Although depositional rates vary, typical average thicknesses observed in deposits suggest yearly accumulations of no more than



Courtesy of EaglePicher Filtration & Minerals, Inc.

Figure 2. Micrograph of lacustrine diatom assemblage from an EaglePicher Filtration & Minerals, Inc., deposit in Nevada



Courtesy of EaglePicher Filtration & Minerals, Inc.

Figure 3. Micrograph of lacustrine absorbent-grade diatom assemblage from an EaglePicher Filtration & Minerals, Inc., deposit in Nevada

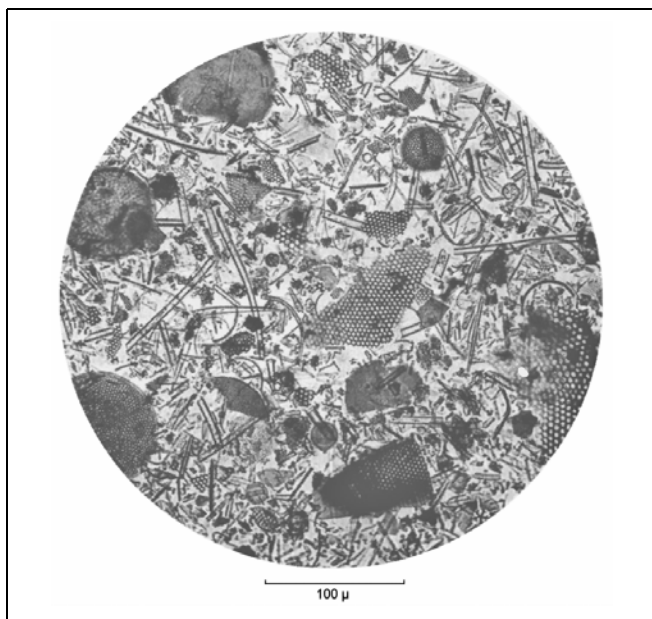


Figure 4. Micrograph of a marine diatom assemblage from Lompoc, California

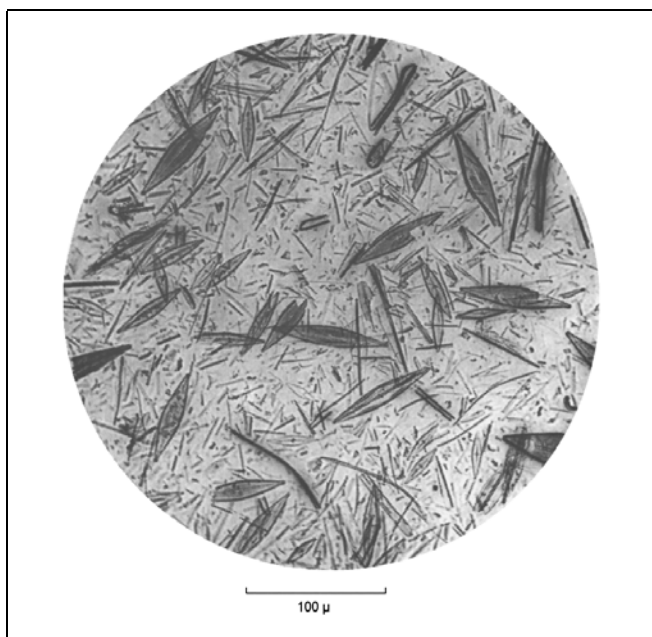


Figure 5. Micrograph of a bog diatom assemblage from Pernambuco, Brazil

several millimeters of compacted sediment. Strata of significant thickness and high purity, therefore, indicate prolonged environmental conditions that favored high diatom productivity and were free of continuous and significant clastic contribution or mineral precipitation. Geologic preservation of the soft sediments requires protection from erosion, such as that offered by overlying volcanic rocks. Preservation also demands that the diatomite not be subjected to geological conditions that promote silica dissolution or diagenetic conversion of opaline silica to chert, porcellanite, or

quartz, such as through deep burial and exposure to high temperature and alkaline groundwater. Figures 6 and 7 show the distribution of many of the well-known diatomite deposits.

Marine environments favorable for deposition of nearly pure diatomite exist in submerged coastal basin areas and shelves that are isolated from significant sources of clastic contribution and in areas adjacent to upwellings where waters are nutrient and silica rich and biologically productive. Such areas occur today along the coastlines of California, Peru, and southwest Africa (Soutar, Johnson, and Baumgartner 1981). Seawater rich in both nutrients and silica has been found to contain as many as 1 million diatom cells per milliliter (Tappan 1980), and diatomites such as those in the Monterey Formation of California have been seen to contain as many as 1.28×10^6 frustules per cubic centimeter (Barron 1987).

Tertiary marine deposits are commonly found along uplifted Pacific Rim coastlines and are associated with interbeds of volcanic ash, clay, and clastic sediments. Thick marine deposits occur in the Monterey Shales and Sisquoc Formation in Santa Barbara and Kern counties in California; in the Miocene Tortugas Formation of Baja, Mexico; in the Miocene Pisco and Zapayal Formations along the Peruvian coast; and in the Miocene Funakawa Formation of northern Japan. Other marine diatomites and diatomaceous sediments occur in the Paleocene-Eocene Fur (Moler) Formation of Denmark; in Oligocene-Miocene sediments in Poland; in the Miocene Tellian Group (Beida Stage) of Algeria; in the Miocene Calvert Formation of Maryland and Virginia in the United States; and within Tertiary sediments in Spain, South Korea, Chile, New Zealand, and Java.

Lacustrine environments typically exhibit greater variability than marine environments in terms of pH, salinity, temperature, and nutrient content, but they can produce diatomite sections that are often tens of meters or more in thickness. Deposits commonly occur in Miocene to Recent volcanic environments and are associated or interbedded with volcanic rocks and sediments. This association is clearly demonstrated by deposits within the lake sediments of caldera moats, such as in the Trout Creek Mountains of Oregon; in lava-dammed rivers (e.g., Terrebonne, Oregon, and in the subsiding valleys of the Nevada basin and range); and within the lake sediments of volcanic maars in France. In many countries, including the United States, Brazil, Australia, and the Philippines, bog or shallow-pond deposits are found in Holocene to Recent nonvolcanic, marshy lowland terrains.

The thick diatom accumulations that are common in Tertiary sediments reflect the exceptional availability of silica from external sources such as runoff, groundwater seepage, and hot or cold springs, as well as from the internal regeneration of silica released from bottom sediments (Hurley et al. 1985). Groundwater that has percolated through silica-rich volcanic rocks and sediments undoubtedly supplies much of the required silica.

Distribution of Deposits

Diatomite deposits of both marine and lacustrine origin are commercially mined throughout the world. Although deposits occur commonly in Tertiary to Recent sediment facies, high-purity deposits suitable for versatile quality-sensitive products are uncommon. It should be noted that classification as high or low grade is dependent on the performance required by the ultimate application, not solely on purity. For example, although low-purity diatomite is unsuitable as a filter aid, it can make a high-quality absorbent.

Although marine deposits account for much of the worldwide production, mining activities at lacustrine deposits are far more numerous. In the United States, diatomite is mined in California, Nevada, Oregon, and Washington. In Canada, impure diatomite is



Figure 6. Diatomite deposits and processing plants in North and South America

mined in British Columbia. Information about foreign producers and production is often lacking or available only as estimates. Notable mining operations in Europe are in France, Denmark, and Spain; as well as in Iceland. Substantial production is reported for the former Soviet republics and the Czech Republic, but little specific information is available about mines and production facilities. African production is reported for Algeria and Kenya. Historically, the U.S. Bureau of Mines reported mining in Morocco. In Asia, mining operations are known in Japan, South Korea, and China. Farther south, production is reported in Australia and New Zealand. In Latin America, Mexico leads production, followed by Peru, Argentina, Costa Rica, Chile, Brazil, and Colombia.

North America

North American production is dominated by the United States where at least five companies operate at 10 locations in four western states. Since 1990, the industry has experienced notable changes in ownership, closure of two operations, the startup of a new operation, and the reopening of an operation that had ceased production. These include the divestiture of Manville Corporation's diatomite operations to Celite Corporation, a subsidiary of World Minerals; Celite's acquisition of CR Minerals' operation in Nevada; the closure of Grefco's Lompoc operations; the closure of the Oil-Dri Corporation facility in Oregon and its 2003 acquisition of operations at Taft, California; the development of high-brightness natural grade diatomites by DiaSource in Oregon for insecticides, fillers, coatings, and the control of pitch in paper manufacturing; and the 2002 attempt by the Atlas Minerals subsidiary Whitecliffs to reopen an operation in Arizona for filler specialty markets such as calcium silicates, asphalt, extenders, and insecticides. At the time of publication, Alleghany



Figure 7. Diatomite deposits and processing plants in Africa, Asia, and Oceania



Courtesy of EaglePicher Filtration & Minerals, Inc.

Figure 8. View showing portion of one of EaglePicher Filtration & Minerals, Inc.'s diatomite quarries at Lovelock, Nevada

Corporation announced it had signed a definitive agreement to sell World Minerals Inc. to Imerys USA, Inc.

In 2002, Nevada became the major producing state in North America. Mines in Nevada include those operated by EaglePicher Filtration & Minerals, Inc., at Clark Station, Lovelock (Figure 8), and near Fernley and Brady; the Grefco operation at Basalt; the Celite Fernley quarries and mill (previously owned by CR Minerals); and the Molten Company facility constructed during 1987 north of Fernley. Until 2002, California was the major producing state with the majority of production sited near Lompoc in Santa Barbara County. The operations at Lompoc consist of the mines and mills owned by Celite Corporation. The marine diatomite at Lompoc is approximately 300 m thick and is the largest center of production in the world. Other operations in California include Grefco's facility in Shasta County, constructed near Lake Britton during 1985 and 1986, and the Oil-Dri Corporation facility that



Courtesy of EaglePicher Filtration & Minerals, Inc.

Figure 9. View of EaglePicher Filtration & Minerals, Inc., quarry at Vale, Oregon



Courtesy of EaglePicher Filtration & Minerals, Inc.

Figure 10. View of EaglePicher Filtration & Minerals, Inc., processing plant at Vale, Oregon

mines lithified diatomaceous earth near Taft for the manufacture of cat litter, pesticide carriers, and oil absorbents.

During 1986, EaglePicher Filtration & Minerals completed construction of the Vale, Oregon, facility (Figures 9 and 10) in Malheur County. Oil-Dri Corporation has reported ending its production of absorbents and agricultural grades of diatomite in Lake County, Oregon. The Celite Corporation operates several mines and plants that produce flux calcined filter aids at Quincy in Grant County in Washington State.

Well-known deposits occur throughout the western states in many of the Tertiary formations that contain lacustrine facies. Deposits have been known for many years in the Truckee, Desert Peak, Carlin, Esmeralda, and Panaca formations of Nevada; within the Juntura, Drewsey, and Trout Creek formations of Oregon; and in the Quincy and Squaw Creek portions of the Yakima Basalt Subgroup in Washington. Diatomites and diatomaceous sediments are also present in the Banbury Basalt and Idaho Formation in Idaho, near Dorris and Lake Britton in northern California, and

within the Quaternary age basin sediments in Utah. Along the U.S. East Coast, bog-type deposits have been identified in New Hampshire, New York, and Florida.

Production in Canada has historically centered on bog-type deposits in Nova Scotia, and more recently on the lacustrine diatomites at Kamloops in British Columbia. The production in Nova Scotia has ceased. Because of the elevated clay and contaminant content of the British Columbia deposit, production has been directed toward manufacture of absorbents, fillers, carriers, and refractory/insulation bricks.

Celite Mexico is the largest of the Latin American producers, with mines and processing facilities near Guadalupe in Jalisco State in Mexico and in Chile. In Mexico, numerous other lacustrine deposits occur in the states of Mexico, Michoacan, and Tlaxcala. Extensive, although impure, marine diatomite deposits crop out for many kilometers along the Baja coast.

South and Central America

Diatomite deposits in Brazil occur along the East Coast in the states of Ceara, Rio Grande do Norte, Bahia, Pernambuco, Santa Catarina, and Sao Paulo. Without exception, the deposits are accumulations in bogs or shallow ponds that contain abundant organic matter that must be burned out through an ignition process. In the past, organic matter was removed in stationary, wood-fired kilns located at or near the deposit. Size classification and/or flux calcination was then used to further process the organic-free diatomite into fillers and filter aids.

Commercial production continues to be reported in Argentina. Historically, lacustrine deposits have been mined in Neuquen, La Rioja, and Rio Negro provinces. Deposits are also known in Catamarca, Chubut, Salta, and Jujuy provinces.

Production in Chile centers on the numerous lacustrine deposits, typically contaminated by salt, near Arica in the northernmost part of the country. Celite acquired these operations in the past decade. Other lacustrine deposits occur throughout Chile from the northern province of Tarapaca south to the province of Chiloe. Marine ores were previously mined near La Serena, 400 km north of Santiago.

Elsewhere in Latin America, production is reported for Peru and has been reported at the Laguna de la Herrera deposit in Colombia. In Peru, numerous lacustrine and marine occurrences are found along the West Coast and in the western Andes. The most notable of these are the marine deposits near Pisco and the marine phosphate-bearing sediments at Bayovar. Undeveloped lacustrine deposits occur to the south of Quito, Ecuador, and at Lake Brava in Venezuela.

Europe

Deposits in France, the former Soviet republics, and the Czech Republic are the most significant of the European diatomite sources. Although production rates are significant, fundamentally different products may be made from the material mined at the various locations. Production in France focuses on premium quality filter aid and filler. Historically, production from the former Soviet republics has been reported to focus on the construction and refractory product industries. Spain and Iceland are also major producers of filter aid and filler. Denmark is the largest producer of moler earth, a diatomite-clay mixture used in the manufacture of insulating brick, absorbents, carriers, and a variety of powders and granules.

Tertiary lacustrine deposits occur throughout the Massif Central of France. Carbonisation et Charbons Actifs SA (CECA), a subsidiary of Atofina, has operations at Murat and to the south near

Privas at St. Bauzile. Celite Corporation mines this same deposit at Murat as a source for filter aids and fillers. The largest of the Spanish mines is operated by the Celite Corporation near Elche de la Sierra. Although carbonate-bearing, the lacustrine ores are bright and produce a broad spectrum of quality filler products. Marine diatomites crop out near the coast in the south of Spain.

Germany was the first country to commercially produce diatomite, although production reportedly ceased during the past decade in the Luneburg Heath Area of Lower Saxony. Other deposits also occur in the Klieken Area and in the Vogelsberg Mountain area of Bavaria. In Italy, lacustrine diatomites have been mined in the Viterbo District.

In northern Iceland, a joint venture between the Icelandic government and the Celite Corporation employs dredging methods to extract the diatomaceous muds that lie beneath Lake Myvatn. From the dredging barge, the muds are pumped as a slurry to landside hydrocyclones where unwanted volcanic ash and other contaminants are removed, and then on to settling ponds. Geothermal steam is used to dewater and dry the resulting crude ore before calcination or flux calcination.

Marine moller earth is mined on the isles of Mors and Fur in Denmark. The crude ore contains up to 30% plastic clay, precluding its use for the production of filter aids. Some lacustrine diatomite has been mined in Portugal at Couto Mineiro de Jardim, but production is minor. Another deposit is located near Rio Maior.

Although production is reported for Romania, the Czech Republic, and the former Soviet republics, little information is available about deposits and processing facilities. Reserves of marine and lacustrine diatomite in the former Soviet republics are believed to be large and to occur in the central Volga region, in Georgia, the Ukraine, Armenia, and in the St. Petersburg area. Mining in Romania has historically been at Adam Clisi, Pătrăcele-Buzău, and at Minis Arad. In Hungary, lacustrine diatomite has been mined at Erdőbénye. Diatomite mining in Yugoslavia has centered on the Prilep and Križva Palanka deposits. Impure marine deposits occur in southeast Poland. Diatomite has also been mined in Bulgaria near Gurmen in the Blagoevgrad District.

Africa

Deposits of marine diatomite occur in Algeria at Sig and at Mostaganem. The Sig diatomite, which is characterized by elevated carbonate content, has been mined by Societe des Diatomites d'Algerie using underground methods. Numerous lacustrine deposits are found in the Kenyan Rift Valley. Although most of the deposits are poorly known or not commercially significant, African Diatomite Industries Ltd. has mined the diatomites at Soysambu and Kariandusi. Small lacustrine deposits occur at several locations in South Africa. During the 1980s, annual production was reported from the Witdraai deposit in the northern part of Cape Province. Lacustrine diatomite has been mined in Morocco at Awinat. Elsewhere in Africa, impure lacustrine deposits are known in Angola; Djibouti; central Ethiopia; Nigeria; Zimbabwe; and within a coastal belt in Mozambique.

Asia and Oceania

Until the past decade, the annual production rates for China and Japan were available only as rough estimates. Both countries, however, now report significant production and are respectively ranked second and third largest in world production.

China is reported to have more than 50 diatomite occurrences located in 14 provinces (Crossley 2000) and to have 34 mines, with major mines located in Inner Mongolia and in Hebei, Jilin, Zhejiang, Sichuan, and Yunnan provinces (Fu Taizhi, personal commu-

nication). The largest and most commercially significant of the high-purity-deposit areas in China occur in Jilin Province near the border with North Korea. Deposits in this area have been jointly commercialized with Celite Corporation. The lacustrine diatomites are extensive and must generally be mined by underground methods. Many other, lesser-known lacustrine deposits occur in Jilin as well as in Heilongjiang Province. Vast reserves of clay-bearing lacustrine diatomite are present in Zhejiang Province and scattered throughout southwestern Yunnan Province.

In Japan, more than 70 lacustrine and marine deposits occur on the islands of Honshu, Hokkaido, and Kyushu. Hakusan Industry, Isoraito Mining, Nittetsu Mining, Sakamoto Mining, and Showakagaku are major producers in Japan (Crossley 2000). All production in the country is controlled by Japanese companies.

Both marine and lacustrine deposits occur in southeastern South Korea. Filter aids, fillers, and other grades have historically been produced at facilities located near Pohang. Although no production is reported for the Philippines, bog-type lacustrine deposits are present. Impure, clay-bearing lacustrine diatomite occurs in Vietnam and in Thailand. The deposits in Vietnam are reportedly being examined for development. Deposits are also known in Indonesia.

In Turkey, numerous deposits of lacustrine diatomite occur in the central portion of the country. Elsewhere, Kamal Abad reportedly produces diatomite in Iran.

Mining of lacustrine deposits in Australia has been undertaken in New South Wales, Victoria, Queensland, and Western Australia. Marine and lacustrine diatomite occur on the North and South islands of New Zealand, but only small-scale production has been reported at several of the deposits.

TECHNOLOGY

Exploration and Evaluation

Exploring and evaluating deposits requires that geology, mining feasibility, and processing feasibility be integrated with the determination of the ore's suitability for the products desired to meet market needs. During the course of these studies, the fundamental elements of an evaluation program must include identification of ore strata and determination of strata mineability (i.e., number, thickness, areal continuity, to mine potential, and the degree of mining selectivity required). In addition, processing requirements—such as the equipment required and the process flow, the determination of economic marketability, and an assessment of logistics, including proximity to utilities, transportation, and work force—must be determined. A basic understanding of these elements will benefit the geologist in designing, guiding, and interpreting the sampling program. There are many diatomite deposits in the world but very few that are of high purity with commercial value. As a high priority, the suitability of the diatomite for product/market end uses must be determined.

Deposits of diatomite occur in Tertiary marine and lacustrine sedimentary facies throughout the world, and many such facies are well described in geologic literature. Aerial photographs can be reviewed to augment study of the literature when selecting target areas. After a promising target is identified, a sequence of sampling programs is initiated. A typical exploration program consists of several sampling phases that may lead to the eventual determination of measured resources or proven reserves. The sampling phases, which are punctuated by go-no-go decisions to proceed, would be followed by development and quality assurance sampling immediately before and after the commercialization of the deposit.

Initially, very widely spaced surface samples are collected and used to determine the general quality of the exposed diatomites, the

quality variations across the deposit and between individual beds, and the tonnage potential. This also permits areas that warrant priority investigation to be identified. During this phase, representative samples are collected from well-exposed outcrops or shallow trenches that have been excavated to adequately expose the near-surface beds. In conjunction with surface mapping, sample testing results and data from microscopic examination of the stratigraphic sequence can be used to direct continued effort.

If the initial sampling, sample test results, and mapping results are encouraging, phases of progressively closer spaced sampling can be considered. Unless the sediments are naturally well exposed, subsurface potential must be determined by drilling or by excavating shaft-like pits. Geophysical prospecting techniques such as very-low-frequency electromagnetic (VLF-EM) and seismic methods are unable to directly distinguish diatomite from other sediments, but they may permit the rapid, if indirect, interpretation of subsurface geology. Consequently, geophysical methods can be used in conjunction with surface data to guide the selection of priority targets and the location of drilling sites.

Final sample spacing is dependent on the continuity of the beds and the quality variations that are observed. To permit pit design and mine planning, a final spacing pattern of less than 50 m to as much as 100 m is generally used. During core drilling, care must be taken to avoid contaminating the core with drilling fluids, and the core diameter must be large enough to ensure high recovery. BQ (36.5 mm) or NQ (47.6 mm) diameter coring using triple tube wireline usually minimizes drilling problems and yields sufficient sample for testing.

If the results of sample tests indicate commercial-grade ore, and mining is determined to be feasible, bulk samples are collected to determine plant-scale performance. Other special samples may be required before mining begins. Even though this is the final phase of exploration sampling, pit-face quality assurance sampling must be undertaken during active mining.

Specialized sampling techniques can be employed when drilling is unnecessary. Where crude ores are soft and less than 5 m thick, hand augering with extension rods is effective, although the auger bucket must be emptied frequently and the cuttings laid out carefully for sampling. Mechanized augering works well in soft, wet diatomite. For sampling muds and oozes, augering can be done with a peat bog sampler.

The goal of optimum sampling is to delineate potential ore strata of uniform or nearly uniform quality. This includes determining the suitability of the ores for product application as well as the delineation of waste strata. Program design thus requires that critical specifications and product/market requirements be identified. Integrating these factors within sampling programs permits the program to be guided through the recognition of critical variations in ore quality. Appropriate qualitative yardsticks must be selected to judge results relative to industrial and health standards as well as to competitive commercial products. Because ore quality can vary between strata in a deposit, or across a deposit within a single stratum, sampling intervals and methods must be selected to maximize recognition of quality variation and to avoid sample bias.

Specialized testing of ore samples and of prepared test product samples is undertaken to examine the suitability and performance of an ore for specific product applications. Testing of physical properties and milling performance can include the determination of lab-scale milling recovery, density of dry milled powder, wet density, particle-size distribution, brightness, flow rate, clarity of filtrate, surface area, abrasiveness, Hegman value, and other properties related to specific market applications. Other testing examines chemistry and composition, including major and minor oxides, trace elements,

heavy metals and toxic compounds, pH, soluble substances, and the determination of crystalline silica content. In addition, many countries require products that contact food and beverages to pass stringent Food Chemicals Codex specifications.

Mining, Milling, and Thermal Processing

Mining Methods

Throughout most of the world, the lower cost of and higher recovery from open-pit quarrying relative to underground mining encourages operators to use surface mining methods. Where the diatomite sequence is thick, benches from 1.5 to 15 m in height are developed. Benching not only facilitates the removal of ore and waste but also permits immediate access to many ore layers and provides the opportunity to blend layers with differing characteristics. Notable exceptions are underground mines in Europe, South America, and Asia, and the dredging operation at Lake Myvatn, Iceland.

Prior to mining, the ore strata are carefully identified in the quarry faces through sampling and evaluation programs that determine and confirm the suitability of each individual stratum. The ore-grade strata can then be rated by quality and carefully segregated from the lower quality waste units using mechanized equipment. Because diatomite is a soft, easily broken sediment, ores are typically dozer ripped or broken from the face by power shovel. Blasting of the ores is neither needed nor possible because of the inherent softness of commercial quality diatomite, its porosity, and its absorptive nature. The broken material is loaded by front-end loader or belt loader into haul trucks for transport to either the crude storage area or the waste piles.

Typically, the moisture content of unprocessed ore ranges from 30% to 60%. Where the climate is favorable for solar drying, significant cost savings can be achieved by reducing moisture before milling. Crude grades may be blended or used separately depending on the final application.

Milling Methods

The objectives of milling are twofold: to disaggregate the crude ore into individual diatoms while preserving the delicate diatom structure, and to remove as much nondiatomaceous contamination as possible. Ore is gently crushed in spike rolls and hammer mills to reduce feed size to approximately -1.27 cm. The crushed feed is then conveyed by heated air into milling fans and simultaneously milled and partially dried. Secondary milling and drying further reduces the moisture content. The dried material is sized by a series of air separators and cyclones, the oversize recycled, and the coarse waste removed. Without further processing, the sequential milled products consist of coarse fractions that may be used for filter aids and finer fractions that are sold as filler grades.

Thermal Processing Methods

Diatomite is thermally processed, or calcined, to achieve fundamental adjustment of particle structure and particle-size distribution. Calcination in a rotary kiln, with or without the addition of a fluxing agent, removes organic matter and reduces the percentage of fine structure through incipient fusion, thereby reducing surface area through the loss of fine structure (Figures 11 and 12). Average particle size is increased through sintering or agglomerating the individual diatoms and fragments. After additional air classification, the coarser fractions or cyclone products are collected for use as filter aids. The finer baghouse products are used as fillers. Permeability and flowthrough rate of the powders used for filtering are thus increased and a more diverse spectrum of products is made possible

through additional milling and classification. Calcination produces a color change as well as the modification of other properties described previously.

Diatomite is calcined without adding a fluxing agent at temperatures that range from 870° to 1,100°C to produce pink or off-white straight calcined product grades. The straight calcined grades of filter aid exhibit flow rates faster than the natural grades but achieve lower filtrate clarity.

Calcination at temperatures up to 1,200°C with a fluxing agent added produces white-colored product and further increases the flow rate of the coarse fraction filter aid grades. The fine fraction recovered from the baghouse is sold as white fillers. In the United States, soda ash (sodium carbonate) is used as the fluxing agent. Historically, sodium chloride has been used as a fluxing agent elsewhere in the world. Temperature, amount of flux used, and retention time in the kiln are used to control the particle-size distribution. In general, fluxing agent is added at 3 wt % to 7 wt % of the feed.

In the manufacture of calcined absorbents, diatomite ores are crushed to -1.27 cm, the fines removed, and the coarse fraction calcined at temperatures lower than those employed for calcinations of filter aids. The product is then crushed and screened.

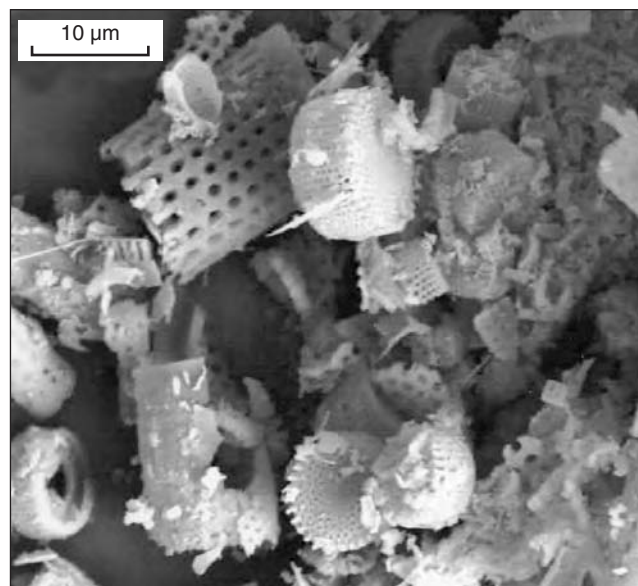
Testing and Specifications

The factors that affect the ultimate properties of processed diatomite products are complex and interrelated; they include the fundamental composition and nature of the diatomite crude ore as well as each of the handling and processing steps that follow mining. Thus, the quality of mill and kiln production can vary, and the implementation of quality and process control procedures is required to ensure that uniform products of acceptable quality are produced.

Control of the manufacturing process can be achieved by the periodic testing of in-stream and finished-product samples and consequently adjusting processing variables such as kiln temperature, flux addition, fines removal, and crude blends. Laboratory testing of samples also permits product performance to be quantified and commercial acceptability to be confirmed. By using standardized testing methods, the commercial quality of a product sample can be judged relative to commercially accepted application-specific specifications and to the performance of standard samples. Stringent product specifications must be established, tested for, and met for each end-product grade.

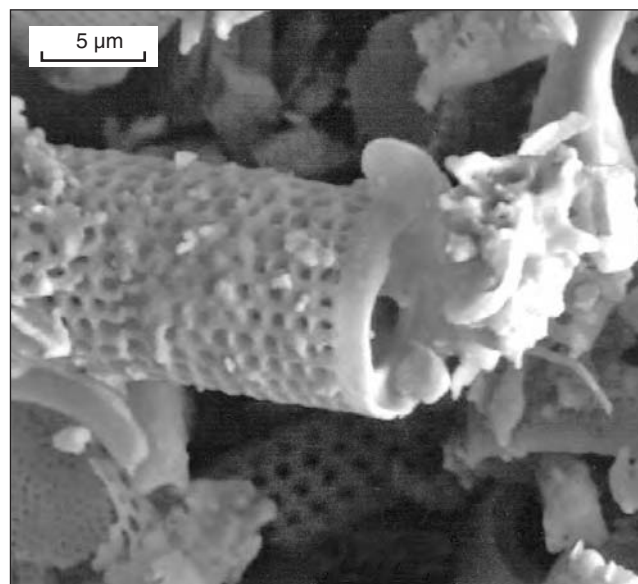
In filtration applications where filter aids must achieve satisfactory clarity at a reasonable flow rate, the flow rate and clarity performance of a filter aid sample can be tested under controlled laboratory conditions and measured directly. Because diatomite is purchased on a weight basis and used by volume, wet cake density must also be determined. The particle- and pore-size distributions, which reflect the ability to trap suspended particles, are also directly measured, as well as are the pH and resistivity of the powder. These latter tests indicate the presence of soluble substances that can affect the quality of the filtrate. Trace element analysis using Food Chemicals Codex methods and limits must also be conducted on food-, beverage-, or cosmetic-related products. With the advent of health-related labeling requirements, the abundance of free crystalline silica is routinely determined to ensure compliance with all regulations. Brightness is tested using the methods of the Technical Association of the Pulp and Paper Industry (TAPPI) or the General Electric Company to determine the whiteness of a product relative to a magnesium oxide or barium sulfate standard. Although brightness is only of aesthetic value for filter aids, the whiteness has great importance for many filler applications.

Samples of functional filler products are typically tested for density, TAPPI brightness, and particle-size distribution. Additional



Courtesy of EaglePicher Filtration & Minerals, Inc.

Figure 11. Fine structure in EaglePicher Filtration & Minerals, Inc., processed natural grade filter aid



Courtesy of EaglePicher Filtration & Minerals, Inc.

Figure 12. EaglePicher Filtration & Minerals, Inc., flux calcined filter aid showing the reduction of fine-structure resulting from thermal processing

testing for paint application can include the determination of Hegman value or fineness, and the liquid vehicle demand expressed as oil or water absorption. The abrasiveness of the product for paper applications can also be measured using the Valley Iron method.

Nearly all applications have their own unique requirements, formalized specifications, or both. As a result, testing methods have been developed for predicting the suitability of products. Evaluation can often be achieved using simple, improvised testing procedures

through which small samples of product are made and pertinent characteristics of the final product can be compared to accepted industrial norms. Similarly, comparison can be made between the performance of traditional materials used in a product formulation and the performance of potential substitutes.

The following test procedures and specifications are available through the American Society for Testing and Materials (ASTM), the U.S. military, and the agencies or governments of other countries:

- ASTM D686-93. *Standard Test Methods of Qualitative Examination of Mineral Filler and Mineral Coating of Paper*
- A-A-59239 NOT 1. U.S. Military Specification, *Diatomaceous Earth*
- BS EN 12913. British Standard. *Products Used for Treatment of Water Intended for Human Consumption: Powdered Diatomaceous Earth*

MARKETING

Worldwide, the production of diatomite is reported for at least 29 countries. Seven countries and a few producers dominate world production. The major producers achieve distinct marketing advantage in the domestic and export marketplaces by offering the customer integrated technical and sales assistance. The ability to provide such services relies largely on technical knowledge of the customer's process and product needs as well as on the ability to deliver a broad spectrum of application-specific products. Related services include supplying reliably available products through well-developed distribution systems and worldwide marketing presence, and furnishing product development and technical support from research and development organizations. Throughout the world, the large producers have established trade or brand names that are synonymous with reliable quality. Many smaller producers compete successfully with the larger manufacturers by supplying local niche markets at lower prices. Commonly, these smaller producers supply local market requirements for which demanding quality specifications and technical sales service are not required.

Uses, Grades, and Specifications

The unique physical properties of the diatom make diatomite and processed diatomite powders suitable for wide-ranging industrial applications. Early uses of diatomite blocks and powders focused on absorption, abrasion, and insulation applications, but the use of diatomite as a filter aid in the mechanical separation of suspended solids from fluids now surpasses all other specialty applications in terms of tonnage. Notwithstanding the importance of filter aid uses, specialty functional fillers and diatomite-based synthetic silicates supply significant markets. Insulation, granulated or powdered absorbent, and agricultural and construction grades continue to serve high-volume markets that can utilize more highly contaminated diatomite that is unsuitable for filtration purposes. Use of diatomite in fluid chemical separation, in natural insecticides, and in granular soil amendments are applications where growth is anticipated.

Worldwide statistics on usage are generally unavailable. Some 1993 estimates suggest filter aids represented 45 % of worldwide consumption, including molar, and that more than 25% was used as filler, 17% for insulation, and roughly 11% for absorption and other applications (Roskill Information Services Ltd. 1994).

Filtration

According to the USGS, 68% of the diatomite produced, sold, or used in the United States in 2003 was for filter aid (Dolley 2003).

The physical and chemical properties required of filter aid-quality diatomite are demanding and must ensure the clearest possible filtrate, a high flow rate of fluid through the filter cake, and a long cycle duration before the filter cake must be replaced. Optimum permeability and flow rate–clarity characteristics of the filter cake are achieved by careful control of the particle-size distribution and porosity of the filter aid cake. These properties are controlled and adjusted through thermal sintering and particle-size classification to produce a broad spectrum of filter aid products and filtering characteristics. Table 5 lists the properties of a range of products. As a rule of thumb, the ability to remove small particles from a fluid decreases as the permeability of the filter cake increases. In general, natural products exhibit slower flow rates but achieve the greatest clarity. Straight calcined and flux calcined products, respectively, exhibit faster flow rate and lower clarity than the natural products. For special applications, diatomite is mixed with cellulose fiber and can be surface treated and acid washed.

The proper grade of filter aid is selected based on the minimum size of the suspended particle that must be removed and on the clarity of the final filtrate that must be achieved. The optimum grade will provide the fastest flow rate while achieving acceptable filtrate clarity. Several filtration steps, each utilizing a specific grade of filter aid, may be required. Nearly neutral pH and low solubles content of the filter aid powder are necessary to ensure that the filter cake is chemically inert and the final filtrate is high in purity.

Diatomite filter aids are used in a wide variety of food and nonfood filtration applications. Brewing, sugars, fats and oils, wines, pharmaceuticals, and fruit juices represent several of the largest food-contact applications. Major industrial end users include the petroleum industry, inorganic and organic chemical manufacturers, the nonferrous metals industry, and industrial wastewater treatment operations. Swimming-pool water filtration is a major consumer market end use.

Fillers

As a class of products, fillers can be divided into the two general categories of nonfunctional and functional, depending on the role that the additive plays in the ultimate performance of the final product. Nonfunctional fillers are used as bulking agents and as cost-reducing agents and extenders. Functional fillers are working additives that alter and enhance the properties of the final product; they may also improve the manufacturing process itself by conditioning the ingredients. The physical properties of functional fillers are tailored to meet the needs of individual applications, and thus must be tightly controlled to meet the rigorous requirements of each end use. Many of the functional fillers command a high sales price.

Most diatomite manufacturers produce filler application grades from baghouse fines. Historically, filler products were developed from the fines derived from filter aid production. Today, the filler applications are highly demanding and filler products must meet rigorous specifications and physical property requirements, and a broad spectrum of natural, calcined, and flux calcined grades are made to meet the needs of diverse end uses. Ideally, filler grades are insoluble and inert in most chemical processes, exhibit low bulk density while maintaining small particle size, and provide suitable particle shape and size distribution. The particle size of functional fillers generally ranges from 1 to 50 μm . Many other properties may be relevant for specific applications, such as color, surface area, liquid absorption capability, abrasiveness, particle rigidity, high melting point, and

Table 5. Typical physical properties* of some EaglePicher Filtration & Minerals, Inc., commercial filter aids

Grade†	Color	Bulk Density, pcf		Screen Analysis % Retained, 150 mesh	pH	Median Particle Size, μm	Permeability, d'Arcy	Typical Filtration Applications
		Dry	Wet					
Natural								
Celatom FN-1	Buff	12	24	0.2	7.0	13.0	0.035	Polishing beer, wine, gelatin, manufacture of filter pads
Celatom FN-2	Buff	14	21	1.1	7.0	16	0.060	
Celatom FN-6	Buff	12	26	0.1	7.0	12	0.020	
Calcined								
Celatom FP-1SL	Buff/pink	12	25	0.5	6.8	12.5	0.07	Polishing beer, fats, oils, citric acid, vinegar, primary filtration of beer
Celatom FP-2	Buff/pink	12	25	1.2	6.8	12.8	0.12	
Celatom FP-4	Buff/pink	12	23	4.3	6.8	15.0	0.35	
Celatom FP-6	Buff/pink	12	23	5.8	6.8	19.0	0.45	
Celatom FP-12	Buff/pink	12	23	11.4	6.8	24.0	1.00	
Flux calcined								
Celatom FW-14	White	14	20	7.7	9.5	28.0	1.3	Primary filtration of acids, fruit juice, solvents, wine, plating solutions, potable water, corn products
Celatom FW-20	White	14	20	11.0	10.0	33.0	2.1	
Celatom FW-40	White	15	20	21.0	10.0	40.0	3.2	
Celatom FW-60	White	15	19	24.7	10.0	48.0	4.8	
Celatom FW-80	White	16	19	46.5	10.0	77.0	10.0	

Courtesy of EaglePicher Filtration & Minerals, Inc.

* English units used where appropriate.

† Brands listed are from EaglePicher Filtration & Minerals, Inc. Celatom is a registered trademark.

Table 6. Typical physical properties* of some EaglePicher Filtration & Minerals, Inc., commercial functional additives

Grade†	Color	Surface Area, m ² /g	Bulk Density, pcf		Screen Analysis % Retained, 325 mesh	Oil Absorption, %	pH	Median Particle Size, μm	Typical Applications
			Dry	Wet					
Natural									
Celatom MN-2	Beige	28	12	21	7.0	170	7.0	15.0	Catalyst support/carrier, polishing agent, abrasive, specialty paper components, natural insecticide, reactive silica source, drilling fluids, paint flattening agents
Celatom MN-4	Beige	30	10	27	0.3	160	7.0	8.0	
Celatom MN-23	Beige	36	11	33	0.3	130	7.0	5.0	
Celatom MN-47	Beige	35	11	33	1.0	130	7.0	9.0	
Celatom MN-51	Beige	78	11	27	6.5	150	7.5	15.0	
Celatom MN-53	Beige	35	11	31	5.0	140	7.0	14.0	
Celatom LCS-3	Off-white	30	10	22	0.5	160	7.0	11.0	
Flux Calcined									
Celatom MW-25	White	2	10	29	0.1		10.0	9.0	Paint flattening agent, adhesives, antiblock agents, catalyst carriers, friction papers, stucco products, asphalt sealers
Celatom MW-27	White	2	12	24	1.0		10.0	13.0	
Celatom MW-31	White	2	13	24	5.0		10.0	16.0	
Celatom Celabrite	White	2	10	30	0.0		9.5	8.5	
Celatom Celablock	White	2	10	32	0.0		9.5	6.0	

Courtesy of EaglePicher Filtration & Minerals, Inc.

* English units used where appropriate.

† Brands listed are from EaglePicher Filtration & Minerals, Inc. Celatom is a registered trademark.

porosity. Although many minerals are crushed and sized as fillers, the inherent properties of diatomite are well suited for, or can be readily modified for, specific filler applications. Table 6 gives typical properties of some commercial fillers.

Because the uses for diatomite fillers are numerous, only a few of the notable applications are discussed here.

Paints and coatings are among the most important of the filler end uses of diatomite. Functionally, the diatomite filler acts to extend more costly pigments and serves as a flattening agent that reduces both the sheen and gloss of the dried paint surface. The small size and

irregular shape of the particles serve well to roughen the paint film, imparting a matte finish as well as tooth for better adhesion of top coats. Toughness and durability of the film are also increased. Rigorous requirements for brightness, pH, absorption, refractive index, particle size, and chemical stability must also be met.

In polyethylene film, the particulate structure and the optical properties of diatomite fillers make them effective antiblocking agents. When added to the film during manufacture, the small and irregularly shaped particles mechanically separate adjacent sheets and prevent adhesion.

In other plastics, diatomite is used to reduce cost and improve heat resistance and surface finish. Diatomite also reduces mold release resistance and improves abrasion resistance.

Absorbents

For more than 50 years, diatomite of lower purity has been used to absorb liquid spills. Both granules and powders of various grades are manufactured and may be calcined to increase hardness, improve durability after absorbing a fluid, and reduce the tendency to produce dust. Since its early use as “floor sweep” absorbent, numerous industrial, environmental, and household spill-control applications have emerged that utilize the low bulk density of diatomite as well as its inherent high surface area and porosity and the resulting ability to absorb and retain up to 2–3 times its own weight in liquids. Diatomite can be used to absorb a wide variety of liquids including water, oil and grease, and chemicals, with the exception of hydrofluoric acid. Floor sweeps and pet litters, particularly for cats, are two of the large volume and widely known applications. Diatomite has been used in areas such as stables to absorb liquids and, reportedly, to control flies.

Soil Amendments

Granules of calcined diatomite are increasingly being used as a high-end soil amendment. Important properties include granule durability and water retention and release. Research has indicated that 10% incorporation by volume in soils can reduce irrigation requirements by up to 50%. As a soil amendment, diatomite is used for preventing soil compaction in sports turf, improving root growth, lessening transplant shock for landscape plantings, and reducing water and chemical consumption for all turf and ornamental applications. New developments include adding diatomite to create specialty soil blends for hanging basket soil and rooftop garden soil (P. Lenz, personal communication).

Natural Grade Insecticides

The use of diatomite dusts in commercial products designed to control insects and mites within stored agricultural products is widespread throughout the world. Public and governmental pressure to reduce reliance on chemical insecticides that are harmful to mammals would appear to offer growth potential for this application and others such as soil and structural fumigation. Although several mechanisms have been proposed to explain diatomite's effectiveness as an insecticide, the adherence of the particles to the waxy surfaces of insect pests and the absorption of body fluids are believed to cause death by dehydration (Crossley 2000). Product effectiveness may be enhanced by adding silica gel and treating with heat.

Cement, Concrete, and Asphalt

Diatomite has been used only to a limited extent in the United States as a supplemental silica source in cement kiln feed where it has been used in conjunction with traditional raw materials. Provided that the diatomite source is within economic transport distance of a cement plant, the chemical composition, fine grain size, and relatively low fusion temperature of diatomite are attributes that may potentially yield advantages in the manufacturing process. Potential benefits that should be considered include reduction in feed and clinker grinding, ease and homogeneity of reaction, energy savings in calcination, mitigation of process bottlenecks, and improvement of the properties of finished product and finish characteristics of the cement.

In concrete, mortar, plaster, stucco, and grout, diatomite filler can improve plastic and hardening properties; enhance cohesi-

ness, homogeneity, and workability; and reduce bleeding and efflorescence. In sprayed-on stucco, the addition of diatomite reportedly reduces rebound. Throughout the world, diatomite and clay-bearing diatomite are used as pozzolans. In asphalt products, diatomite can decrease cracking tendencies associated with rapid temperature change, improve cohesive strength, control viscosity, and improve the application characteristics of mastics.

Other Uses

Diatomite filler is used as a processing aid in rubber manufacture, and as a mild abrasive in polishes and cleansers. Fineness, absorptive capability, and low abrasiveness make diatomite powders and granules effective carriers and diluents for use in agrochemicals.

Diatomite provides the source of low density, heat resistance, and porous silica in catalyst carriers such as those used in hydrogenation processes and sulfuric acid manufacture. Similarly, diatomite is used in porous, inert chromatographic supports. Diatomite powders are also used as a silica source for the production of synthetic calcium and magnesium silicates. These unique products exhibit extremely high surface area (105 to 190 m²/g) and are able to absorb up to 5½ times their weight in water. Some commercial synthetic silicates are able to absorb 3 to 4 times their weight in water and remain dry, free-flowing powders. In some parts of the world, diatomite is formed directly into insulating brick.

Other miscellaneous applications include use in match head and welding rod composition, as an anticaking agent on ammonium-nitrate prills, as a stabilizer in explosives, and as a silica source for calcium silicate filler for acetylene cylinders.

Product Pricing

Based on statistics compiled by the USGS and the U.S. Bureau of Mines, the weighted average price of diatomite per metric ton sold or used by U.S. producers rose from \$219 in 1990 to \$258 in 2003, reaching a peak of \$271 in 2001 (Table 2). The USGS reported that the average price per ton for most end uses in 2002 and 2003 decreased from that of 2001.

Competitive Substitutes

Many minerals and materials are used in filtration applications in which a porous filter bed is used to mechanically remove suspended solids from a liquid. In addition to diatomite, other commonly used materials include expanded and milled perlite, sand, garnet, asbestos, cellulose, and carbon. Although diatomite is acknowledged as a superior performer for a broad range of commercial and municipal filtration problems, each of the other materials can be suitable for specific or niche applications and can exhibit advantages in terms of effectiveness, cost, durability, and availability. In the last decade, the use of ultrafiltration and synthetic membranes has become more widespread. The performance and suitability of alternative filtration systems, however, must be considered in terms of the specific application. The filtration system installation and operational costs of common membrane filtration units must be taken into account, because they are more expensive than typical diatomite systems (Crossley 2000).

Talc, silica sand, ground mica, clay, expanded and milled perlite, and ground calcite are a few of the many mineral fillers sold into the large and diverse filler markets in addition to diatomite.

Chemically modified or synthetic fillers represent a second important group of fillers. Selection of appropriate fillers is based on cost, availability, and performance. The physical properties of diatomite make it useful as a functional filler in a broad spectrum of industrial applications. Although substitute fillers may be used, replacement may require that the final product be reformulated.

Minerals that can compete with diatomite as absorbents include sepiolite, attapulgite, and bentonite, among others. Although these minerals share some market applications, each has its various niches.

Packaging

Powdered diatomite products are sold in both 22.68-kg (50-lb) bags and in bulk form. In the United States, powdered diatomite is primarily sold in 50-lb bags, although it is also available in 800- and 1,000-lb sacks and in bulk form via pressure differential railcars and trucks. Bagged products are palletized and can be stretch- or shrink-wrapped for shipment. In Europe, powdered diatomite has been sold in 20-kg bags and in 1,000- to 2,000-L sacks.

Bags are labeled with the product and trade name and can be labeled with a customer's specific in-house identification if requested. Labels may also be placed on the shrink wrap that covers palletized loads at the customer's request. Caution labels are placed prominently on each bag or on the palletized load advising the product handlers of the health issues associated with the crystalline silica present within diatomite products. Caution advisories may be printed in several languages on each of the labels, and in addition, special labeling may be required for different locations. Great care must be taken to comply with labeling requirements.

Transportation

Freight costs have a significant impact on the overall cost of products to the customer. Diatomite products are bulky because of their low density; as a result, transport cost per ton is high. After palletizing and wrapping, bagged products are transported to distribution centers or directly to customers by truck or by rail and ocean freight in containerized loads. Alternatively, pneumatic railcars and truck tankers are used to transport diatomite powders in bulk directly to the customer's storage bin. In the United States, the majority of products are bagged and shipped by truck in palletized form.

In the United States, products destined for export are typically palletized and transported to port in containers as large as $12.2 \times 2.7 \times 2.7$ m that are easily transferable to ship, truck, or rail systems. The major elements of export contracts that must be routinely negotiated include inland freight obligations at both ends of the transport, marine cargo insurance, and currency and fuel adjustment factors. Tariffs and taxes associated with export are considered separately in the next section.

ECONOMIC OR COMPETITIVE FACTORS

Import Tariffs, Taxes, and Depletion Allowance

Most of the major trading countries now use the international Harmonized Commodity Description and Coding System (HS) to classify products for tax purposes. Under this system, imported natural diatomite products and products calcined without sintering agents are classified under designation 2512 as siliceous fossil meals and similar siliceous earths. This heading includes tripolite, diatomite, and molar earths. Diatomite products that are calcined with the addition of sintering agents such as sodium chloride or sodium carbonate are classified under a separate heading, 3802, as activated products. Bricks, blocks, tiles, or other ceramic goods of siliceous fossil meals are classified under heading 6901. Import duties and other taxes vary throughout the world and are set by the fiscal and customs authorities of each country.

No tariffs are applied to 2512 diatomites and straight calcined diatomites imported into the United States. A duty of 2.5% is imposed on flux calcined diatomite imported in the United States. Products are exported from the United States under general license with no restrictions. Depletion allowance is set at 14%.

Costs and Timing

In the United States, the cost of production can be approximately divided as follows: 10% mining, 60% processing, and 30% packaging and shipping (Benton 1983). Energy is the largest single element of direct cost, representing roughly 30% of the total cost (P. Lenz, personal communication). Freight costs, which are discussed generally here (see the section on Transportation), have a great impact on the cost to the customer.

The cost of and time required for exploration, mine development, and plant development vary widely and depend on the unique requirements of any given project. For example, the cost of building a new plant will be dictated by such factors as the products that are to be made, the need for a kiln, and the production capacity that is required. In general, a greenfield facility capable of manufacturing calcined filter aids and fillers might cost \$20–\$25 million or more. In the United States, bonding is required and such plans must be approved by the U.S. Bureau of Land Management. Individual states manage the plans. In determining the bond amount, health issues, land use and zoning, environmental concerns, and reclamation, closure, and decommission issues are considered. Additional costs may include royalties paid to mineral owners for extraction. The contractual agreements employed for determining royalty payments can vary from mine to mine, but royalty payment is quite commonly calculated as a percentage of the value of the annual sale of finished goods. Minimum annual royalty may also be a feature of individual royalty agreements.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Health and Safety

In the United States, exposure to diatomite is primarily an occupational issue. Prolonged and excessive exposure to respirable crystalline silica dust is a known cause of silicosis (pneumoconiosis). As discussed previously, diatomite can contain crystalline silica species in varying abundance. In 1996 the International Agency for Research on Cancer (IARC) reclassified crystalline silica as a Group 1 known human carcinogen. Crystalline silica is also listed as a human carcinogen by the U.S. National Toxicology Program, and under California Proposition 65, airborne crystalline silica of respirable size is listed as a substance known to the State of California to cause cancer (Anon. 1998; W. Miles and M. Mirliiss, personal communication). IARC has classified amorphous silica as a Group 3 substance, not classifiable as to carcinogenicity.

The diatomite industry has addressed the health issues associated with mining, processing, and handling of crystalline silica dusts for many years. In the United States, worker exposure to such dusts is regulated under the Occupational Safety and Health Administration (OSHA) and by the Mine Safety and Health Administration. Classification as Group 1 triggers the regulation of respirable crystalline silica under the Hazard Communication Standard as administered by OSHA, and producers must appropriately label their diatomite products that contain more than 0.1% of this substance. In addition, health and safety information is provided on material safety data sheets (MSDSs), which include information on the carcinogenicity of respirable crystalline silica.

Manufacturers are responding directly by conducting worker and consumer protection, education, and training programs, and by implementing and maintaining industrial hygiene programs in plants. MSDSs have been and will continue to be revised to meet OSHA requirements.

Because crystalline silica occurs as a principal or minor accessory mineral in most mineral products, the designation of crystalline silica as a carcinogen affects nearly all mineral-related industries. The diatomite industry formed the International Diatomite Producers

Association (IDPA) in 1988 to study and report on the health, safety, and environmental issues related to the industry. In addition to sponsoring health-related research, the IDPA has published educational literature on crystalline silica for workers and users of diatomite products. Information is available through the IDPA (Long Beach, California), and also from the American Chemistry Council (Arlington, Virginia).

The health regulation issues associated with respirable crystalline silica continue to evolve in both the United States and Europe. The European Union does not currently have an occupational exposure level limit for respirable crystalline silica, although one is under consideration by the Scientific Committee on Occupational Exposure Limits, a subcommittee of the European Commission (M. Mirliss, personal communication).

Other Regulatory Issues

In the United States, land use and zoning issues associated with mining, plant construction, and production can be of significant concern depending on the location of the operation and its proximity to sensitive environmental areas and/or to residential and urban development. In general, reclamation requirements are becoming more restrictive and more stringently enforced. Reclamation that is concurrent with mining is commonly employed. Control of fugitive dust emissions has become a key issue as regulations have become increasingly stringent and subject to enforcement.

There are no U.S. federal disposal restrictions, although some states may impose restrictions. Landfill disposal costs for used or spent filter cake have long been of concern to the end user. To avoid such cost, some end users may seek to recycle their waste through secondary usage such as land farming or use in animal feed. Alternatively, some end users have examined the viability of other filtration technologies.

OUTLOOK AND FUTURE TRENDS

United States

From 1980 to 1990, production capacity in the United States for fillers, absorbents, and filter aids increased through the development of five new operations. Following the construction of the new filler and filter aid plants, U.S. overcapacity was estimated to be in excess of 25% (Anon. 1987a, 1989). Since 1990, the industry has experienced a net reduction of domestic production capacity by the closure of the large Grefco mining and manufacturing operations at Lompoc, California, and by the closure of the Oil-Dri facility in Oregon. These capacity decreases have been somewhat offset by the startup of Dia-Source operations in Oregon and by Atlas Minerals Inc.'s intermittent operations during 2002 at Mammoth, Arizona. Even though emerging applications such as natural grade insecticide, biotechnology, and pharmaceuticals continue to develop, no major new market applications that will greatly increase usage have been announced. In general, consumption in the filter aid and absorbent market segments is not expected to grow during the first half of the current decade, whereas modest growth is expected for filler and natural grade insecticide market segments.

The free crystalline silica associated with diatomite persists as an industry concern.

Exploration of deposits has continued throughout the western United States and in the state of Virginia.

The Rest of World

Since 1992, world output was estimated by the USGS to range from 1.93 to 2.02 Mt, and for 2002, it was estimated at 1.95 Mt (Dolley 2002).

During the past decade, attention has focused on the development of Chinese resources at Changbai, Jilin, and on investigation of deposits in Australia, New Zealand, Vietnam, and the former Soviet Union.

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Feldspars

Michael J. Potter

INTRODUCTION

Feldspars make up the most abundant mineral group in the earth's crust. They account for an estimated 60% of the exposed rocks, as well as soils, clays, and other unconsolidated sediments, and are principal components in rock classification schemes.

Feldspars are aluminum silicate minerals that contain varying proportions of calcium, potassium, and/or sodium. The principal feldspar species are albite (sodium feldspar), anorthite (calcium feldspar), and microcline and orthoclase (potassium feldspars). These species are almost never found in pure form in nature but occur as mixtures of varying proportions.

Pegmatites, which are one source of feldspar, are exceptionally coarse-grained igneous rocks and have a composition similar to that of granite. The composition may be simple or complex and may include minerals rich in such elements as lithium, rare earths, tantalum, and others (Jackson 1997). Perthite is a variety of alkali (sodium-potassium) feldspar in which the potassium-rich phase (typically microcline) appears to be the host from which the sodium-rich phase (typically albite) exsolves (i.e., unmixes). The exsolved areas are visible to the naked eye and typically form irregular veinlets, strings, and so forth (Jackson 1997). Antiperthites have sodium-rich plagioclase as the host feldspar and intergrowths of potassium-rich feldspar. What is commonly known as Spruce Pine alaskite is an important feldspar ore-bearing rock that occurs in the Spruce Pine District of North Carolina. This alaskite has been described as a coarse-grained pegmatitic granite (Kaufman and Van Dyk 1994). According to A. Glover (personal communication), a true alaskite has a higher potassium than sodium content, whereas the Spruce Pine alaskite has a higher sodium than potassium content. Alaskite generally contains microcline, orthoclase, and quartz; plagioclase may or may not be present (Rogers, Neal, and Teague 1983). Aplite that was mined in 2003 (in only one U.S. location, in Virginia) is a metanorthosite (metamorphosed anorthosite) with a high proportion of plagioclase feldspar.

Feldspars are widely used in the glass and ceramic industry. Nepheline syenite, which is covered in a separate chapter in this book, is a light-colored, silica-deficient feldspathic rock made up mostly of sodium and potassium feldspars and nepheline. Although not mined in the United States for glass and ceramic use, nepheline syenite has been imported from Canada for a number of years for that use. A single operation in Arkansas has been producing nepheline syenite for its internal use in manufacturing roofing granules and related products.

The first commercial production of feldspar in the United States occurred in about 1825 and was mined from pegmatite bodies located in Connecticut. The feldspar was hand sorted and shipped to England. During the nineteenth and twentieth centuries, feldspar production grew with new production locations, integrated mine and processing facilities, and the development in 1939 of the flotation process for feldspar by the U.S. Bureau of Mines (USBM) and the feldspar industry. The first commercial feldspar flotation plant began operations in Kona, North Carolina, in 1946 (Feitler 1967; Rogers, Neal, and Teague 1983).

In 2003, U.S. production of feldspar, based on reported and estimated data, was about 800,000 t. World production of feldspar, excluding China, was an estimated 10.8 Mt (Potter 2005).

Since 1980, the U.S. feldspar industry has seen some expansion of plant capacity, a few plant closures, and changes in ownership of existing operations. In its glass end-use market, the industry has been affected by glass recycling and by competition from metal, paper, and plastic containers. In ceramics, the other major market for feldspar, much of the manufacturing of plumbing fixtures and tiles is in Brazil, China and other Asian countries, and Western Europe (Roskill Information Services Ltd. 2002). Brazil, China, Colombia, Italy, Mexico, and Spain are significant exporters of plumbing fixtures and tile to the United States (Ceramic Industry 2004; Grahl 2004).

PRODUCTION AND TRADE

North America

U.S. production of feldspar comprises hand-cobbed, flotation concentrates, feldspar-quartz mixtures (feldspathic sand), and aplite. Beginning in 1992, aplite has been included with feldspar production data. Table 1 shows U.S. feldspar production from 1980 to 2003. Flotation concentrates comprised about 70% to 80% of output through 1991 and about 40% to 45% thereafter. Feldspar-silica mixtures and hand-cobbed material made up about 20% to 30% through 1991, and thereafter, with aplite being included, about 55% to 60% of the output.

Feldspar was mined in seven states in 2003, which were, in descending order of output, North Carolina, Virginia, California, Georgia, Oklahoma, Idaho, and South Dakota. North Carolina accounted for about 45% of the total. Ten companies mined feldspar, nine of which operated 12 beneficiation facilities—four in North Carolina, three in California, and one in each of the five remaining states mentioned (Table 2). U.S. production data for feldspar are collected by the U.S. Geological Survey (USGS) by means

Table 1. Feldspar production in the United States, kt

Year	Flotation Concentrate	Percentage	Other*	Percentage	Total
1980	513	80	131	20	644
1985	442	70	193	30	635
1990†	440	70	190	30	630
1995†	400	45	480	55	880
2000†	330	42	460	58	790
2003†	330	41	470	59	800

Source: USBM 1981–1996; USGS 1997–2005.

* Includes hand-cobbed feldspar, feldspar-quartz mixtures (feldspar content), and (beginning in 1992) aplite.

† Data rounded to no more than two significant figures because of partially estimated data.

of a voluntary survey. Of the 12 known beneficiation facilities in 2003, 6 responded with production data by the survey deadline. These 6 facilities represented about 64% of the production shown in Table 1. In 1985, the response rate, by tonnage, was 81%; in 1990, 75%; and in 2000, 60%. As a result, U.S. production data in Table 1 for 1990 and after have been rounded to no more than two significant figures because of partially estimated data.

Canada has had no feldspar production for a number of years, although some projects are being developed. Avalon Ventures Ltd. of Toronto, Ontario, continues work on its Warren Township, Ontario, anorthosite (calcium plagioclase feldspar) project. Also under development is the company's Separation Rapids project near Kenora, Ontario, which has a deposit containing high-lithium feldspar, for potential use in glass and ceramic manufacture (Avalon Ventures Ltd. 2004). Another company, i-minerals inc. of Vancouver, British Columbia, continues to test and develop two feldspar deposits at its Helmer-Bovill property in Latah County, Idaho. Its Kelly's Basin deposit contains sodium feldspar, and the "WBL" tailings (previously owned by Washington Brick and Lime Co.) contain potassium feldspar and quartz (i-minerals inc. 2004).

U.S. imports of feldspar increased from 864 t in 1985 to a high of 17,900 t in 1991. Between 1999 and 2003, imports fluctuated between about 5,500 tpy and 8,000 tpy. Most of the imported material from 1986 to 2002 came from Mexico. Beginning in 2003, Turkey became a significant exporter of feldspar to the United States (Table 3). U.S. feldspar trade and apparent consumption statistics are shown in Table 4.

Production of feldspar in Mexico increased from 163,000 t in 1990 to an estimated 330,000 t in 2003. Mexican exports between 1997 and 2003 fluctuated between about 5,900 tpy and 11,400 tpy, with 98% to 99% going to the United States. Mexican imports of feldspar between 1997 and 2003 were between 1,200 tpy and 5,150 tpy. The United States supplied between 86% and 98% of the total (U.N. Statistics Division 2004).

Rest of World

Feldspar is produced in more than 50 countries. According to preliminary data and estimates by the USGS for 2003, the following countries produced these estimated amounts of feldspathic materials:

- Italy—2.5 Mt
- Turkey—1.8 Mt
- France—650,000 t
- Germany—450,000 t
- Spain—450,000 t
- Czech Republic—350,000 t
- Egypt—350,000 t

Significant production also has come from China and countries in Southeast Asia. Table 5 shows exports from selected countries.

In Italy, output in 2002 included a plite, feldspathic sand, sodium feldspar, sodium-magnesium feldspar, and sodium-potassium feldspar. Gruppo Minerali SpA and Maffei SpA are among the largest producers. Aplite mined by Maffei contains sodium feldspar (20%), potassium feldspar (40%), quartz (30%), and other minerals (10%). End uses for feldspathic products include floor and wall tile, glass, sanitary ware, and tableware. A major development in recent years has been gres porcellanato (i.e., glazed and unglazed porcelain tiles), which contain a high percentage of feldspar. Most Italian feldspar production is consumed domestically, and large quantities of the mineral are imported for the ceramics industry. Italian imports of feldspar increased from 246,000 t in 1992 to 1,865,000 t in 2001 and about 2,290,000 t in 2003 (U.N. Statistics Division 2004; 2003 data given in Table 6). Most of the imported material came from Turkey (Roskill Information Services Ltd. 2002; Crossley 2003; U.N. Statistics Division 2004).

In Turkey, the majority of feldspar produced in 2003 was albite, although potassium feldspar had a small output. There were six main and six smaller producers. Two of the large companies, Çine Akmaden Madencilik Tic. A.Ş. and Esan Eczacıbaşı Endüstriyel Hammaddeler San. ve Tic. A.Ş., produced flotation feldspar. A third company, Kallitun Madencilik San. ve Tic. A.Ş. had plans for a new flotation plant in the works in 2003. Flotation feldspar, with its increased whiteness, was being consumed by porcelain tile producers in Italy and other countries (Crossley 2003).

Turkish exports of feldspar grew from 163,000 t in 1991 to 2.1 Mt in 2000. The main reason for the rapid increase in shipments was a sharp rise in demand from ceramics companies in Italy and Spain (Roskill Information Services Ltd. 2002). Turkish exports were reported to be around 2.2 Mt in both 2001 and 2002 and about 3 Mt in 2003. About 90% of the exports in 2003 went to Italy and Spain (Crossley 2003; U.N. Statistics Division 2004).

In Asia, sodium feldspar is probably the most widely used feldspar because of its relative abundance, especially in China and Thailand, both of which are major exporters (Lines 2003). Although official data are not available, Chinese production of feldspar may exceed 2 Mtpy (Roskill Information Services 2002). Estimated production in 2003 for Thailand was 780,000 t and for the Republic of Korea, 400,000 t. Japan produced an estimated 50,000 t of feldspar in 2003 and an estimated 300,000 t or more of aplite (Potter 2005). Table 7 shows feldspar production for a number of selected countries.

Chinese exports of feldspar in 2001 were 557,000 t, with at least 400,000 t probably being exported to Taiwan, some of which was shipped via Hong Kong. In 2003, Chinese exports were about 600,000 t, with major destinations of Indonesia, Japan, Malaysia, the Republic of Korea, Taiwan, and Vietnam. In 2001, exports of feldspar from Thailand were reported to be about 330,000 t, with about 200,000 t going to Malaysia. In 2003, Thai exports were again about 330,000 t, with major destinations of Malaysia, United Arab Emirates, and Vietnam (Roskill Information Services Ltd. 2002; U.N. Statistics Division 2004).

Potentially economic deposits of feldspar occur in at least 70 countries, and the potential supply throughout the world is presumed to be large. Feldspar reserve and resource data have only been assessed for a few countries: Reserves in Brazil have been estimated at 23 Mt; in Italy, 14 Mt; and in the Republic of Korea, 36 Mt. Detailed estimates of world reserves and resources for most countries are not available or have not been compiled (Roskill Information Services Ltd. 2002).

Table 2. U.S. feldspar operations

Company	Ore Body	Mining	Milling Process	Products	Size, μm	Typical Analysis, %					By-products and Coproducts
						Al ₂ O ₃	Fe ₂ O ₃	CaO	K ₂ O	Na ₂ O	
Aplite											
U.S. Silica Co., Montpellier, Virginia (Hanover County)	Pegmatite	Open pit	Processing	Aplite	600	21.7	0.18	5.6	2.9	5.5	None
Feldspar-Quartz Mixtures											
Arkhola Sand and Gravel, division of APAC, Arkansas, Inc., Muskogee, Oklahoma (Muskogee County)	River sands	Dredging	Washing, magnetic separation, leaching	Glass sand	600	5.40	0.10	0.08	3.04	0.78	Industrial sand, construction sand
	Marine sands	Open pit	Processing	Glass sand	425	9.50	0.23	0.80	4.07	1.85	Clay, other sand products
	Pegmatite	Open pit	Flotation	Glass sand	na [†]	na	na	na	na	na	Feldspathic sand is a by-product of mica and kaolin clay production.
Deltaic conglomerates, sandstone, siltstone	Open pit	Washing plant with flotation	Amber grade	600	9.0	0.35	1.0	4.0	3.50	3.50	Construction sand, industrial sand
		Regular	600	5.0	0.15	0.50	2.0	1.25	1.25		
P.W. Gillibrand Co., Simi Valley, California (Ventura County)	Open pit	Flint grade-high grade	600	4.0	0.04	0.30	1.5	1.0	1.0		
		Glassil glass sand [‡]	425	4.10	0.12	0.06	2.85	0.37	0.37	Industrial sand, construction sand	
Unimin Corp., Bryon, California (Contra Costa County)	Sandstone	Open pit	Washing, flotation		425	8.31	0.13	0.77	2.99	2.06	Industrial sand
Unimin Corp., Emmett, Idaho (Gem County)	Lake deposits	Open pit	Washing	Glassil glass sand [‡]	425	8.31	0.13	0.77	2.99	2.06	Industrial sand
Sodium-Potassium Feldspar											
K-T Feldspar Corp., Spruce Pine, North Carolina (Mitchell County)	Alaskite	Open pit	Flotation	Minspar 1	600	18.5	0.05	1.5	4.1	6.5	Mica, industrial sand
				Minspar 200	75	18.5	0.06	1.5	4.1	6.5	
				Minsilpar [§]	90	14.0	0.06	1.1	2.8	4.9	
				Minspar [§]	**	na	na	na	na	na	
The Feldspar Corp., Spruce Pine, North Carolina (Mitchell County)	Alaskite	Open pit	Flotation	NC-4	75	18.8	0.07	1.40	4.10	6.82	Mica, industrial sand
				F-20	600	18.8	0.065	1.40	4.10	6.82	
				Silo-o-spar [†]	90	13.5	0.057	1.05	2.86	4.86	
				Felex	**	18.6	0.07	1.85	3.80	7.20	
Unimin Corp., Spruce Pine, North Carolina (Mitchell County)	Alaskite	Open pit	Flotation	F-1	600	19.3	0.08	1.5	4.5	6.7	Mica, high-purity quartz
				F-4	90	19.3	0.08	1.5	4.5	6.7	
				F-4	75	19.6	0.04	1.7	6.9	4.8	
				Unispar 40	**	na	na	na	na	na	
				Unispar 50	**	na	na	na	na	na	
Potassium Feldspar											
Pacer Corp., Custer, South Dakota (Custer County)	Pegmatite	Open pit, selective mining by contractors	Dry grinding	Custer potash feldspar	75	17.0	0.15	0.3	10.0	3.0	Mica
				Custer potash feldspar	45	17.0	0.15	0.3	10.0	3.0	
				Custer potash feldspar	38	17.0	0.15	0.3	10.0	3.0	
				Crystalline feldspar	45	15.0	0.15	0.3	7.0	3.0	
The Feldspar Corp., Monticello, Georgia (Greene and Jasper counties)	Granite	Open pit	Flotation	G-40	425	18.0	0.076	0.8	10.2	2.85	Industrial sand
				G-200	75	18.5	0.082	0.81	10.75	2.85	

* Nominal top size.

† na = not available.

‡ Mean values, do not represent a specification.

§ Feldspar-silica mixture.

** Submicron grind feldspar extender and filler product.

Table 3. U.S. imports* of feldspar, by country, t

Country	1997	2000	2003
Mexico	8,200	7,100	6,100
Turkey	0	0	1,800†
Other	400	100	100
Total	8,600	7,200	8,000

Source: International Trade Administration 2004; U.N. Statistics Division 2004.

* Data rounded to two significant figures.

† U.N. statistics show exports to the United States as 16,600 t.

Table 4. U.S. feldspar statistics, kt

Year	Production	Imports	Exports	Apparent Consumption*
1980	644	0.4	11.8	633
1985	635	0.9	8.4	628
1990	630†	11.3	24.8	620†
1995‡	880†	9.0	14.7	870†
2000	790†	7.2	11.4	790†
2003	800†	8.0	9.0	800†

Source: USBM 1981–1996; USGS 1997–2005.

* Calculated as production plus imports minus exports.

† Data rounded to no more than two significant figures because of estimated data.

‡ Beginning in 1992, aplite data are included.

Table 5. Exports of feldspar, by selected countries,* kt

Country	1997	2000	2003
China	591	607	599
France	122	296	286
Germany	83	61	102
Italy	43	122	165
Malaysia	21	24	53
Norway	68	71	68
Spain	25	57	66
Thailand	241	294	330
Turkey	950	2,114	3,000

Adapted from U.N. Statistics Division 2004.

* Includes countries with feldspar exports of 50,000 tpy or higher in 2003.

Table 6. Imports of feldspar, by selected countries,* kt

Country	1997	2000	2003
Germany	42	52	51
Indonesia	81	105	186
Italy	714	1,573	2,292
Malaysia	267	281	262
Poland	36	82	155
Portugal	36	60	81
Spain	229	552	777

Adapted from U.N. Statistics Division 2004.

* Includes countries with feldspar imports of 50,000 tpy or higher in 2003.

Table 7. Feldspar world production, by selected countries,* kt

Country	1980	1985	1990	1995	2000	2003†
Brazil	123	110	105	199	118	75
China‡	na§	na	na	na	na	na
Colombia	27	34	35	58	55	100
Czech Republic	na	na	na	na	337	350
Egypt	4	19	10	75	330†	350
France	210	172	420†	632	642†	650
Germany	381	322	418†	330	450†	450
India	59	46	54	100	110†	150
Iran	3	32	32	80†	156	190
Italy	345	1,116	1,610	2,199	2,500	2,500
Korea, Republic of	72	145	237	368	330	400
Mexico	117	100	163	122	334	330
Poland	40†	60	32	46	165	240
Portugal	41	29	44	107	120	120
Spain	103	136	214	379	460†	450
Thailand	24	104	311	670	626	780
Turkey	73†	20†	182	760	1,148	1,800
United States	644	635	630	880	790	800
Venezuela	6	43	91	227	130	150
Other	928	977	1,412	668	699	915
Total (rounded)	3,200	4,100	6,000	7,900	9,500	10,800

Source: USBM 1981–1996; USGS 1997–2005.

* Includes countries with estimated feldspar production in 2003 of 100,000 t or higher.

† Estimated.

‡ Official data are not available. In 2000, estimated production may be 2 Mt or more (Roskill Information Services Ltd. 2002).

§ na = not available.

GEOLOGY

The common feldspar minerals can be represented in a ternary phase system that shows feldspar mineralogy; the end members are KAlSi_3O_8 (orthoclase), $\text{NaAlSi}_3\text{O}_8$ (albite), and $\text{CaAl}_2\text{Si}_2\text{O}_8$ (anorthite). The end-member compositions also are referred to as potassium, sodium, and calcium feldspar (Table 8). The feldspars whose chemistry ranges between the potassium and sodium end members are known as alkali feldspars, whereas those between the alkali and calcium end members are plagioclase feldspars. The plagioclase series is arbitrarily subdivided and named according to increasing mole fraction of the anorthite component: albite, oligoclase, andesine, labradorite, bytownite, and anorthite (Jackson 1997). The feldspar groups can be further subdivided based on structural and compositional features within the alkali or plagioclase feldspar series (Kauffman and Van Dyk 1994). The feldspars have become the primary tool in the classification of igneous rocks (Deer, Howie, and Zussman 2001). Table 8 gives theoretical end-member compositions of the principal feldspars.

Minerals of the feldspar series have some similar physical properties: a Mohs hardness of 6, a specific gravity range of 2.54 to 2.76, and a vitreous luster. Color can range from colorless, white to gray, green, yellow, and red; feldspars may be translucent to transparent.

Geologic Occurrence and Major Deposits

The major U.S. commercial feldspar deposits in 2003 were Spruce Pine alaskite; the aplite in Hanover County, Virginia; pegmatites; and various sand deposits, including certain beach, dune, and river sands, derived from granitic source rocks.

Alaskite

Spruce Pine alaskite is a granitic rock that is composed principally of plagioclase, quartz, orthoclase, and muscovite, in decreasing order of abundance (Feitler 1967). Mined only in North Carolina, it is a major source of feldspar production in the United States. Alaskite occurs in three principal areas, referred to as the Spruce Pine, Penland, and Crabtree alaskite bodies, which are located, respectively, in Mitchell, Avery, and Yancey counties, North Carolina (Olson 1944). The largest mass of alaskite is between Spruce Pine and Chalk Mountain in Mitchell County. A 1981 mineral analysis of Spruce Pine alaskite showed 42.9% sodium (sodic plagioclase) feldspar, 28% quartz, 14.7% potassium feldspar (microcline, generally perthitic), 7.5% muscovite, 6.4% calcium feldspar, and small amounts of iron minerals and garnet. A corresponding average chemical composition of alaskite was SiO_2 , 74.4%; Al_2O_3 , 15.4%; Fe_2O_3 , 0.4%; CaO , 0.9%; K_2O , 3.4%; Na_2O , 5.1%; and LOI (loss on ignition), 0.4% (Redeker 1981). A 2004 analysis of Spruce Pine alaskite generally had the following mineral composition: 35% sodium feldspar (sodic plagioclase), 25% quartz, 30% potassium feldspar, 6% muscovite, and 4% calcium feldspar (A. Glover, personal communication).

For comparison, an average chemical composition for granite was given as SiO_2 , 70.2%; Al_2O_3 , 14.5%; Fe_2O_3 , 1.6%; FeO , 1.8%; CaO , 2.0%; K_2O , 4.1%; Na_2O , 3.5%; and small amounts of other components (Reed 2004).

Historically, in this region of North Carolina, pegmatites containing large amounts of microcline are thick (about 8 to 46 m) and occur near the abundant alaskite extending along the southeast side of the district from near Ingalls through Spruce Pine to the Crabtree Creek area. Prior to 1940, all the feldspar was mined from pegmatites by hand, but since 1940, the commercial production of feldspar has been revolutionized by feldspar flotation. Alaskite

Table 8. Theoretical end-member compositions of the principal feldspars, %

Type	K_2O	Na_2O	CaO	Al_2O_3	SiO_2
Microcline	16.9	0	0	18.4	64.7
Orthoclase	16.9	0	0	18.4	64.7
Albite	0	11.8	0	19.4	68.8
Anorthite	0	0	20.1	36.6	43.3

replaced pegmatites as a source of raw material because bodies of alaskite are larger than the pegmatites. Also, compositional and mineralogical uniformity are greater, making the alaskite a more desirable flotation feed (Brobst 1962).

Aplite

Aplite is defined as a light-colored igneous rock consisting essentially of quartz, potassium feldspar, and sodic plagioclase (Jackson 1997). Commercial aplite mined near the Piney River area in Virginia until 1980 was identified previously as a pegmatite, a syenite, and Roseland anorthosite (Brown 1962). A description of rock from the same locality (Castle and Gillson 1960) suggests that the rock originally contained very coarse feldspar, which was subsequently granulated to give it a marked variability in texture. Aplite mined from Hanover County, Virginia, is the one current (2003) source of commercial production. The deposit is part of the Montpelier metanorthosite where rock is mined by U.S. Silica Co. (formerly by The Feldspar Corp.) at a quarry near Montpelier, Virginia (Bice and Clement 1982; Clement and Bice 1982). The metanorthosite intruded the Sabot gneiss and consists of two phases: a coarse-grained, gray, nonfoliated phase and a granulated, medium-grained foliated phase. The coarse-grained phase contains plagioclase crystals up to 25 to 35 cm that constitute 85% to 90% of the total rock.

Feldspar-Quartz Mixtures (Sands)

Feldspar is an abundant constituent in modern sands of diverse origins (Pettijohn, Potter, and Siever 1973). These sands most commonly occur as beach sands, sand dunes, and river sands. River sands tend toward more feldspathic compositions than either dune or beach sands. Although relatively few petrographic analyses give a breakdown of feldspar varieties, a survey of those that do suggests that potassium feldspar (orthoclase, microcline) is most abundant, followed by sodium plagioclases and the calcium plagioclases.

Feldspar-quartz mixtures currently make up part of the current feldspar market and have been a significant portion of the industry. A major part of this production comes from the feldspar-rich quartz sand deposits located in California, Idaho, and Oklahoma. Some feldspar-quartz mixtures are a coproduct from feldspar flotation operations.

The primary active California deposits are sandstone and deltaic deposits that contain quartz, and a range of 10% to 35% contained feldspar (Silva 1985). The Idaho deposit is a lacustrine (derived from a lake bed) sand with an estimated feldspar content of 30%. The Oklahoma operation processes an Arkansas River sand deposit containing 25% feldspar, of which about 72% is potassium feldspar (Bowditch 1978). In most cases, these silica deposits have been identified as extensive.

Although they have not been developed thus far, the Kankakee dune sands in Kankakee County, Illinois, contain an average of about 21% feldspar. The sands are composed of quartz, plagioclase feldspars, potassium feldspar, mica, pyrite, and some other accessory minerals (Bhagwat et al. 2001).

Granite

Granite is a plutonic (igneous) rock that contains largely feldspar and quartz and in which the alkali feldspar/total feldspar ratio generally is restricted to the range of 65% to 90% (Jackson 1997). Granite is mined from only one state: Georgia has two granitic sources, which have been mined for feldspar for a number of years. The Shadydale granite, mined in Jasper County, has a chemical composition of 13.9% Al_2O_3 , 0.9% CaO , 3.6% K_2O , and 4.7% Na_2O . The Siloam granite, mined in Greene County since 1980, is a porphyritic granite containing perthitic microcline—47% microcline, 25% plagioclase, 20% quartz, 3% perthite, and 5% biotite. Ore from the two mines is blended and processed in a plant to produce a potassium-grade feldspar.

Pegmatites

Exceptionally coarse-grained igneous rocks, pegmatites have a composition similar to that of granite (Jackson 1997). Granitic pegmatites, widely distributed throughout the crystalline rock areas of the United States, occur in rocks of many geologic ages and are most abundant near the margins of granitic intrusions. Most of the important pegmatite districts are included in three broad geographic belts:

- Appalachian Belt, which extends from Alabama to Maine
- Rocky Mountain Belt, which encompasses Colorado, Idaho, Montana, New Mexico, South Dakota, Texas, Utah, and Wyoming
- Western Belt, which covers Arizona, California, Nevada, Oregon, and Washington

From about 1865 to 1991, pegmatites in the Middletown, Connecticut, area were mined almost continuously for feldspar and other minerals. Pegmatite occurrences in the Middletown Area have been recorded in the hundreds. These pegmatites are composed essentially of perthite, quartz, plagioclase, and muscovite. Approximately 42% of the pegmatites contain more than 40% plagioclase. The Middletown pegmatites are largely granitic in composition and form a vast resource of feldspar, quartz, and scrap mica. The relative abundance of potassium and sodium feldspar-rich pegmatites is not related to the formation in which the pegmatite occurs, but rather shows a regional pattern in which potassium feldspar-rich pegmatites are more numerous to the south (Stugard 1958).

North Carolina pegmatites are located in the Kings Mountain Belt within the Shelby District covering Cleveland, southwestern Lincoln, and western Gaston counties. The area currently has one producing operation (Bundy and Carpenter 1969); the feldspar that is obtained is a by-product of mica production (in 2003 as a feldspar-quartz mixture). At the south end of the district, a coarse-grained phase of the Cherryville quartz monzonite is mined for mica, feldspar, quartz, and kaolin. The coarse-grained granite is gradational into pegmatite and also is cut by pegmatite dikes. Depending on weathering, the total feldspar content ranges from 13% to 40%, and the potassium feldspar content ranges from 6% to 7% (Horton 1981). Lithium pegmatites are located northwest of Kings Mountain and the Bessemer City area and were mined until 1998. The average composition of the lithium pegmatites going to mill feed was 20% spodumene, 32% quartz, 27% albite, 14% microcline, 6% muscovite, and 1% trace minerals. The pegmatites are generally not zoned, and the fairly uniform grade of the crude ore allows recovery of feldspar and mica by-products (Kesler 1976). Feldspathic sand was recovered as a by-product from lithium production until 1998, when the last spodumene mine was closed.

The pegmatites of the Black Hills, South Dakota, occur in two main areas. The Harney Peak area encompasses the Keystone Dis-

trict in Pennington and Custer counties, the Hill City District in Pennington County, and the Custer District in Custer County. The second area is the Tinton District in Lawrence County. Although the greater part of the pegmatite-bearing area is in Custer County, the Keystone District has a record of significant mineral production from pegmatites. The most abundant minerals of the South Dakota pegmatites are plagioclase feldspars (oligoclase and albite), potassium feldspars (perthite and microcline), and quartz. The minerals are uniformly distributed in many pegmatites, but in others they tend to be concentrated in specific structural units. South Dakota pegmatites have been classified on the basis of mineral distribution, texture, and their structural relationships to the wall rocks (Page 1953; Norton 1964).

The following gives detailed descriptions of other feldspar occurrences:

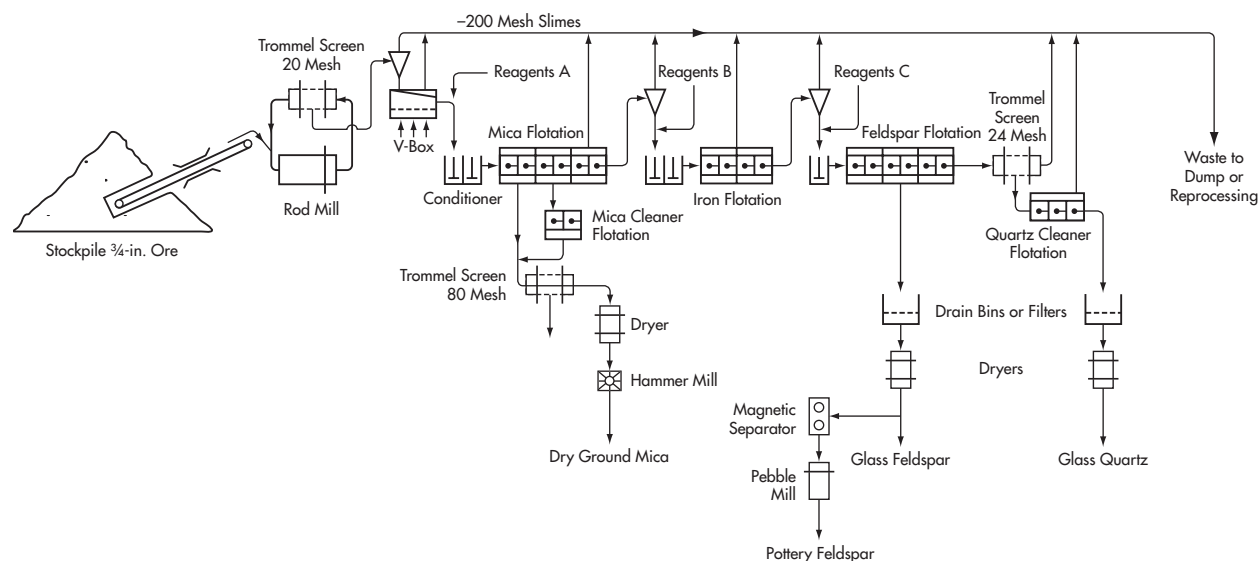
- Barium feldspars have mineral structures very similar to those of potassium feldspars but are rather rare and are not being mined commercially. Barium feldspar with more than 90% of the $\text{BaAl}_2\text{Si}_2\text{O}_8$ molecule is described as celestian (Deer, Howie, and Zussman 2001). Occurrences of barium feldspar have been reported in Australia, Italy, Japan, Namibia, Sweden, Wales, the United States, and a few other countries (Mineralogy Database 2005).
- Amazonite is a gem variety of microcline feldspar and often is polished as a cabochon (i.e., cut so the top of the gemstone forms a convex surface). It displays a Schiller of light, which is a lustrous reflection, also known as iridescence. Amazonite is usually light green to blue green and is found in Australia, Brazil, Namibia, Russia, the United States, and Zimbabwe (Bernardine Fine Art Jewelry 2004).
- Labradorite is plagioclase feldspar. Although much of the stone is dark gray, a Schiller effect can produce blue, green, gold, and yellow iridescent colors. Slabs of labradorite rocks are available in very large sizes, suitable for facings of office buildings. The material also is cut into cabochons. Labradorite is found in Australia, Finland, Labrador, Madagascar, the United States, and other countries (Arem 1987).
- Moonstone refers to a feldspar of widely varying composition and from a wide variety of localities. For example, moonstone from Burma and Sri Lanka displays a white to blue sheen.
- Sunstone is oligoclase or labradorite that contains hematite (Fe_2O_3) or goethite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$) and inclusions of silicate or clay minerals, which reflect light and create a sparkling sheen in gold to brown color shades. Sunstone is found in Australia, Canada, India, Norway, Russia, and the United States (Arem 1987).

TECHNOLOGY

Commercial feldspar mining in the United States includes mining of feldspathic sand deposits and of hard-rock material such as alaskite. Dredging of river sand occurs at one operation in Oklahoma. In general, after mining of sand deposits or dredging of sand, processing steps can include washing, screening, classifying, leaching to remove surface stains, flotation, and drying. The Spruce Pine alaskite has been a major ore source since the mid-1940s, and a description of a typical alaskite feldspar operation that employs differential froth flotation for the recovery of a pure feldspar product follows.

Mining

Hard-rock mining is done by open-pit methods, either by the mine owner or by contractors. Stripping ratios are nominal, less than 1:1.



Courtesy of Minerals Research Laboratory, North Carolina State University.

Figure 1. Typical flowsheet for feldspar production with alaskite ore

After the feldspar ore is drilled and blasted, secondary breakage is with a conventional drop ball. Ore is then loaded with a hydraulic shovel onto trucks and hauled to the crushing plant, which is adjacent to the flotation plant.

Processing

Figure 1 is a simplified flowsheet of a typical feldspar flotation plant and is intended to acquaint the reader with the concepts involved in feldspar production. Primary crushing is done with a jaw crusher in open circuit. Secondary crushing is with a standard or shorthead gyratory crusher in two or three stages, sometimes in closed circuit with a screen. The final crushed product is -25 m (-1 in.).

Grinding is normally done with rod mills in order to minimize slime generation, although one company uses ball mills without any apparent ill effects. The grinding mills are normally operated in closed circuit with a classifier in order to maximize grinding capacity. Although the feldspar mineral grains are liberated at $850\text{ }\mu\text{m}$ (20 mesh) or larger, grinding is usually carried out to $-600\text{ }\mu\text{m}$ (-30 mesh) in order to optimize the efficiency of subsequent flotation steps. To reduce reagent consumption and produce a higher grade product, the feed to flotation must be sized to eliminate the slimes or $-38\text{ }\mu\text{m}$ (-400 mesh) material. The fact that container glass customers prefer a $+75\text{ }\mu\text{m}$ ($+200\text{ mesh}$) product is also a factor. Desliming is normally done with hydrocyclones.

Once the feldspar feed is properly sized, the differential flotation process can begin. All the unit operations after crushing are operated in a continuous circuit, 24 hours a day, 5 days per week. The first flotation step is to remove mica, which later can be sold as a coproduct. Mica flotation is achieved by conditioning with a cationic collector (an amine) at pH 3 using sulfuric acid. The mica is removed in a froth product and is usually cleaned once prior to being dewatered and sold. Iron-bearing minerals such as garnet and ilmenite are removed next, this time using an anionic collector, petroleum sulfonate, again at pH 3. The iron-bearing minerals are collected in the froth product and pumped to tailings.

The previous unit operations of grinding, sizing, mica flotation, and iron flotation have produced an essentially pure mixture of feldspar and quartz. Some of the traditional feldspar producers are marketing or have marketed this mixture for ceramic use under various trade names such as Min silspar and Silospar. The product is filtered, dried, and cleaned with high-intensity magnetic separation or dry ground and sold, usually in bulk. Other company products are shown in Table 2.

The production of a high-grade feldspar product requires a third flotation step, again at pH 3. The collector is the same cationic amine as used in mica flotation, but this time the pH is controlled with hydrofluoric acid to depress the quartz. The fluorine ion is a powerful depressant in the quartz-feldspar separation. A feldspar product is produced with good recovery in a single rougher flotation step. The feldspar-containing froth product is filtered, dried, and, if necessary, cleaned with high-intensity magnetic separation and stored in bulk prior to sales.

A particular plant generally will produce several different products, all with the same chemistry (because of the same source rock), but with different physical specifications. For ground feldspar for ceramic and filler use, the dried flotation product is ground in a ceramic-lined ball mill in closed circuit with air classifiers to produce a $-74\text{ }\mu\text{m}$ (-200-mesh) or a $-44\text{ }\mu\text{m}$ (-325-mesh) product. As can be seen in Figure 2, this step is one of the more expensive unit operations in the whole processing scheme, and the ground feldspar commands a higher price.

While feldspar producers strive to sell as high a percentage of the ore as possible, tailings (i.e., waste residue left from the processing of feldspar ore) inevitably account for 30% to 40% of the head feed. Tailings are dewatered in settling ponds, by filtration, or in tailings plants. Solid material generally is sent to a landfill, although some could be used as fill material in, for example, mine excavations (A. Glover, personal communication). Figure 2 shows the relative costs of the various unit operations as compared to the total cost of producing feldspar. The data have been derived by using cost experience for the various unit operations and costs that

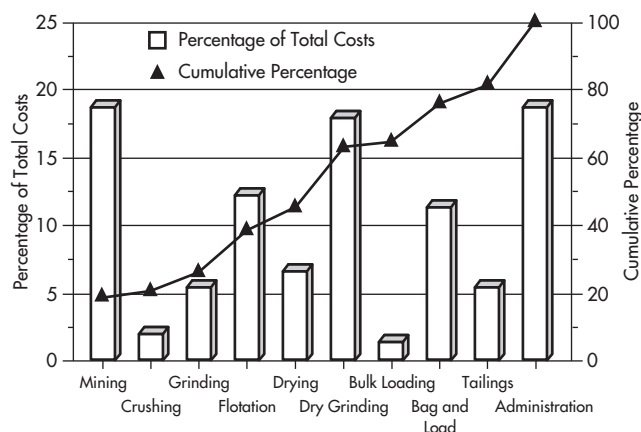


Figure 2. Distribution of feldspar production costs

Table 9. Feldspar sold by U.S. producers, by use

Year	Glass*		Ceramic and Other		Total†	
	Quantity, kt	Value, thousand \$	Quantity, kt	Value, thousand \$	Quantity, kt	Value, thousand \$
1980	367	12,700	278	13,600	644	26,300
1985	353	15,600	285	16,400	638	32,000
1990	340‡	17,900	260‡	16,200	600	34,100
1995§	570‡	27,000	260‡	18,900	830‡	45,900
2000	520‡	26,700	270‡	19,200	790‡	46,000
2003	560‡	29,000	240‡	16,000	800‡	46,000

Source: USBM 1981–1996; USGS 1997–2005.

* Includes container glass, fiberglass, and other glass.

† Data may not add to totals shown because of independent rounding.

‡ Data rounded to no more than two significant figures because of partially estimated data.

§ Beginning in 1992, aplite data are included.

have been published in cost-estimating manuals (Kaufman and Van Dyk 1994; A. Glover, personal communication).

MARKETING

Uses

In the United States, feldspar for glass manufacturing is usually ground to 850 μm (20 mesh) to 425 μm (40 mesh) and contains 4% to 6% K_2O ; 5% to 7% Na_2O ; approximately 19% Al_2O_3 ; and 0.08% Fe_2O_3 . Pottery-grade feldspar for white ware and similar ceramic products usually ranges from 5% to 14% in K_2O and is ground to 75 μm (200 mesh) with Fe_2O_3 content in the 0.07% range (Potter 1993).

Table 9 shows the consumption of feldspar by major end-use markets from 1980 to 2003. Until 1991, glass (including containers, fiberglass, and other glass) accounted for more than half of consumption. Beginning in 1992, aplite was included in U.S. feldspar statistics, and, because aplite is largely used for glass, glass increased to about 65% to 70% of consumption. Ceramic and other uses were about 40% to 45% of feldspar consumption until 1991 and then decreased to about 30% to 35% thereafter.

Glass

Glass manufacturing is complex and encompasses an enormous range of compositions and product types. Materials for glassmak-

ing can be classified in three groups: glass formers, fluxes, and stabilizers. Glass formers are basic ingredients that can be melted and cooled into a glass, such as silica (quartz sand) (Elert 2005). Fluxes are oxides, including potassium oxide (K_2O) and sodium oxide (Na_2O), which are added to lower the melting temperature of a glass batch. Stabilizers, which can be oxides such as alumina (Al_2O_3) and calcium oxide, impart to the glass a high degree of resistance to physical and chemical attacks. In conjunction, the fluxes and stabilizers control the working characteristics of the glass-forming (Tooley 1984).

Although alumina does not represent a large part of the composition of most glass, it is important because it increases the resistance of glass to chemical corrosion, improves the hardness and durability, and enhances the working characteristics of the glass (Pincus and Davies 1983).

Feldspar provides both alkaline oxides (K_2O and Na_2O) for fluxing and alumina and calcium oxide as stabilizers. An important source of alumina for glassmaking, feldspar has a low iron and refractory mineral content, a low cost per unit of alumina, no volatile constituents, and no waste. The products usually melt between 1,100° and 1,200°C and dissolve readily in the glassmaking batch. A typical batch for container glass contains about 8% feldspar, and a batch for glass fiber insulation contains about 18% (Roskill Information Services Ltd. 2002).

The consumption and selection of glass raw materials are influenced significantly by the economics of the glass-manufacturing process and the glass product market. Therefore, specifications for raw materials vary based on particular circumstances and economics. However, raw materials for the glass industry require rigid physical and chemical specifications.

Ceramics

Ceramic and pottery products are the second largest consumer of feldspar products in the United States. The ceramic products generally consist of ceramic glazes, ceramic tile, dinnerware, electrical porcelain, and sanitary ware.

Feldspars are used in the fine ceramic industry as a flux to form a glassy phase in bodies, thus promoting vitrification and translucency. They also are used as a source of alkalis and alumina in glazes. Feldspars also provide one of the few sources of water-insoluble alkali compounds (Norton 1970).

Consumption of feldspar varies depending on the finished product. Dinnerware and various china products may contain 17% to 20% feldspar; floor tile, 55% to 60%; high-tension electrical porcelains, 25% to 35%; kitchen and ovenware, 10%; vitrified plumbing fixtures, 25%; wall tile, 0% to 11%; and other special ceramic products, including dental porcelain, may require 60% to 80% feldspar (Singer and Singer 1963).

The selection of a potassium versus a sodium feldspar for ceramic applications has been the subject of many investigations (Norton 1970). Feldspar fluxing differences also have been studied (Weinstein 1985) for deformation and the effect of the alkali type in feldspars on the glassy phase formed.

Fillers

Feldspar use as a functional filler and extender in the paint, plastic, rubber, and sealants industries has evolved in recent times as an application that improves product performance. In these uses, feldspar competes with other minerals and nepheline syenite and requires increased levels of research and technical marketing efforts. Feldspar products developed for these markets must comply with the following specifications: dry brightness, oil absorption, Hegman grind, particle-size distribution, surface area, and bulk density.

Feldspar gives paints and coatings favorable properties such as low vehicle demand, which means that the feldspar is not demanding or taking up polymer (binder) out of the paint mixture. Other opportune characteristics of feldspar are low viscosity at high pigment loading; high dry brightness and low tint strength; good film integrity; resistance to abrasion, chemical attack, and chalking (the formation of an easily crumbled powder on the surface of a paint film); excellent tint retention; and ease of dispersal. Compared to nepheline syenite, feldspar has exceptional resistance to frosting (whitening of a painted surface) but may exhibit slightly greater health hazards owing to the presence of free crystalline silica (Mommensen 1988; S. Robinson, personal communication).

Product Pricing

Published prices for feldspar can vary according to the application, particle size, quality, quantity purchased, source, and type of material. Therefore, price quotations serve only as a general guide. From 2000 to 2003, U.S. sodium feldspar prices have shown little or no increase. During the same time period, prices for potassium feldspar increased by about 10% to 30%.

Published prices for U.S. ceramic-grade feldspar at year-end 2003, ex-works (i.e., cost, not including insurance or transport cost), bulk (not in bags), per metric ton, were about \$66 to \$83 for sodium feldspar and \$138 for potassium feldspar. For glass-grade feldspar, prices were about \$44 to \$57 for sodium feldspar and \$94 to \$99 for potassium feldspar. Prices for Turkish sodium feldspar, f.o.b. Gulluk (i.e., free on board at Gulluk port), per metric ton, were \$13 to \$14 for crude, -10 mm, bulk; \$75 to \$80 for ground, -63 µm, bagged; and \$54 to \$56 for glass grade, -500 µm, bagged (*Industrial Minerals* 2003).

Transportation

Feldspar is shipped either in bulk or in 50-lb (23-kg) or larger bags. In the feldspathic minerals industry, the cost of transportation is often equal to the value of the material transported. In 2002, rail transport was still the dominant form of shipping. Rates generally were increasing 2.5% to 3% per year, and fuel surcharges were an additional 2% to 3%. With faster delivery and reasonable costs, truck transport was gaining market share (Rogers 2002).

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

In the United States, because of its crystalline silica (quartz) content, feldspar falls under the Occupational Safety and Health Administration's Hazard Communication Standards, 29 CFR Section 1900.1200. The standard requires labeling and other forms of warning, material safety data sheets, and employee training for products containing identified carcinogens with concentrations greater than 0.1%.

OUTLOOK

The container glass industry, a major end user of feldspar, continues to face strong competition from other forms of packaging, such as metal, paper, and plastic containers. Use of recycled glass containers (as cullet) in glassmaking decreases consumption of mineral raw materials, including feldspar. Government legislation and regulation are also providing momentum for increased use of recycled glass (Roskill Information Services Ltd. 2002). With escalating production costs and resistance to price increases by consumers, feldspar producers will continue to face a challenging business environment for the foreseeable future (Rogers 2002).

Beer and wine packaging is probably the single largest market for container glass in the world. Countries with large beer industries—including Brazil, the Czech Republic, Germany, Japan, Mex-

ico, the Netherlands, Poland, Russia, Spain, the United Kingdom, and the United States—have substantial glass production capacity. In the immediate future, the fastest-growing markets for container glass are projected to be in Asia and Latin America, where countries have fast-growing populations. At present, glass packaging is said to have a cost advantage over aluminum and plastic containers in most of these countries. For example, the Chinese and Indian container-glass markets are potentially very large (Roskill Information Services Ltd. 2002).

The strong U.S. market in 2003 for new home construction and remodeling consumed about 267 million m² of tile. Imports supplied about 78% of this demand with Italy providing 34% and Spain 17%. Consumption of porcelain tile continued to grow, partly because of its durability. Also, demand is increasing for larger-sized tiles, in sizes ranging from about 30 cm × 30 cm (12 in. × 12 in.) to 51 cm × 51 cm (20 in. × 20 in.) (*Ceramic Industry* 2004).

Although U.S. vitreous china sanitary-ware consumption data are not available, U.S. demand is increasingly being filled by imports. In 2004, Mexico and China were the largest U.S. suppliers, providing about 58% of imports. According to The Freedonia Group, Inc., U.S. demand for vitreous plumbing fixtures may remain flat for the next several years. Instead, regions outside the United States, such as Asia, Eastern Europe, and the Middle East, may provide growth opportunities (Grahl 2004; The Freedonia Group 2004).

Demand for ceramic grades of feldspar is projected to remain relatively stronger than demand for glass grades. The main centers of ceramics production are China, Italy, Spain, Latin America, and Southeast Asia. These areas, and Chinese, Italian, and Spanish companies in particular, have been the major consumers of feldspar during the past 20 years and are projected to remain so in the immediate future (Roskill Information Services Ltd. 2002).

ACKNOWLEDGMENT

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Fluorspar

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Fluorspar is the commercial name for fluorite, a mineral that is calcium fluoride (CaF_2). The name, derived from the Latin word *fluere* (to flow), refers to its low melting point and its early use in metal-lurgy as a flux. It is the principal industrial source of the element fluorine.

Two other minerals, cryolite and fluorapatite, have significant fluorine content. Cryolite (sodium aluminum fluoride, Na_3AlF_6), is a rare mineral that has been found in commercial quantities in Greenland. It has also been produced as a by-product of tin mining in Brazil. The natural material has been supplanted by synthetic cryolite for its principal industrial use in the manufacture of aluminum. Fluorapatite [$\text{Ca}_5(\text{PO}_4)_3\text{F}$] is a source of phosphate for fertilizer manufacture and contains a small percentage of fluorine. Commercially mined deposits of apatite have varying amounts of fluorine, chlorine, hydroxyl, and carbonate.

HISTORY

Fluorspar was used by the early Greeks and Romans for ornamental purposes such as vases, drinking cups, and tabletops. Various cultures, including the Chinese and the Native Americans, carved ornaments and figurines from large crystals. Its usefulness as a flux was known to Agricola in sixteenth-century Europe.

Fluorspar mining began in England about 1775 and started at various places in the United States between 1820 and 1840. Production grew substantially following the development of basic open-hearth steelmaking, where it was used as a flux. Use was stimulated by growth of the steel, aluminum, chemical, and ceramic industries, particularly during World Wars I and II. Fluorocarbons entered the picture in 1931, although significant production of these compounds did not occur until after World War II. The use of anhydrous hydrogen fluoride (HF) as a catalyst in the manufacture of alkylate for high-octane fuel began in 1942.

Differential flotation for separating fluorspar from galena, sphalerite, and common gangue minerals in the 1930s and the application of heavy media-concentrating methods to the treatment of low-grade ores in the 1940s were outstanding technological advances that facilitated increased production.

Pelletizing and briquetting of flotation concentrates for use in steel furnaces and the development of flotation schemes for beneficiating ores containing abundant dolomite and barite have been major improvements in the industry.

PRODUCTION, RESERVES, AND TRADE

Major producing countries have been China, England, France, Italy, Mexico, Mongolia, South Africa, Spain, Thailand, the United States, and the former USSR. Other smaller producers have included Argentina, Brazil, Canada, Czechoslovakia, Germany, India, Iran, Kenya, Korea, Morocco, Namibia, Tunisia, and Romania. In 2002, the major producing countries (in descending order of production) were China, Mexico, South Africa, Mongolia, Russia, and Spain. The largest exporters were (in descending order) China, Mexico, South Africa, Mongolia, Kenya, Morocco, and Namibia. World production in 2002 was about 4.55 Mt, and world reserves (measured as 100% CaF_2) are estimated at 230 Mt (see Table 1).

Natural phosphate rock contains approximately 3.5% fluorine as a component of the mineral fluorapatite. Silica, in the form of sand or gravel, occurs with the phosphate rock ore. In phosphate rock processing, the fluorine reacts with the silica and volatilizes as silicon tetrafluoride, which hydrolyzes to fluorosilicic acid when the gas is passed through water scrubbers. Currently, most of this acid

Table 1. World production and reserves, *kt**

Country	Production in 2002	Reserves
China	2,450	21,000
France	105	10,000
Kenya	98	2,000
Mexico	650	32,000
Mongolia	200	12,000
Morocco	96	na†
Namibia	73	3,000
Russia	200	Moderate
South Africa	227	41,000
Spain	130	6,000
Other countries	310	110,000
World total (may be rounded)	4,550	230,000

* Production data rounded to three significant digits. Reserves rounded to two significant digits, measured as 100% CaF_2 .

† na = not available.

Table 2. U.S. imports for consumption*

Country	2001		2002	
	Quantity, kt	Value, thousand \$	Quantity, kt	Value, thousand \$
Acid grade				
China	353	48,500	344	44,400
Mexico	28	3,690	35	4,340
South Africa	114	14,400	83	10,300
Others	<1	160	3	435
Total	495	66,800	466	59,500
Metallurgical grade				
Mexico	26	2,040	23	1,970
South Africa	na†	na	5	492
Others	<1	115	<0.5	68
Total	27	2,150	28	2,530
Grand total, all grades	522	69,000	494	62,000

* Data are rounded to three significant digits; values are cost, insurance, and freight (c.i.f.), U.S. ports.

† na = not available.

is neutralized with lime. In some countries, however, fluorosilicic acid is converted to a aluminum fluoride and also silica fluorides of sodium, potassium, and ammonium. Although numerous attempts have been made to develop processes to produce hydrofluoric acid from phosphate rock in fertilizer manufacturing, no one has, to date, developed a viable and economic method to separate the silica from the fluorine.

The quantity of fluorine present in phosphate rock deposits is enormous. Current U.S. reserves of phosphate rock alone are estimated to be 1.0 Gt, which at 3.5% fluorine would contain 35 Mt of fluorine, equivalent to about 72 Mt of fluor spar. World reserves of phosphate rock are estimated at 18 Gt (Jasinski 2004), which converts to 630 Mt of fluorine and 1.29 Gt of fluor spar equivalent.

With the exception of fluor spar purchased from the U.S. National Defense Stockpile and some synthetic fluor spar recovered as a by-product of uranium processing, petroleum alkylation, and stainless-steel pickling, the bulk of U.S. fluor spar requirements are imported. In 2001, the United States imported 522 kt of fluor spar, and in 2002, imports totaled 494 kt (466 kt of acid grade and 28 kt of metallurgical grade). Table 2 shows the quantity and value of U.S. fluor spar imports by country and grade.

GEOLOGY

Composition and Properties

Theoretically, pure fluorite contains 51.3% calcium and 48.7% fluorine. Substitution of small percentages of cerium and yttrium for calcium has been noted. Inclusions of gases and fluids, such as petroleum and water, and of solid minerals such as pyrite, marcasite, and other sulfides, are common. Rarely, free fluorine is present in some crystals. Commercial fluor spar may contain various amounts of attached and admixed mineral impurities, such as calcite, quartz, barite, celestite, various sulfides, or phosphates.

Fluorite tends to occur in well-formed isometric crystals, forming cubes and octahedrons. It also occurs in both massive and earthy forms, and as crusts or globular aggregates with radial fibrous texture. Crystalline fluor spar exhibits a great range of colors, from colorless to yellow, blue, purple, green, rose, red, bluish

and purplish black, and brown. The colors may occur in alternating bands parallel to crystal faces. Coloration may be altered by exposure to x-rays, heat, ultraviolet light, and pressure. Colors are caused by a variety of factors, including the presence of trace impurities and displaced ions in the lattice. Long exposure to sunlight, such as in mine dumps, frequently results in the fading of the original coloration.

Some varieties fluoresce blue or violet under ultraviolet light or cathode rays. Some specimens phosphoresce when heated or after exposure to sunlight or ultraviolet light, and some forms exhibit triboluminescence.

Fluorite has a hardness of 4, and is the mineral type of that hardness on the Mohs scale. Its normal specific gravity is 3.18 when crystalline but ranges from 3.01 to 3.6 in various forms. The luster is vitreous. The mineral has perfect octahedral cleavage, and octahedrons, made by cleaving off the corners of cubic crystals, often are seen in collections.

Crystalline fluorite has a very low index of refraction ($n = 1.4339$) and low dispersion, is isotropic, and has an unusual ability to transmit ultraviolet light. These are the properties that make it useful as prisms in optical systems and as components of high-quality, special-purpose lenses. Synthetic fluorite has replaced the natural mineral for optical uses.

Modes of Occurrence

Fluorite occurs in a wide variety of geological environments, evidencing deposition under an extended range of physical and chemical conditions. At one extreme, it is present as an accessory mineral in granites and related igneous rocks; at the other extreme, it is sometimes found as crystals in geodes and as botryoidal linings in limestone caves. From an economic standpoint, the most important modes of occurrence of the mineral are

- Fissure veins in igneous, metamorphic, and sedimentary rocks
- Stratiform replacement deposits in carbonate rocks
- Replacements in carbonate rocks along contacts with acid-igneous intrusives
- Stockworks and fillings in shattered zones
- Deposits in association with carbonatite and alkalic rock complexes
- Residual concentrations resulting from the weathering of primary deposits
- Occurrences as recoverable gangue in base metal deposits

Less common modes, although commercially important in some places, include fillings in breccia pipes, fillings in open spaces, and pegmatites. Least common are deposits in lake sediments.

Fissure Veins

Fissure veins, usually along faults or shear zones, are the most readily recognized form in which fluor spar deposits occur. Silica, calcite or other carbonates, iron, lead and zinc sulfides, and barite are the typical associated minerals. In some vein deposits, such as those in the Rosiclare District of southern Illinois, fluorite appears to have replaced a prior vein filling of calcite. Along some veins in carbonate rocks, fluor spar has replaced the wall rock at intersections with favorable beds, providing large minable tonnages. Although vein structures are remarkably persistent, the fluor spar commonly occurs as lenses or ore shoots separated by barren or poorly mineralized portions of the veins. Ore-shoot widths of 0.5 to 10 m and lengths of 60 to 300 m are common, but there is great variation from deposit to deposit. Vein systems may be up to several kilometers in length, and ore may be present to depths of 300 m or more.

below the surface. The CaF_2 content of minable portions of veins normally ranges from 25% to 80%, although grades above 90% occur in limited areas.

Important vein deposits have been developed in China, adding to the world's great vein deposits that include the Osor deposit in northeastern Spain, the Torgola deposit in northern Italy, the Muscadroxiu-Genna Tres Montis vein system in Sardinia, the Hucklow Edge and Longstone Edge-Sallet Hole vein systems in England, the Rosiclare-Goodhope vein system in Illinois, and the El Hammam vein system in Morocco.

Stratiform Deposits

Stratiform, manto, or bedded deposits occur in carbonate rocks. Certain beds are replaced along or adjacent to structural breaks such as joints or faults. This relationship to structural features is very clear in some deposits but obscure in others. Frequently, there is a sandstone, shale, or clay capping. Typically, there is evidence of loss of volume in the replaced zones with attendant development of gentle synclinal structures in overlying strata or of collapse structures, the latter sometimes pipelike in shape. In some districts, no connection is recognized between the mineralization and any igneous activity. In southern Illinois, mafic dikes, offset by the younger mineralized structures, intrude host rocks superjacent to a rift complex (Baxter and Bradbury 1989). Post-dike igneous activity, related to rift reactivation, is invoked as a deep-seated source of fluorine. In other districts, such as the Encantada District in northern Coahuila, Mexico, the presence of rhyolite plugs and sills in the general vicinity of the spar deposits, and the association of spar with rhyolite injections along bedding planes, suggests a more direct association.

Stratiform deposits are known in many parts of the world and are particularly well developed in the Cave-In-Rock District of southern Illinois, in the northern part of the state of Coahuila in Mexico, and in the Ottoshoop (Zeerust) District in the Republic of South Africa. In Illinois, the deposits range from a few centimeters to 6 m thick, are 15 to 150 m wide, and are up to 7 km long. In Coahuila, the individual ore bodies are smaller but relatively more numerous and widespread. In the Ottoshoop District, bedded deposits occur in an area that is 16 km in length and 10 km wide, in a dolomite facies that underlies a prominent chert bed.

In stratiform deposits, textural features, such as sedimentary banding of the parent rock, are commonly preserved. A massive, crystalline ore type, frequently associated with the banded ore, appears to have filled open spaces left from the dissolution of limestone by the ore-bearing solutions or their precursors. Minerals accompanying fluorspar in stratiform deposits include calcite, dolomite, quartz, galena, sphalerite, pyrite, marcasite, barite, and celestite. Calcium fluoride content in minable deposits ranges from 11% upward. A few ore bodies in Illinois yielded direct-shipping, metallurgical-grade fluorspar containing 85% or more calcium fluoride.

Replacement Deposits

Replacement deposits in carbonate rocks are well developed along contacts with intrusive rhyolite bodies in the Rio Verde, San Luis Potosi, and Aguachile districts in Mexico. They include some of the largest and highest grade fluorspar deposits. The fluorspar, not thought to be contact metamorphic in origin, was apparently introduced later by ore solutions that followed conduits along the contact zone and, either massively or selectively along certain beds, replaced the limestone outward from the contact. At Agua Chile, cross sections show ore shoots resembling one side of a Christmas tree.

Stockworks

Fluorspar often occurs as stockworks and fillings in shear and breccia zones. Many occurrences in the American West are of the stockwork type and, though wide, usually have low overall calcium fluoride content and are consequently uneconomic; deposits in the Zuni Mountains of New Mexico and near Jamestown, Colorado, are examples. The Zwartkloof deposit, in the Transvaal Province of South Africa, consists of three vertical breccia zones containing stockworks of fluorite-carbonate veins. The mineralized breccia zones are in an east-west line and developed in felsite. The largest zone is 60 m by 180 m in plan and persists to 900 m below the surface. The fluorspar grade is about 14%. The Buffalo deposit, near Naboomspruit in the Transvaal, consists of a network of fluorspar veinlets that occur in sill-like bodies of fine-grained, pink granite in the coarse, red granite of the Bushveld Complex.

Carbonatite and Alkalic Rock Complexes

Fluorspar is a common mineral in carbonatite and alkalic rock complexes, although rarely in sufficient abundance to be economically recoverable. The Okorusu deposit in Namibia is an economic deposit of this type and consists of a number of bodies of fluorspar in limestones, quartzites, and related rocks that have been intruded and metamorphosed by an alkaline igneous rock complex that includes a nepheline syenite stock. The fluorspar replaces bedded and brecciated limestone, marble, and quartzite, forming large lenticular masses. Apatite, magnetite, and quartz are abundant accessory minerals. At Amba Dongar, India, veins and replacement bodies of fluorspar occur in carbonate rocks that border an eritic carbonatite in trusives. Fluorite is also present in the carbonatite itself at both Okorusu and Amba Dongar.

Residual Deposits

Concentrations of fluorspar in clayey and sandy residuum, from surficial weathering of fluorspar veins and replacement deposits, are, principally, sources of metallurgical spar. This category includes detrital deposits blanketing the apex of veins, as well as deeply weathered upper portions of the veins themselves. Such deposits, extending to depths of 30 m or more, were of major importance in Illinois and Kentucky. Similar deeply weathered ore has been mined in England, Thailand, and the Asturias District of northwestern Spain. Weathered residuum, called kokoman, is mined in the Marico District in South Africa, where it is the result of the weathering of gently dipping replacement bodies.

Gangue Mineral

Fluorspar occurs as a major gangue mineral in lead-zinc veins in many parts of the world, and in some, averaging 10% to 20%, is economically recoverable. Acid-grade fluorspar has been produced on a large scale from lead-zinc mill tailings in the Parral District in Mexico.

Breccia Pipes

Fluorite occurs in breccia pipes in the Thomas Range in Utah, and near Beatty, Nevada. Pipes in the Thomas Range are circular to oval in plan, up to 45 m in diameter and more than 60 m in depth. They formed in dolomite by replacement along shattered zones associated with faults and intrusive breccias. The fluorspar occurs as soft, friable masses and in boxworks of fine-grained, more resistant veinlets, and is nearly unrecognizable. At the former Daisy mine near Beatty, fluorspar replaces brecciated dolomite in pipe-like bodies bounded by gouge zones along two sets of intersecting faults.

Fillings in Open Spaces

Fluorspar occasionally partially fills open spaces, both in veins and stratiform deposits. Spectacular examples of this type occur in the San Vicente District of northern Coahuila, Mexico, where fluorspar occurs in veins and mantos as pure massive incrustations of mamillary, stalactitic, and stalagmitic forms. The Fluorspar-Gero-Pember vein system of the Northgate mine in Colorado is a similar occurrence where fluorspar occurs in botryoidal layers on the walls of open fissures and as concretionary coatings surrounding loose fragments of country rock. The lower parts of open areas of these fissures are partly filled with concretionary pebblelike masses, in places cemented into porous, rubbly aggregates.

Pegmatites

Many pegmatites contain minor amounts of fluorspar. Grade in three ore bodies was high enough to once support a mining operation at the Crystal Mountain occurrence in Montana. These large, tabular bodies of massive fluorspar, which occur in coarse-grained biotite granite, also contained minor amounts of biotite, quartz, feldspar, and other igneous-type accessory minerals. This deposit is of particular interest because of the presence of scandium.

Lake Sediments

Fluorspar occurs in unconsolidated clayey and sandy pyroclastic sediments in the beds of former lakes near Castel Giuliano, about 40 km north of Rome, Italy. Fluorine of volcanic origin permeated the lake sediments, resulting in deposition of minute disseminated crystals of fluorspar, which make up as much as 50% to 60% of the clayey parts and 15% of the sandy parts of the deposits. It is accompanied by barite, apatite, calcite, dolomite, and opal.

DISTRIBUTION OF DEPOSITS AND CURRENT ACTIVITIES

Fluorspar deposits occur worldwide. The average ore grade of major fluorspar deposits that have been mined has ranged from a low of about 11% CaF_2 (South Africa) to 85% CaF_2 (Mexico). The following discussion addresses the major countries that currently produce fluorspar. The section on the United States is primarily a review of historical production and the geology of the Illinois–Kentucky Fluorspar District. Production is known to occur in other countries, such as Hungary, Iran, Romania, South Korea, and Turkey, but production is limited and information is scarce.

North America

Canada

The only large fluorspar production in Canada was from the St. Lawrence Area of the Burin Peninsula in southern Newfoundland. More than 4.2 Mt of ore was produced by underground mining between 1933 and 1978, when operations ceased. Production resumed in 1987 under new ownership, but ended in 1990 when the mining company went into receivership. In 2004, plans to restart mining as an open-pit operation were under consideration.

On the Burin Peninsula, fluorspar occurs in veins in granite and rhyolite porphyry along steeply dipping faults. The average thickness of higher grade veins is 1 to 2 m and that of lower grade veins is 4 to 6 m. Some veins have been traced on the surface for more than 2 km.

Other deposits occur in British Columbia, Ontario, and Nova Scotia. In British Columbia, the rare deposits at Birch Island, Eaglet, a group of significant occurrences north of the Laird River, and the Rock Candy fluorspar mine. The Rock Candy fluorspar mine, located 25 km north of Grand Forks, operated between 1918

and 1929, and briefly during World War II. The Birch Island deposit, 130 km north of Kamloops, contains reserves estimated at 1.8 Mt grading 29% CaF_2 , and the Eaglet deposit, located near Quesnel Lake, contains 24 Mt of ore grading 11.5% CaF_2 . In Ontario, deposits are located at Madoc and also near Wilberforce and Cobden (Andrews and Collings 1993). Between 1905 and 1961, nearly 122 kt of mostly metallurgical grade were shipped from mines in southern Ontario. The dominant fluorspar-producing area was near Madoc, where five properties—the Rogers, Bailey, Noyes, Kilpatrick, and Perry mines—accounted for 93% of Ontario's recorded fluorspar shipments. At Madoc, fluorspar occurs as small veins that have been worked principally in wartime (Kilborn Ltd. and Mineral Development Section, Ministry of Northern Development and Mines 1991). In Nova Scotia, there is the Lake Ainslie deposit on Cape Breton Island (Zurowski 1972).

Mexico

Mexico has been a major producer of fluorspar since the mid-1950s when major deposits were first developed in the state of San Luis Potosi. Production peaked in the period from 1971 to 1975, when annual production regularly reached 1.0 to 1.2 Mt. Production has varied tremendously in the period since 1975, hitting a high of 1.1 Mt in 1981 and a low of 235 kt in 1994. In 1995, production jumped to above 500 kt, and from 2000 to 2002, it averaged between 600 kt and 635 kt, according to official government statistics. In 2002, production was reported at 622 kt, including 279 kt of metallurgical grade and 343 kt of acid grade (U.S. Bureau of Mines 1955–1994; U.S. Geological Survey 1995–2004). Industry estimates put production even higher. The producing mines and mills, in descending order of production, are Cia. Minera Las Cuevas (in San Luis Potosi), Fluorita de Mexico (in Coahuila), Minera Musquiz (in Coahuila), Minerales y Productos Metallurgicos (in Durango), and Minera Ramos (in Coahuila). There are also a number of small mines that produce metallurgical grade and/or feed material to some of the larger producers.

Many types of deposits are mined. In the Musquiz District of northern Coahuila, mantos in Cretaceous limestones are most important. Northwestern Coahuila has vein deposits and replacement deposits in limestone associated with rhyolite sills and plugs. Deposits in the Paila District of central Coahuila are veins. In San Luis Potosi and adjoining Guanajuato, there are several large replacement deposits in Cretaceous limestone unconformably overlain and intruded by Tertiary volcanic rhyolites. Generally, the ore bodies occur along the contacts between intrusive rhyolites and the limestone. The largest is at Las Cuevas where the fluorite is mostly cryptocrystalline in texture and varies in color from near white through various shades of red and purple to near black. Las Cuevas has one of the largest ore bodies in the world with the highest ore grade (on average 85% CaF_2) of any major producer and is a major producer of both metspar (metallurgical-grade fluorspar) and acid-spar (acid-grade fluorspar). Numerous small-vein deposits occur in Chihuahua. Occurrences of fluorspar gangue in metal sulfide mines have provided significant production from differential flotation of the sulfide mill tailings near Parral.

United States

There are no active fluorspar mines in the United States. Hastie Mining (at Cave-In-Rock, Illinois), Seaforth Mineral & Ore Company (at East Liverpool, Ohio), and Oxbow Carbon and Minerals LLC (at Aurora, Indiana) all wash, screen, and dry fluorspar imported or purchased from the U.S. National Defense Stockpile.

Fluorspar deposits, all now idle, are known in 15 states: Alaska, Arizona, California, Idaho, Illinois, Kentucky, Montana, Nevada, New Mexico, Oregon, Tennessee, Texas, Utah, Washington, and Wyoming. They are numerous and are described in previous editions of *Industrial Minerals and Rocks* or in *Geology and Resources of Fluorine in the United States* (Shaw and Van Alstine 1976).

The bulk of all fluorspar mined in the United States came from the Illinois–Kentucky Fluorspar District, which was the source of the last major fluorspar mining operation in the United States (Ozark–Mahoning Company, closed in late 1995). For a number of years, the Illinois–Kentucky District was the world's largest producer (Baxter, Bradbury, and Hester 1973). Shipments of fluorspar concentrates of all grades during the period 1880 through 1995 are estimated to have totaled 11.5 Mt, which is probably equivalent to mine production of approximately 35 Mt of crude ore. Activity in the district is now confined to Hastie Mining.

The following is a general description of the geology and ore deposits of the district. Although vein deposits are numerous, after 1950, bedded deposits near Cave-In-Rock became the source of most of the district's output and outranked the vein deposits in terms of total district production.

Vein deposits of the Illinois–Kentucky District occur along an extensive and intricate system of faults in sedimentary rocks of Mississippian age. Most of these faults are the steeply dipping normal type, trending northeast, with displacement ranging from a few meters to more than 300 m. The most important deposits are on faults of 15 to 150 m displacement. Veins generally range in width up to 4 m and to as much as 18 m in exceptional cases. They have been mined for as much as 270 m vertically and for as much as 3 km along faults. Veins pinch and swell horizontally and vertically with the proportion of fluorspar to total vein material ranging from 0% to 100% within short distances. Near the surface, and to depths as great as 75 m, the veins contain much clay because of the dissolution of vein calcite and limestone wall rock by circulating groundwater, which leaves behind the argillaceous material originally in the limestone. Strong walls are found at depth in most places. A large inflow of water at high pressure was characteristic of the deeper mines, particularly those at Rosiclar (Baxter, Potter, and Doyle 1963; Baxter and Desborough 1965; Baxter, Desborough, and Shaw 1967).

Major replacement deposits occur in Illinois adjacent to a major structure, the Rock Creek Graben (Baxter, Potter, and Doyle 1963). These include deposits of the Cave-In-Rock District, located on the southeast side of the graben, northwest and north of the village of Cave-In-Rock, and the Harris Creek District, approximately 6 km northwest of the Cave-In-Rock ore trend and on the northwest side of the graben (Baxter and Bradbury 1989). Other replacement deposits are in Kentucky, south of Carrsville, and near Hampton, in Livingston County.

Fluorite, accompanied by sphalerite and galena in many ore bodies, is the principal mineral in replacement deposits. Quartz, barite, and calcite are common, along with pyrite, marcasite, witherite, and strontianite. Banded ore, known locally as coontail ore, is characteristic of some deposits and may be a relic from the replaced limestone or may result from rhythmic metasomatic deposition. Crude ores have 15% to 90% calcium fluoride; some contain up to 3.5% zinc and 5% lead.

Residual deposits have been less important producers but have yielded high-quality fluorspar. These gravel-spar deposits are as much as 20 m wide and extend to depths of 30 m or more. The fluorspar occurs as weathered fragments, which range from boulder-size down to that of sand grains, dispersed in a clayey matrix.

Hicks Dome, an intrusive structure in southern Illinois, has been explored for fluorspar with inconclusive results.

South America

Argentina

Vein deposits have been mined intermittently in the Sierra Comechigones, 50 km northwest of Córdoba, and some have been developed for production in the southern part of Rio Negro Province and the adjoining northern part of Chubut. In recent years, metspar has been produced from a group of veins in the Sierra Grande District of Rio Negro, including the Delta vein, reportedly with 4.0 Mt of drill-indicated ore of 51% CaF_2 grade. A small flotation mill at Valcheta formerly produced concentrates for domestic use. In Chubut, a number of veins were discovered west of Puerto Madryn. The ore was used to supply a small 10-ktpy flotation mill that was operated in Chubut from 1984 through 1990. Production was 9.1 kt in 2001 and 7.7 kt in 2002.

Brazil

Brazilian fluorspar reserves, estimated at 1.7 Mt, are located in the states of Santa Catarina (55%), Paraná (33%), and Rio de Janeiro (12%). Production in 2002 was 48 kt from three operations in Santa Catarina and one in Rio de Janeiro, divided into acid grade (68%) and metallurgical grade (32%) from a run-of-mine output of 132 kt (Peçanha 2003). In 1989, at Cerro Azul, a 55-ktpy flotation mill started operation based on output from an alkaline replacement deposit. It proved to be uneconomic and was closed in 1999. The open-pit workings were backfilled and seeded according to Brazilian environmental standards. Small-scale, intermittent production has been reported from deposits in the provinces of Rio Grande do Norte, Paraíba, and Bahia. Brazilian production was 43.7 kt in 2001 and 47.9 kt in 2002.

Europe

France

Deposits occur in the departments of Haute-Loire, Pyrénées-Orientales, Var, Tarn, Saône-et-Loire, and Puy-de-Dôme. Details have been described in a series of articles by Chermette (1972–1973, 1979).

Epithermal vein deposits occur in the Morvan, Auvérgne, Limousin, and Albi districts of the Massif Central, the Maures and Esterel districts of the Mediterranean coastal area northeast of Toulon, in the eastern Pyrénées west of Perpignan, and in the Vosges. The vein deposits contain about 50% CaF_2 , 20% silica, 5% to 10% barite, and 3% to 5% sulfides.

Stratiform deposits with about 35% CaF_2 and 15% barite occur in the Morvan District. Deposits having stratiform characteristics have been important producers in the Escaro District in the Pyrénées southwest of Perpignan. Deposits at Le Beix, Chailac, Chavaniac, and Le Maine in the Massif Central are exhausted. Fonte Sante, La Charbonnière, and Langeac have also closed. Le Burg and Montroc (near Albi) are the only mines currently active. Fonte Sante was noteworthy for the economic occurrence of sillite (MgF_2), which was blended with fluorspar when fed to an HF plant.

Société Générale de Recherches et d'Exploitation Minière (Sogerem), a subsidiary of Groupe Pechiney (now part of Alcan), is the sole remaining producer and operates mines and a beneficiation plant about 20 to 30 km southeast of Albi in the Tarn region. The ore is in silicified breccia in Cambro-Ordovician sericitic schists and averages about 50% CaF_2 with negligible arsenic, bismuth, and lead. Mill capacity is about 110 ktpy, although the flotation plant was recently upgraded and the capacity may be higher.

Germany

The former East Germany normally produced about 100 ktpy of acid-grade fluorspar, in a market insulated from outside competition. Its two principal flotation mills were located at Ilmenau-Gehren in Thuringia and at Lengenfeld in Saxony, each deriving its feed from nearby mines exploiting vein deposits. Following reunification in 1989 and the freeing of markets, these operations were noncompetitive and production ceased in late 1990 and early 1991.

Production in the former West Germany is limited to one surviving mill, operated by Sachtleben Bergbau GmbH, at Wolfach in the Schwarzwald, using ore from vein deposits in the nearby Clara mine. Acid-grade fluorspar rated capacity is about 50 ktpy, produced in conjunction with barite from two parallel veins. The barite vein averages about 48% barium sulfate (BaSO_4) with 15% CaF_2 ; the fluorspar vein has about 39% CaF_2 and 11% BaSO_4 . Fluorspar production in 2002 was estimated at about 32 kt.

Italy

Italy produced 30 to 35 kt in 2003, down markedly from about 80 kt in 1990. Mines in the Gerrei District of Sardinia are the only significant producers, producing ore from one of the world's longest and most persistent vein systems on which four underground mines have been linked along the strike into a single producing unit. The Genna Tres Montis-Muscadroxio-S'Acqua Frida vein system in southern Sardinia, near the village of Silius, is credited with 8 Mt of ore reserve averaging 40% to 45% CaF_2 , making it one of the world's largest deposits. Vein widths are 5 to 8 m. Barite and galena are recoverable accessory minerals. Underground workings have demonstrated a strike length of about 3 km. Numerous other vein deposits and a skarn deposit occur in southern Sardinia.

Nuovo Mineraria Silius SpA is now the only producer, operating a flotation plant at Assemini, near Cagliari. The plant has a capacity of about 100 ktpy of acid-grade concentrate and metspar briquettes, in addition to barite and galena concentrates. An older mill with acid-grade capacity of 40 ktpy is idle.

In northern Italy, important deposits have included Prestavel and Vallarsa near Bolzano, Torgola near Brescia, and Camerata Cornello near Bergamo, all of which are now closed.

The Pianciano deposits in the Castel Giuliano Area, 40 km northwest of Rome, consist of fluorspar that impregnates lake beds of volcanic ash (Spada 1969). The fluorspar content, ranging from 20% to 55%, was derived from volcanic emanations along with barium, strontium, and phosphorous. The fluorspar is too fine-grained to be recovered economically.

Spain

Spain is estimated to have produced about 140 kt of metgrade and acid-grade fluorspar in 1990—20 kt metallurgical grade and 120 kt acid grade, all from the Asturias region. Output remained essentially level at 130 kt in 2002.

Principal deposits are in the Asturias region of northern Spain, near the ports of Ribadella and Aviles; in southeast Spain, near the port of Almeria; and in south-central Spain, near Seville and Cordoba. Deposits are both vein and replacement bodies. Acid-grade material was formerly derived by the retreatment of old lead mine wastes in the Almeria-Berja Area. In 1980, seven companies produced acid-grade fluorspar—four in Asturias, two in the Seville-Cordoba region, and one near Berja. Grades of ore range from 40% to 45% for some of the vein mines, down to 15% to 20% in the case of the old lead mine waste. The large Oso vein in Gerona is exhausted. Weakening market conditions and competition from China have led to closure of all except one mill, located at Ribadesella and belonging to Minerales y Productos Derivados (Minersa).

United Kingdom

Among numerous fluorite occurrences in the United Kingdom, the most recent operations are located in the Southern Pennine Ore-field of north Derbyshire and in the Northern Pennine Ore-field of west Durham. Production is from fissure veins and bedded replacement deposits, together with associated old lead mine waste and tailings dumps. The deposits occur in rocks of the Carboniferous Limestone Series (Mississippian). Ore is currently mined both underground and by open pit. The deposits contain variable amounts of galena, sphalerite, calcite, barite, quartz, and iron sulfides. Some were originally mined for lead, even before written record.

Fluorspar and barite-bearing ores have been processed in Derbyshire since 1938, initially by Glebe Mines and then by Laporte Minerals. LRM Ltd. acquired the business assets of the Laporte operation in November 1999. The operation continues as a wholly owned subsidiary of LRM, renamed Glebe Mines. The underground mining operations are on Glebe Mines' property and external contributors provide ore from nearby privately owned open-pit operations for processing at Glebe's Cavendish Mill. Glebe Mines is the only remaining producer of fluorspar in the United Kingdom and supplies acid grade to both of the hydrofluoric acid producers; production in 2002 was about 45 to 50 kt and rose in 2004 to its previous output of 60 ktpy. The operation at Broadwood on the Northern Pennine Ore-field ceased producing fluorspar in 1999 and now functions as a limestone quarry.

Africa

Kenya

All production is from a single acid-grade plant, formerly jointly owned by the Kenyan government, International Minerals and Chemical Corporation, and the Bamburi Portland Cement Company, then solely by the Kenyan government from 1979 to January 1997, when it was fully privatized under entirely new management. Acid-grade production was 103 kt in 2002. In 2003, it was approximately the same, and will expand to about 135 kt in 2006. It produces concentrates relatively high in phosphorous pentoxide (P_2O_5 ; about 0.43%) from epithermal vein and replacement deposits in the Kerio Valley, about 130 km northwest of Nairobi. Ore ranging from 30% to 45% CaF_2 is open-pit mined. Concentrates are trucked 45 km to rail at Kaptagat, near Eldoret, and then 884 km to port at Mombasa.

Morocco

The El Hammam deposit near Meknes consists of two nearly vertical veins, mineralized in a fish-bone pattern at intervals along an east-west fault in sericite schist and shales. Overall length is more than 2.5 km with ore widths of 2.5 to 5 m, grading about 45% CaF_2 . The mine and the flotation plant, with a capacity of 110 ktpy of acid-grade concentrate, are operated by Societe Anonyme d'Entreprises Minières (Samine) and are owned by Omnium Nord Africain (58%) and by the Moroccan government through the Bureau de Recherches et de Participations Minières (42%). Three other deposits are recognized in this region. Other veins occur in the Djebel Tirremi area, 10 km northeast of Taourirt, in eastern Morocco (Van Alstine and Schruben 1980).

Namibia

The principal fluorspar deposits are on the Marburg farm, with lesser deposits on the adjacent Okorusu, Belvedere, and Brandenburg farms, located about 20 km northwest of Ojijwarango, which is 425 km northeast of the port of Walvis Bay. These fluorspar deposits are part of an alkalic complex that forms an erosionally broken ring

structure about 5 km in diameter. The fluorspar bodies lie mainly in the southern part of the complex where they occur, with accompanying thin magnetite cappings, as late metasomatic replacements of syenite, fenitic rocks, and carbonatite (Schneider and Seeger 1990). Reserves exceed 6 Mt, grading about 60% CaF_2 and about 5% P_2O_5 . A flotation mill, rated at 50 ktp y, began operation in 1988 under Okorusu Holdings Ltd. The mine and mill were sold to Solvay Group of Brussels, Belgium, in 1997. It is managed through Solvay Fluor und Derivate in Hannover, Germany, which instituted significant expansion of the mine and mill to provide an output of about 100 ktp y, all of which is consumed by Solvay for production of HF at Bad Wimpfen in Germany and at Porto Maghera in Italy (*African Mining* 2003).

South Africa

Fluorspar, mainly acid grade, is produced at two mine/mill operations: Vergenoeg Mining near Pienaar srivier, 80 km nor theast of Pretoria, and the Witkop fluorspar mine near Zeerust, about 250 km west of Johannesburg.

Vergenoeg Mining, which is 70% owned by South Africa's Metorex Group and 30% by Spanish fluorspar producer Minersa, has an open-pit mine in a nearly 2-billion-year-old volcanic pipe that constitutes the fluorite ore body. The ore body is hosted by the Rooiberg Group rhyolites, centrally located between the four lobes of the Bushveld Complex. The ore body has a vertical funnel-like shape about 900 m in diameter at the surface, tapering sharply at depth to where it is still open-ended below 650 m. The pipe is horizontally zoned, with a hematite-fluorite or gossan cap at the surface, below which is a deeper zone of magnetite-fluorite, then a magnetite-fayalite transition zone, and finally a fayalite zone at the deepest levels. Hematite-fluorite, magnetite-fluorite, and magnetite-fayalite assemblages make up more than 90% of the mineralogical composition. Fluorite occurs in both massive and disseminated form and is present in variable quantities throughout the pipe. The fluorite-rich part of the ore body extends to a depth of approximately 360 m. The ore grade is between 35% and 40% CaF_2 , and present mining depth is 55 m. The mine produces about 120 ktp y of acid grade and 10 to 20 ktp y of metallurgical grade (Metorex Limited, undated).

In the Zeerust District, fluorspar occurs as replacements in dolomite and in associated residual deposits. Much of the ore is disseminated in dolomite along intersecting fractures. For many years, metspar was produced by screening coarse fragments from residual surface deposits. The current operation is the Witkop fluorspar mine, a subsidiary of South African Land & Exploration Company (Sallies). The previous mine owners were selectively mining the high-grade ore, but after a thorough investigation of the ore body, new management has found it possible to maintain a target ore grade of 11%, which will prolong the life of the mine. Current reserves from the Wintershoek deposit (currently being mined) plus the company's Buffleshoek reserve total 27.5 Mt, reportedly at a final grade of 14.5% CaF_2 . The company recently purchased new mining equipment and performed extensive drilling to establish best mining practice. Additional milling and flotation capacity was added and intensive metallurgical research performed to determine the best combination of flotation collectors and depressants to improve flotation recovery. Capacity increased to 180 ktp y with improvements completed in 2004 (Lanham 2004).

The former Buffalo open-pit mine of Transvaal Mining and Finance, a subsidiary of General Mining and Finance near Naboomspruit, exploited 14% to 16% grade deposits consisting of a network of fluorspar veinlets in sill-like bodies of fine-grained, pink granite in coarse, red Bushveld granite. In 2000, International Metals Process-

ing acquired the mine and attempted to produce acid-grade product by processing feed from preexisting high-grade stockpiles and tailings dumps. Operations ceased in 2002, apparently as a result of legal problems.

Acid-grade fluorspar is exported to Australia, Europe, Japan, and North America through the port at Durban. Domestically, acid grade is consumed by African Exploratives and Chemical Industries Ltd. to make hydrofluoric acid, and the steel industry consumes essentially all of the metallurgical-grade fluorspar.

Tunisia

A former flotation mill, located at the Hammam Zriba deposit near Zaghouan, 54 km south of Tunis, produced about 30 ktp y of acid-grade concentrate from a bedded deposit in Jurassic limestone, averaging 35% CaF_2 with considerable barite. In the same general area, replacement vein deposits occur at Djebel Staa, Hammam Djedida, Djebel Oust, and Djebel el Kohol. Other deposits are at Bourchiba, Cap Bon, and Bou Ja ber. Production in Tunisia ceased in 1992, and the country now imports about 75 ktp y of acid-grade fluorspar to supply the aluminum fluoride plant of Industrie Chimique de Fluor (ICF) in Gabes.

Asia

China

This country is the world's largest fluorspar producer with a production of about 2.45 Mt in 2002, of which about 1.25 Mt was acid grade and 1.2 Mt metallurgical or submetallurgical grade. Principal deposits are in the central and northern parts of Zhejiang, in eastern Fujian, northeastern Hebei, eastern and southern Hunan, northern Guangdong, northeastern Anhui, eastern Shandong, Inner Mongolia, and Liaoning. In all, fluorspar occurrences are reported in 17 provinces.

In 2002, according to the United Nations Statistics Division, Commodity Trade Statistics Database (Comtrade), exports of acid-grade fluorspar were about 807 kt (902 kt in 2001) and exports of metallurgical grade were 200 kt (208 kt in 2001). Of the acid-grade exports, 359 kt went to the United States (344 kt according to U.S. import statistics) and 202 kt went to Japan. These figures compare to exports of 170 kt of acid grade to Japan and about 125 kt to the United States in 1990.

Acid-grade production has mushroomed with production from as many as 40 flotation mills (down from more than 80 in the mid-1990s). Some originated from conversion of preexisting mills and others from new construction. Most of the fluorspar deposits now being mined in China are veins in acidic terranes. One in De An in Jiangxi Province is a series of large replacement ore bodies.

India

At Amba Dongar, 560 km north of Bombay in Gujarat State, veins and replacement bodies occur in the carbonate wall rock around ankeritic carbonatite intrusives, similar to the occurrences at Okorusu in Namibia (Deans et al. 1972). A heavy media and flotation concentration plant has been constructed nearby at Kadipani, with a nominal capacity of 37.5 ktp y of product, of which 30% is acid grade with a high P_2O_5 content and 70% is metallurgical grade. Reserves are reported to be 11.6 Mt of 30% fluorite content, of which proven reserves are said to be 4.7 Mt (Moorthy 1997).

Other mineralized areas are reported at Chandri-Dungri in the Drug District of Madhya-Pradesh and at Mando-ki-Pal in the Durgapur District of Rajasthan.

Mongolia

The major fluorspar production site in Mongolia is the mill at Bor Undur, which is fed by four mines at Bor Undur, Khajuu Ulaan,

Ayrag, and Urgun. Fluorspar deposits occur in breccia and veins composed of fluorite, calcite, and quartz associated with Late Permian faults. Fluorspar production at Bor Undur started in 1982 as a joint venture (Mongolrostsvetmet) of the Mongolian Peoples Republic and the former USSR. Mining was followed by the construction of the flotation mill in 1985. Improvements were made to the mill beginning in 1998 that increased its capacity from 130 ktpy to 160 ktpy. Production in 2002 was reported to be about 130 kt of acid grade (95.5% to 97.2% CaF_2) and 80 kt of metgrade (75% CaF_2).

In 2003, a new joint venture was formed (Mongolia Minerals Corporation) to mine, process, and export fluorspar. They are apparently reselling acid grade purchased from Mongolrostsvetmet and producing metallurgical grade from a mill in the Ayrag region. The company is studying plans to build a flotation plant to produce acid grade and an aluminum fluoride plant to add value to its exports (Crossley 2004).

Russia

There are reportedly four major active companies in the Russian fluorspar industry: JSC Yaroslavsky, JSC Zabaikalsky, JSC Kalanguisky, and Suran Cooperative Quartz, with production concentrated in southeast Russia and Siberia. By far, the largest producer is Yaroslavsky GOK (also known as Yaroslavsky Mining and Dressing Complex), which mines the Vosnesensky and Pogranichny deposits in the Primorsky region of the Russian Far East. Russia produced 169 kt of fluorspar concentrate in 2002, of which Yaroslavsky accounted for 70% to 80%. The South-Ural and Polevskoy cryolite plants consume more than 90% of Yaroslavsky's output, but domestic production satisfies only half of Russia's needs. The balance is imported from Mongolia (Crossley 2004).

Thailand

Fluorspar deposits occur in a region extending from the northern border with Burma southward for more than 1,280 km to a point about 640 km southwest of Bangkok. Mining was concentrated in three areas: Chiangmai, Lamphun, and Mai Hong Sun provinces in the north; Kan Chanaburi, Petchaburi, and Ratchaburi provinces southwest of Bangkok; and Krabi Province in the south (Gardner and Smith 1965; Hodge, personal communication), but production has fallen to less than 5 ktpy, all from Mai Hong Sun.

Vietnam

Tiberon Minerals Ltd., a Canadian corporation, is studying development of acid-grade fluorspar production in connection with a new polymetallic mine and mill planned for start-up in 2007 in northern Vietnam at Nui Phao. The Nui Phao deposit is primarily a polymetallic intrusive skarn (tactite) and greisen ore body. The mineralization is characterized by an assemblage of tungsten-gold-copper-bismuth-fluorine-bearing minerals that occur within and proximal to a biotite-muscovite granite. Project interest is held 77.5% by Tiberon, 15% by Thai Nguyen Mineral Company, and 7.5% by Export-Import Investment Company Thai Nguyen. An exploration license on 91 km^2 is held by Tiberon. Drilling of 180 holes has indicated a resource of 88 Mt grading 0.22% WO_3 (tungsten trioxide), 8.0% CaF_2 , 0.22% Cu (copper), 0.24 g/t Au (gold), and 0.11% Bi (bismuth). Preliminary plans are to produce about 200 ktpy of low-arsenic, acid-grade fluorspar from ore mined at the rate of 3.5 Mtpy. An existing railroad crosses the property and links it to the port at Hai Phong, 160 km away (Tiberon Minerals Ltd. 2004).

Australia

Deposits of fluorspar have been found in all the Australian states except the Northern Territory (Liddy 1971) but are undeveloped

because they are small and remote. There have been investigations in the Chillagoe-Mungana-Almaden and Forsyth areas of northern Queensland, and in western Australia in the Pilbara District, 217 km southeast of Port Hedland; the Yinnietharra Area, 320 km from Carnarvon; and the Speewah Valley area 180 km southwest of Wyndham.

As reported at the 2003 Fluorspar Conference in Rome, recent activity at Speewah involves feasibility work started in August 2003, anticipating an 18-month construction program aimed at 180 ktpy production of low-arsenic acid grade.

EXPLORATION AND MINING METHODS

Because fluorspar resists chemical weathering, it can be traced in the soils of heavily weathered veins. Cleavage fragments, washed clean by rainwater or exposed in anthills or spoil piles from animal burrows, are useful clues. Silicified veins, resisting erosion, may stand up like a reef. Bedded deposits are less discernable, but, in areas of sufficient topographic relief, the outcropping edges of deposits or slumped fragments of ore may be found. Because of its softness and cleavability, fluorspar does not survive in the beds of streams and ordinarily cannot be traced by panning.

The search for bedded deposits usually involves locating a mineralized horizon and following it down dip with vertical drill holes, drilled to intersect the favorable beds. Geophysical prospecting methods are not applicable. Photogeology can be of assistance in locating and tracing structures and outcrops, and as an aid in geologic mapping to determine the areal distribution of stratigraphic units known to be favorable for veins or replacement deposits.

Geochemical methods have been employed with varying degrees of success. Fluorine anomalies have been found in groundwater and surface streams, in soil samples, and in stream sediments, but using such anomalies as a prospecting tool for the discovery of ore deposits has not been very successful. Various nonfluorine elements that can be detected geochemically can be guides to fluorspar deposits, and in soluble residues of potential host-rock limestones can serve as a sample medium (Erickson et al. 1987). Once mineralization has been detected, core or churn drill holes, prospect shafts, and drifts may be used to probe the structures.

Mining Methods

In some areas, veins may be weathered to depths of as much as 75 m. Such weathered ore, a mixture of clay and fragments of fluorspar and detached wall rock, may be mined open pit with draglines, scrapers, or power shovels to depths of as much as 50 m. Below that, underground mining methods, involving modified top slicing or overhead shrinkage stoping, are used.

Vein mining is commonly done by shrinkage stoping, cut-and-fill, and open stoping where strong walls occur. Closely spaced shrinkage stope bins may give way to widely spaced bins, with electric and air slushers being used in the tops of stopes to transport the overbreak to the ore pass. Air-operated, rubber-tired, muckhaul units can be adapted to in-stope work. Where shrinkage stoping is used, broken ore is commonly moved to the shaft by track haulage using battery-powered locomotives and 1- or 2-t side-dump cars.

With the introduction of diesel haul units of less than 1.5 m in width, mining can be changed from shrinkage stoping to ramp subleveling in veins. Loaders can be served by small diesel trucks carrying 3 to 4 t. Ventilation for the diesel equipment is usually handled by lines of woven plastic tubing. In shafts, bucket hoisting is supplanted by lifting in larger skips. In larger mines, crushers are installed over skip-loading pockets at the shaft bottom, which improves skip loading.

In bedded deposits, room-and-pillar patterns are used, with the widths of rooms governed by roof conditions. Newer equipment has rubber tires and is diesel operated, including the muck haul units—which have buckets ranging in size from 0.9- to 4.6-m³ capacity—and rubber-tired diesel trucks with 3- to 18-t capacity. Drilling is done by diesel-propelled jumbos in the bedded ore mines, but the jackleg drills are still used in narrower working places and drifts. In multileveled ore bodies, haulage ramps on 12% to 15% grades connect the levels. Vertical raises are used to facilitate ventilation requirements. Most drilling uses tungsten carbide bits, or the throw-away-type hardened steel bits. In blasting, the trend is increasingly toward the use of ammonium nitrate-fuel oil mixtures. Mine crews, supervisors, and mechanics are usually provided with diesel personnel vehicles to facilitate mobility.

Wherever widths of ore bodies, depths of overburden, economic stripping ratios, and the strength of the sidewalls permit, it is common practice to mine by open-pit methods, as is the case in Kenya and South Africa. This optimizes the obvious advantages to be gained by using lower cost explosives, large-scale earth-moving equipment, and economical quarry bench mining methods.

Methods of Beneficiation

Most fluorspar must be upgraded for marketing. The beneficiation techniques used are tailored to meet the character of the ores and the specifications for particular uses.

In countries with abundant low-cost labor, metallurgical spar with a calcium fluoride content in the range of 75% to 85% is often produced by the hand sorting of high-grade lump crude ore, followed by crushing and screening to remove most of the +10-mesh fraction. In the case of ores of lower grade, and/or ores with relatively coarse interlocking of minerals, gravity processes of concentration are used for producing metspar based on the specific gravity of spar and less than 2.80 for most gangue minerals.

Heavy media cone and drum separators are particularly effective in the size range of 0.5 to 3.8 cm, either for producing metallurgical gravel or for preconcentrating the crude ore for flotation feed. For the finer sizes, the heavy media cyclone process is frequently used. The high tonnage capacity and low operating costs of heavy media methods give very satisfactory results. The sink can be soild as metspar and the sands for flotation feed, and the float is frequently marketed for road gravel and concrete aggregate. Ores as low as 14% CaF₂ are being preconcentrated to yield a flotation feed of 40% CaF₂ or more. Lead and zinc sulfides and barite, because of their high specific gravity, concentrate with the fluorspar to enrich the flotation feed in these valuable minerals. Many ores that would otherwise be too low grade to warrant mining and processing can be preconcentrated to acceptable flotation feed grade with a tailings loss of less than 12% of the CaF₂ in the crude ore. Washing plants are also used ahead of flotation to remove clay or wad (manganese oxides) in some areas. Barite, a fairly common accessory mineral in fluorspar deposits, can be effectively separated from the fluorspar by flotation and, in most instances, made into a salable product.

Acid-grade concentrates are produced by the froth flotation process, which takes advantage of the varying surface properties of different minerals allowing separation in flotation cells. The run-of-mine ore is crushed and ground to a size that liberates the individual minerals, enabling their separation. Care is taken in grinding to avoid producing extremely fine sizes, known as slimies, which are not amenable to subsequent separation in the flotation process.

The flotation feed first goes to conditioners for reagent addition. The resulting pulp is agitated in the presence of injected air, which creates minute air bubbles that attach to the desired mineral by means of a collector reagent that is then floated off in a froth. If

sulfides are present, they are floated first by use of a xanthate collector in a circuit ahead of the fluorspar; first lead sulfide, then zinc sulfide. Next, easily floated fluorspar is collected in a rougher flotation circuit and is routed directly to the cleaner circuits. Less-easily-floated fluorspar is recovered in a scavenger circuit, and the scavenger tailing is discarded. Where necessary, middlings from up to six stages of cleaning are reground to liberate interlocking grains of fluorspar and gangue minerals. The reground product is then recycled to maximize the recovery of the desired acid-grade concentrate. Commonly used reagents include fatty acids to collect the fluorspar; quebracho or tannin to depress calcite and dolomite; sodium silicate, starch, or dextrin to depress iron oxides and silicates; and dichromates (where environmental regulations allow) to reject barite. Cyanide may be used to depress sulfides. Soda ash and occasionally caustic soda can be used for pH control. In the past, the temperature of the slurry was raised from ambient to as high as 80°C to optimize flotation performance, but the rising cost of energy in recent years has almost eliminated this procedure. Most fluorspar ores can be successfully treated at ambient temperature, even if the source of the water is from below ice, provided that a modern flotation collector containing emulsifying additives is in use.

From the final cleaner circuit, the resulting fluorspar-concentrate slurry with a pulp density of about 25% solids goes to a thickener tank where the density is raised to about 55% solids and the overflow water is recycled to the milling circuit. More water is removed when the thickened slurry passes through vacuum filters where a fluorspar filter cake, usually with less than 10% moisture, is obtained ready for shipment. In some operations, the filter cake is dried prior to shipment in bulk tankers or bags.

The International Organization for Standardization (ISO) has approved 24 standards for testing fluorspar. Some of the more important ones include the following:

- ISO 5439 Acid-grade fluorspar: Determination of a available fluorine content—potentiometric method after distillation (ISO 9503 for metallurgical grade)
- ISO 6676 Acid-grade and ceramic-grade fluorspar: Determination of total phosphorus content—reduced-molybdophosphate spectrometric method (ISO 9438 for metallurgical grade)
- ISO 9505 All grades of fluorspar: Determination of arsenic content—silver diethyldithiocarbamate spectrometric method

Other ISO standards include tests for antimony, barium sulfate, calcium carbonate, iron, lead, manganese, moisture, silica, sulfides, and sulfur. There are additional ISO standards testing other chemical and physical characteristics (ISO 2004).

Internationally traded fluorspar is usually analyzed according to the American Society for Testing and Materials (ASTM) E1506-97 (2003) standard, *Standard Test Methods for Analysis of Acid-Grade Calcium Fluoride (Fluorspar)*. This analytical standard covers the precise procedures to assay the fluorspar filtercake for silica (SiO₂), calcium fluoride (CaF₂), soluble chloride as NaCl, calcium carbonate (CaCO₃), phosphorus (P) as P₂O₅, arsenic (As), mixed oxides (R₂O₃), sulfide sulfur (S), and volatiles as moisture (H₂O).

LOCATION OF BENEFICIATION FACILITIES WORLDWIDE

It is difficult to maintain a comprehensive and up-to-date list of fluorspar flotation mills. Some are major and prominent producers that are well known in the export market; many others are small and little known outside their country of operation. In China, for example, there are so many that it is impractical to list them all, but Wei (1999) and Will and Ishikawa (2002) provided comprehensive lists in their reports.

Some of the major active flotation mills are located as follows:

Location	Company	Capacity, ktpy
Africa		
Kenya	Kenya Fluorspar Company	103
Morocco	Samine	110
Namibia	Okorusu	100
South Africa	Vergenoeg	120
	Witkop	100
Asia		
China	Various	Various
India	Gujarat	20
Mongolia	Mongolrostsvetmet	160
Russia	Yaroslavsky	200
Europe		
France	Sogerem	110
Germany	Wolfach	50
Italy	Nuovo Mineraria Silius	100
Spain	Minersa	130
United Kingdom	Glebe Mines	60
North America		
Mexico	Las Cuevas	500
	Fluorita de Mexico	115
	Minerales y Productos Metallurgicos	20
	Minera Ramos	15

MARKETING

Product Specifications

Traditionally there have been three principal market grades of fluorspar—acid, ceramic, and metallurgical. Specifications for acid grade and metallurgical grade are fairly well defined although the requirements set by individual consumers may vary in detail.

Acid-grade fluorspar is defined as containing more than 97% CaF_2 , but some manufacturers of hydrofluoric acid, both in the United States and in Europe, can use 96%, or slightly lower, if the remaining impurities are acceptable. The Russian specification for acid spar from the Mongolian flotation mill at Bor Undur is not less than 92% CaF_2 . Users specify limits for silica, calcium carbonate, arsenic, lead, sulphide sulfur, phosphorus, and other deleterious constituents. Moisture content of dried concentrates for acid and ceramic grades is usually specified to be not more than 0.10% H_2O , but in some ceramic uses, up to 1% or 2% may be required to relieve dust problems in handling bulk materials.

In the United States, the use of ceramic-grade fluorspar has declined, but it is still offered by some suppliers. There are basically two grades—ceramic no. 1 (90% to 95% CaF_2) and ceramic no. 2 (85% to 90% CaF_2)—although some former consumers of ceramic grade now use an acid grade. Some foreign fluorspar suppliers still offer ceramic grade, but because practically every ceramic-grade user has its own specifications, suppliers (foreign or domestic) may tailor their products accordingly or offer several product grades that fall between metallurgical grade and acid grade. Customers may specify limits on silica, calcite, ferric oxide, and lead and zinc sulfides.

In the United States, metallurgical-grade fluorspar generally contains a minimum of 80% CaF_2 and can range as high as

93% CaF_2 . Impurities of concern for steel customers are silica (4% to 10% maximum) and calcium carbonate (4% to 9% maximum). Standard size specifications for metallurgical-grade fluorspar gravel are 100% passing a 63-mm (2.5-in.) screen and a maximum of 15% passing a 9.5-mm (3/8-in.) screen. In markets outside the United States, CaF_2 content may be lower (depending on the country) and acceptable silica content may be higher than the U.S. specification.

Primarily in the steel industry, there was once significant usage of fluorspar as briquettes (containing varying amounts of fluorspar), but with the steel industry's decrease in consumption in the United States, this practice is no longer widespread. There may still be some fluorspar combined with other fluxing materials, such as lime into briquettes; the quantities are, however, thought to be small.

Uses of Fluorspar

Fluorspar is used to make HF (also called hydrogen fluoride or hydrofluoric acid), which is an intermediate for fluorocarbons, aluminum fluoride, and synthetic cryolite. Fluorspar is also used as a flux in the steel and ceramic industries and in iron foundry and ferroalloy practice, and it has many minor specialized uses. Hydrogen fluoride is produced by reacting acid-grade fluorspar with sulfuric acid in a heated kiln or retort to produce HF gas and calcium sulfate. After purification by scrubbing, condensing, and distillation, the HF is marketed as anhydrous HF, a colorless fuming liquid, or it may be absorbed in water to form the aqueous acid, usually 70% HF. Synthetic cryolite, organic and inorganic fluoride chemicals, and elemental fluorine are made from hydrofluoric acid. The acid itself is important in catalysis in the manufacture of alkylate, an ingredient in high-octane fuel for piston-driven aircraft and automobiles; in steel pickling, enamel stripping, and glass etching and polishing; and in various electroplating operations (Roskill Information Services 1993). The manufacture of 1 t of virgin aluminum requires about 12 to 29 kg of fluorine content in synthetic cryolite and aluminum fluoride. Through improved technology (prebaked) and recovery practices, this quantity is being lowered significantly in countries with the most advanced technology (e.g., in the Middle East); others using older technology remain at the high end (e.g., Russia; Cox 1989).

Elemental fluorine is prepared by electrolysis from potassium fluoride and anhydrous HF. Gaseous at room temperature and pressure, fluorine is compressed to a liquid for shipment in cylinders or in tank trucks. Elemental fluorine is used to make uranium hexafluoride, sulfur hexafluoride, and halogen fluorides. Gaseous uranium hexafluoride is used in separating U^{235} from U^{238} by the diffusion process. Sulfur hexafluoride is a stable high-dielectric gas used in coaxial cables, transformers, radar wave guides, and magnesium casting. Halogen fluorides have important applications, mostly as substitutes for elemental fluorine, which is more difficult to handle.

Emulsified perfluorochemicals—organic compounds in which all hydrogen atoms have been replaced by fluorine—are undergoing investigation as synthetic blood substitutes and therapeutic oxygen carriers. They transport oxygen and may be useful in treating surgery and trauma patients. Such blood substitutes would carry no risk of disease transmission, would have a shelf life of up to 2 years, and could be used in patients regardless of their blood type (Robinson 2003).

Inorganic fluorides are used as insecticides, preservatives, antiseptics, ceramic additives, and fluxes, and in electroplating solutions, antioxidants, and many other products. Boron trifluoride is an important catalyst.

Organic fluorides are volume leaders in the fluorine chemical industry. Fluorinated chlorocarbons and fluorocarbons are prepared

by the interaction of anhydrous HF with chloroform, perchlorethylene, and carbon tetrachloride, and are characterized by low toxicity and notable chemical stability. They perform outstandingly as refrigerants, aerosol propellants, solvents, and cleaning agents, and as intermediates for polymers such as fluorocarbon resins and elastomers. Fluorocarbon resins, which are inert compounds that have unusually low coefficients of friction, have found a number of applications as lubricants for parts that cannot be oiled; for example, in bearings for window-raising equipment located inside automobile doors, in small electronic equipment, for the manufacture of chemical resistant gaskets and valve parts, as pipe and tank linings, in flexible tubing and containers, and on nonstick cookware.

In the steel industry, fluorspar is used as a flux in basic open hearth (older technology, no longer widely used), basic oxygen, and electric arc furnaces where it is added to the heats in amounts ranging from 1 to 10 kg/t of steel produced. The average in the United States is at the low end of this range, and many steel plants have discontinued its use entirely. Fluorspar promotes fluidity of the slag (by reducing its melting point) and thus facilitates removal of sulfur and phosphorus from the steel into the slag. It serves the same purpose in iron foundries, where it is added to the cupola charge in the proportion of around 7 to 9 kg/t of metal melted.

In the ceramic industries, fluorspar is used to make flint glass, white or colored opal glasses, and enamels. Flint glass mixtures commonly contain 3% fluorspar. Opal glasses, containing 10% to 20% fluorspar, are used in containers for foods, drugs, and toiletries, and in ornamental glassware and laboratory and restaurant fixtures. Opaque enamels are used to cover steel stoves, refrigerators, cabinets, bathtubs, and cookware, and for facings on brick, tile, and other structural materials. Fluorspar makes up 3%–10% of the weight of the enamel. Many types of welding rod coatings incorporate fluorspar or fluorspar mixtures. Ceramic-grade fluorspar has been used in the manufacture of magnesium and calcium metals, and in the preparation of some manganese chemicals. In current industrial practice, users typically buy acid grade rather than ceramic grade and dilute it proportionately.

Ceramic- and metallurgical-grade fluorspar may be used in making fiberglass insulation, in zinc smelting, as an inhibitor of vanadium green scumming in the manufacture of buff-faced brick, and as an abrasive on certain types of sandpapers. Various grades of fluorspar are used in electric furnace manufacture of calcium carbide, in making electrodes for arc lamps, and as a bonding material for abrasive wheels, among numerous minor uses.

Metallurgical- or submetallurgical-grade fluorspar is used as a flux in cement production. It is added to the mix of cement raw materials before introduction to the rotary kiln. The addition of fluorspar saves fuel by allowing the kiln to operate at a lower temperature. It also helps produce a softer clinker product that is easier to grind, thus saving electrical energy.

Product Pricing

Published fluorspar prices, as reported monthly in *Industrial Minerals* magazine, conform to the two harmonized tariff codes for fluorspar (2529.21.0000 for metallurgical grade and 2529.22.0000 for acid grade). Prices differ by country of supply and are listed on a free-on-board (f.o.b.) basis at the country of origin or on a delivered basis to the first port of entry, which includes the c.i.f.

Historically, normal competition determined product pricing in world markets, but this pattern has been distorted by specific countries that dominated international fluorspar markets at different times. This was evident in the early 1990s, when China drove prices down to levels not seen for years. In 1994, China instigated a program of export quotas and export license fees, which added US\$9,

US\$16, and US\$20 per ton in successive rounds of bidding. These export license fees increased through the 1990s and by 2003 were more than US\$50 per ton.

China's economy has been growing at such a remarkable rate that its domestic fluorspar requirements have grown much faster than anyone could have foreseen. As a result, China has reduced its annual export quota from 1.2 Mt in 2000 to an expected 750 kt in 2004. Initially, the decrease in exports did not have a major impact on world prices, but by 2003 the supply shortage resulted in a major runup in acid-grade fluorspar prices.

Transportation

The United States is dependent on imports for the majority of its fluorspar supply. Most acid-grade fluorspar is transported in bulk to customers by rail, barge, and ship. Acid grade is shipped routinely in the form of filtercake containing 8% to 10% moisture to facilitate handling and to reduce dust. This moisture is removed by drying in rotary kilns, or other kinds of dryers, before treating with sulfuric acid to make HF. Metallurgical grade is shipped routinely as lump or gravel in barges, ships, or railroad cars. Some acid grade and ceramic grade is marketed in bags for small users and shipped by truck.

Fluorspar is shipped by ocean freight using the "tramp" market and time charters. Bulk carriers of 10,000 to 50,000 t deadweight normally are used. Participants negotiate freight levels, terms, and conditions within the limits defined by International Maritime Organization regulations.

Depletion Allowance and Duties

In the United States, the depletion allowance is 22% for domestically mined fluorspar and 14% for foreign operations of U.S. companies. There are no duties on fluorspar imported into the United States; tariffs on metspar (97% CaF_2 or less) and acidspar (more than 97% CaF_2) were eliminated in the late 1990s.

ENVIRONMENTAL FACTORS

In September 1987, the United States and 22 other nations signed the Montreal Protocol on Substances That Deplete the Ozone Layer. The Montreal Protocol and subsequent amendments mandated a freeze on production of chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and halons, and the eventual phaseout of these compounds. All three are fluorine-containing compounds. Under the umbrella of the Montreal Protocol, specific phaseout schedules have been set for different classes of compounds with different deadlines depending on the country or region. These schedules have been revised periodically as new scientific data have become available. In the early 1990s, the allocated amount of CFCs allowed for production and consumption by developed countries was reduced to 25% of the amount produced in 1986. Production of CFCs had been a major downstream market for fluorspar, and this reduction had a major impact on fluorspar production and demand. World production prior to the phaseout was about 5.46 Mt in 1989 but had decreased to 3.75 Mt by 1994. The market has recovered to some extent, but it is still about 1 Mt below its peak in 1989. This recovery resulted from the development of replacement hydrofluorocarbon (HFC) compounds designed to perform the same or similar functions as the banned CFCs. These consist of compounds such as HFC 134a, which is widely used in refrigeration and air-conditioning systems. HFC 134a actually requires more fluorspar to manufacture than the main compound it replaces (CFC 12).

The fluorspar, HF, and fluorocarbon producers face an uncertain future. HFCs have a relatively high global warming potential, and there is a push to have them phased out as part of the Kyoto

Protocol to the United Nations Framework Convention on Climate Change. This is already having an impact in the European Union, which is a strong supporter of the Kyoto Protocol.

OUTLOOK

Fluorocarbon production from HF is the single largest market that drives acid-grade fluorspar demand. In 2003, the ban on production and importation of the widely used blowing agent HCFC 141b went into effect. The expected loss of market share to nonfluorocarbon replacements will be significant. Some sources estimate that fluorocarbons will lose one half of this market to not-in-kind replacements, such as carbon dioxide, water, and pentane isomers. In North America, growth potential in the refrigerant market looks fairly positive for the next few years, and the fluoropolymer precursors market will continue to display solid growth. In Europe and Japan, however, concerns about the global warming potential of HFCs are causing the growth of non-HFC refrigerants, and fluorocarbon demand is expected to experience a negative growth rate (Will 2004). It is difficult to forecast how these mixed factors will affect fluorspar consumption. A factor to consider is that many of the replacement HFCs use more fluorspar than the CFCs or HCFCs being replaced. Overall, the North American outlook for HF demand during the next several years is for slow growth of maybe 1% per year.

Worldwide aluminum consumption is expected to increase by 1% to 3% per year during the next few years, and consumption of aluminum fluoride (AlF_3) should mirror this forecast. The strongest growth is expected in China and the Commonwealth of Independent States where the largest increases in aluminum production are expected, and where there are high consumption rates because of the continued use of older smelters. The small increase in AlF_3 consumption is expected to be met by output from fluorspar rather than fluorosilicic acid.

Growth is expected in the cement market. This market has been growing in Mexico, Central America, and South America, and metspar suppliers are hoping to duplicate such growth in Canada and the United States.

What may truly roil world fluorspar and fluorochemical markets is the emerging fluorochemicals industry in China. For the past decade, China has been the world's largest fluorspar exporter but has consumed a relatively small amount of fluorspar (mostly metallurgical and submetallurgical grades) for domestic use. This has now changed, and China is exporting less fluorspar and is actually exporting HF and lesser amounts of downstream fluorochemicals (aluminum fluoride, cryolite, fluorocarbons, etc.). Fluorochemical exports are expected to increase dramatically in the next few years. The only factor that may slow these exports is the growing demand for the same chemicals by the domestic market in China. China's aluminum industry has been growing at a rapid pace, and this requires increasing amounts of aluminum fluoride and cryolite. Fluorocarbon demand in China has increased to the extent that it may already be the largest air-conditioning market in the world. In the near term, these changes mean that other fluorspar-producing countries may find greater demand (and be able to charge higher prices) for their product as China continues to reduce its exports. In the longer term, HF and fluorochemicals plants outside of China may be unable to compete with Chinese exports and be forced to close as Chinese exports increase (Miller 2001, 2002, 2003).

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Garnet

R. Randolph Rapp

Garnet refers to a group of similar complex silicates that crystallize as rather dense, tough minerals in the isometric system. Because of the relative hardness and abundance in nature of some garnets, ancient humans used them as an abrasive material. And the deep red color of common garnet created a demand for the mineral as a semi-precious gemstone, an important niche that garnet continues to fill. Today, two members of the garnet group are used as industrial abrasives and in specialized uses as a water filtration medium.

GEOLOGY

Mineralogy

The general formula $A_3B_2(SiO_4)_3$ defines the garnet group. The most common elements filling the “A” position include calcium, magnesium, ferrous iron, or manganese. The “B” position is filled with aluminum, ferric iron or, rarely, by chromium or titanium. Although the crystal structure allows for an almost infinite number of garnet species to form, in reality, only a half dozen or so garnet minerals are commonly found in nature, and only two or three have economic significance.

Table 1 illustrates the most common garnet varieties, their chemical formulas, and some physical characteristics of each.

Between them, almandine and pyrope form a solid-state solution series. Similar series are found—at least on a theoretical basis—throughout the garnet group. Evidence from field analyses, however, suggests that “pure” examples of any of the garnets are extremely rare.

Of the minerals listed in Table 1, only the almandine–pyrope and the andradite–grossular series are common in nature. Minerals of the former series constitute nearly all of the garnet mined for industrial applications. Locally, smaller quantities of andradite are produced for select markets.

Hardness and specific gravity are the key physical properties that create utility for garnet grains and powders in industrial applications.

Modes of Deposition and Occurrence

Members of the pyrope–almandine–spessartine solid solution (the pyrope series) are common accessory minerals in acid igneous and metamorphic rocks in nearly all ancient terranes worldwide. Garnetiferous schists and gneisses are abundant in the cratonic cores and surrounding deformed belts. The garnet minerals occur as discrete grains scattered throughout the host formations and also

Table 1. Garnet types and properties

Mineral	Formula	Color	Mohs Hardness	Specific Gravity
Pyrope	$3MgO \cdot Al_2O_3 \cdot 3SiO_2$	Deep red	6.5–7.5	3.5–3.8
Almandine	$3FeO \cdot Al_2O_3 \cdot 3SiO_2$	Dark red/brown	7.5+	3.9–4.2
Spessartine	$3MnO \cdot Al_2O_3 \cdot 3SiO_2$	Brownish red	7.0–7.5	4.1–4.3
Uvarovite	$3CaO \cdot Cr_2O_3 \cdot 3SiO_2$	Green	7.5	3.4–3.5
Grossular	$3CaO \cdot Al_2O_3 \cdot 3SiO_2$	Pale green	7.0	3.5–3.7
Andradite	$3CaO \cdot Fe_2O_3 \cdot 3SiO_2$	Brownish green	6.5–7.0	3.7–3.8

occur as associated veins and pod-like masses. The hardness and resistance to chemical attack ensure that the garnet crystals survive the erosional process and are concentrated with other heavy minerals in stream placers, or in marine bar and strand deposits.

Members of the grossular–andradite solid solution (the ugrandite series) are enriched in calcium and often are formed as a result of contact or regional metamorphism of limestone-bearing terranes. The most important such occurrences are contact skarn deposits in which many sulfide mining districts are found. The garnet minerals in skarn deposits often crystallize as platy replacement bodies; discrete crystal forms are less common than in the pyrope–almandine deposits. Although concentrated in very large deposits, the lack of markets for andradite and grossular limits production to a few isolated locations, usually as a by-product of other mining operations.

Distribution of Major Deposits

In the United States pyrope–almandine garnet is found in many locations where older crystalline and metamorphic rocks occur; similar deposits are known in many areas of the Canadian Shield. A few of the more important occurrences are described in this section. Most of the garnet produced in North America comes from three unique deposits:

- The Barton Ruby Mountain mine, a hard-rock mine in New York
- The WGI Emerald Creek mine, a stream placer in northern Idaho
- The NYCO wollastonite mine in New York, where andradite is produced as a by-product

Each location serves a different market, and the relative value of the garnet production cannot be compared on a tonnage basis. In recent

years, domestic production in the United States and Canada has been supplemented by imports from Australia, India, and, to a lesser extent, South Africa and China. The increased use of imports largely reflects the economics of mining and transportation rather than insufficient domestic reserves.

United States

California. Large tailings, rich in andradite, are found in the tungsten mining areas on the eastern Sierra front. Skarn-type occurrences are common, but none were developed successfully.

Maine. A high-grade deposit of almandine garnet is located near the town of Rangely, in western Maine. The host rock is probably a granulite (andesine plagioclase with a little quartz and biotite) that locally contains more than 50% garnet crystals. Reserves are likely to exceed several million tons, but commercial development has stalled because of concerns over quartz content in the deposit and the availability of lower-cost resources elsewhere.

New York. The Barton Mines Company operates a well-established hard-rock mine on Ruby Mountain in Warren County. This area is famous for the size and purity of the pyrope-almandine crystals found in metamorphic and igneous rocks there. Many of the garnet crystals have a reaction rim of black hornblende, giving the rock an unusual appearance.

Garnet from the Barton operation exhibits a strong laminar pattern that allows the grains to fracture along predictable planes, a trait that improves performance in certain abrasives' applications.

Similar local concentrations of almandine occur throughout the region, but development is hindered because of their location in Adirondack Park and because of high operating costs relative to other garnet deposits.

Less than 100 miles (167 km) northeast of Ruby Mountain, the NYCO mine produces andradite as a by-product of high-quality wollastonite, which is used in plastics and other applications. Limited quantities of the andradite are used as a high-density water filtration medium.

Idaho. The Emerald Creek mine in Fernwood is located about 90 miles (150 km) southeast of Spokane, Washington. Under various owners for nearly 40 years, the mine currently is owned by WGI Heavy Minerals Inc.

Almandine garnet is eroded from a thick mica schist in the nearby highlands. Mountain streams transport, concentrate, and deposit the garnet in placer gravels, which average 1.0 to 1.5 m in thickness and average 10% to 15% garnet by weight.

Montana. Several alluvial andradite deposits have been identified in the Ruby River drainage system near Dillon. Archean schists and gneisses in the Tobacco Root and Greenhorn mountains are the source rocks for the garnet. At Alder Gulch, garnet has been recovered from local gold-mine tailings. The garnet-bearing alluvium is about 10 m thick and has a garnet content of less than 5%.

When lower-cost imports from India and Australia became available, the Montana deposits suffered in the marketplace, and none are currently active.

Southwestern United States. Andradite garnet associated with local skarn deposits is found in a number of mining districts in the western states. One deposit near Las Vegas, Nevada, was tested for possible use in Southern California markets, and a deposit near Carlsbad, New Mexico, currently is being evaluated. The andradite deposits generally are not well suited to supply garnet for abrasive blasting, and they must compete with lower-cost imports in many locations.

Eastern United States. Almandine garnet occurrences are found throughout the eastern United States in crystalline and meta-

morphic regions along regional orogenic belts and mountains. Several of these were in production briefly in the late 19th and early 20th centuries, but none currently appear to have potential. Most of these occurrences are described in local "rock hound" literature.

Australia

Australia is the world's leading garnet producer. At the GMA Garnet Ltd. mine, located about 100 km north of the West Australia port city of Geraldton, the deposit is an almandine-rich, elevated beach bar or strand line occurrence amenable to low-cost, open-pit mining methods. An associated dune field also is enriched in garnet. The GMA deposit is the result of two cycles of erosion and deposition, and, as a result, the garnet grains are well rounded and well sorted—traits that make the garnet especially attractive in many markets.

Small amounts of almandine are produced as a by-product at the Cable Sands heavy minerals operation in Western Australia. Several other alluvial and hard-rock garnet occurrences are known in Australia, but none are currently in operation.

South Africa

Fine-grained alluvial almandine garnet is produced as a by-product at the Richards Bay heavy minerals complex on the northeastern coast. Although somewhat limited in available size grades, the garnet is suitable for some markets and is exported to Europe.

Canada

Canada contains well over 100 known garnet occurrences, but none of these are in commercial operation because of their low grade and anticipated high mining costs. Nonetheless, several continue to be reevaluated. Chief among these are the following:

- Hutton Strand—a deposit in extreme northern Labrador, where almandine concentrations in beach terrace deposits are similar to deposits in India and Australia.
- Crystal Peak—an andradite deposit in British Columbia where a very high grade, large deposit has been isolated.
- Stralick—an almandine-rich metasomatic structure located near Sudbury. Its low grade has restricted commercial development.
- Mattawa—although several almandine deposits are located in the Mattawan Township, low grades and the high cost of hard-rock mining preclude development.

India

Almandine is a common constituent of both the granitic rocks of the interior highlands and of the heavy mineral beach and stream deposits found along the southern and eastern coasts. India has become a major world supplier of garnet for international markets because of its low production costs and its easy access to marine transport. Major producers include the following:

- V.V. Mineral—Tamil Nadu State
- Transworld Garnet—Tamil Nadu State and Andhra Pradesh State
- Beach Minerals—Tamil Nadu State
- Indian Rare Earths—Tamil Nadu State

China

China apparently has significant reserves of almandine garnet, but all of the deposits discovered to date have been hard rock in nature. While low labor costs benefit the Chinese producers, the limited marketability of hard-rock garnet and the high cost of inland and distant ocean transport have restricted access to commercial markets.

Europe

Several garnet deposits have been evaluated over the years, including several small alluvial deposits in southwestern Europe and several hard-rock deposits in northern and eastern Europe. As of this writing, there are no active deposits on the European continent.

EXPLORATION AND DEVELOPMENT

Almandine–pyrope garnet is among the most common accessory mineral found in acidic igneous terranes and in common metamorphic and metasedimentary rock assemblages. Its high specific gravity, hardness, and resistance to both chemical and physical attack ensure that garnet grains survive even the most energetic geologic environments to form recognizable alluvial concentrations. The durability of the grain makes it a useful indicator mineral for other minerals (e.g., diamonds).

Exploration for new almandine–pyrope garnet follows the usual pattern of terrane recognition based on general geological characteristics associated with acidic igneous and metamorphic rocks—and the presence of the minerals themselves. Standard techniques of stream sediment sampling for heavy mineral concentrations and geologic mapping are important. In addition, areas containing garnet and having good access are well documented because of their long history of garnet production both as a natural abrasive and as an attractive gemstone.

Exploration for andradite and grossular garnet has taken a different route. Prospectors unfamiliar with the demands of the marketplace for the almandine–pyrope varieties have explored for andradite bodies in known areas of skarn-type mineralization, and so most “new” andradite deposits are actually tailings piles from older mining operations. The only significant andradite production in North America is a by-product at the NYCO wollastonite mine in New York, where a portion of the output is sold to a niche filtration market.

Development programs typically involve delineation of sufficient resources to justify acquisition of mineral title and mining rights and anticipated capital spending. Sampling programs designed to ensure grade quality and to determine the dimensions of the deposit are critical; they are usually site specific and are a response to the market. The development activities of a small producer operating on a beach in southern India, therefore, will differ radically from those of a large integrated heavy minerals producer operating in Western Australia.

It is a common requirement for operators to produce bulk samples for commercial testing and evaluation prior to finalizing mine planning and processing design. In some cases, bulk samples may exceed several thousand tons. Development plans also include the creation of channels for sales and distribution.

MINING AND PROCESSING

Mining methods for the extraction of garnet vary depending on the geologic environments responsible for the host rock. At hard-rock locations, such as the Barton mine in northern New York, open-pit methods have been employed for decades. In China, hard-rock mining may consist of more primitive methods including hand mining.

Garnets are extracted and processed more easily from alluvial deposits. For example, at the Emerald Creek mine in Idaho, garnet is recovered from stream gravels from slots cut by backhoes or small draglines. The stream gravels are passed through a tramnel to reject the oversize, and garnet is concentrated on large wet-jigging tables. The garnet is then shipped to the mill for final processing and packaging.

Beach deposits, such as those mined in Western Australia and in southern India, lend themselves to low-cost earth-moving techniques using scrapers and bulldozers to cut and excavate benches

parallel to the trend of the beach and/or bar deposit. Because manual labor remains central to the operator's community responsibility in India, mechanized mining provides only a portion of the mine activity there.

In general, processing involves separation of the heavier garnet from lighter gangue minerals and the further separation of garnet into discrete size classes designed to meet the needs of specific markets. Following crushing (which is determined by the nature of the specific deposit or the market served), ores typically are washed to segregate material by specific gravity. Most operators employ traditional spiral classifiers for this step, some in conjunction with hydrosizers. At least one company uses flotation methods for the separation of garnet from heavy nonmagnetic fractions. Concentrates are dried and then sorted by both high-intensity magnetic and electrostatic separators. One producer that markets very fine grades for precision grinding and polishing markets also relies on wet-separation techniques for quality control. Final separation yields a product exceeding 95% garnet minerals, which usually contains less than 0.5% quartz by weight. The final production step is dry screening and classifying into marketable sizes, then packaging for sales and distribution.

GARNET MARKETS AND TECHNICAL CONSIDERATIONS

The market for almandine–pyrope-type garnet for use in abrasives is probably thousands of years old. In ancient times, garnet is thought to have been substituted for emery (corundum), and its unique physical properties established it as the abrasive of choice for certain precision applications. These factors led to the development of a “high end” specialized abrasives business, which was served by a few well-established suppliers that shipped product to markets throughout the world.

Some of these market characteristics are still in place today, but the demands of garnet markets have evolved in several directions. The markets of the 21st century bear little resemblance to those of the 20th, and the 1990s saw profound changes that continue to shape the production and sales of garnet. Because few deposits contain either the grain sizes or other characteristics necessary to serve all markets efficiently, production has become segmented. Overdevelopment in the 1990s created oversupply in many markets; it most likely will take many years for market demand to catch up to worldwide production capabilities.

For the purpose of this review, garnet markets can be divided into two broad categories: traditional high-end, technical applications that formed the early basis of the industry; and less technical, higher-volume markets for loose-grain material that forms the basis of the current market. Each is described in the next two sections.

Technical Uses

Coated and bonded abrasives (e.g., sandpaper and grinding wheels) using angular crushed grains of almandine have been in the market for generations. With the advent of harder, more aggressive media (e.g., aluminum oxide), these products have evolved into narrower, more specialized applications, but they retain an important niche in the manufacturing and woodworking sectors. In the late 1800s, the New York almandine products opened up this market and today continue to dominate the supply. The unique ability of New York garnet to fracture and break along parallel parting planes gives it an advantage over competing materials.

Finely crushed and pulverized almandine is processed and precisely sized to make optical glass polishing and lapping compounds. Historically, this market sector also was dominated by material from the New York deposits, but as television picture-tube manufacturing has grown in the Far East, almandine powder plants were established in Australia, India, and China. The advent of flat-screen TVs

has altered this market significantly. In recent years, many traditional TV plants have closed, and, as a result, the garnet suppliers have closed or restricted operations accordingly.

Demand from the coated and bonded abrasives market is expected to remain flat or to decrease slightly in coming years. And, as the use of flat screens for TVs becomes the staple, the demand for garnet powders is expected to continue its decline.

Loose-Grain Applications

Almandine–pyrope garnet currently fills three loose-grain applications: (1) abrasive blast media, (2) abrasive grains for water-jet cutting, and (3) a high-density medium in water filtration.

Abrasive Blast Media

In abrasive blast cleaning (i.e., sandblasting), grains of abrasives are accelerated under pressure to impact and clean a surface prior to application of a protective coating system. Abrasive blasting is generally thought to be the most efficient and cost-effective means of preparing surfaces prior to painting. The process yields a clean, roughened surface to which coatings will bond.

The physical traits of garnet are the basis for its use as a blasting abrasive in certain markets. The characteristics of the selected abrasive—grain size, shape, hardness, mass, chemical content, and even color—all have a bearing on efficiency and performance. Specific jobs may call for relatively large angular grains that can cut through thick coatings and layers of rust. Other jobs, such as the removal of mill scale on newly manufactured steel, require the use of hard, durable grains that are more rounded and smaller in particle size.

Abrasive blasting is a means of transferring kinetic energy from the abrasive to the surface being cleaned. As such, the specific gravity—the mass, in this case—is the most important characteristic of garnet. Heavier blast media carry more energy than lighter media and therefore should create a superior blasting agent. The specific gravity, however, must be balanced with the air stream's ability to accelerate the abrasive. Low-pressure air streams or media that are too heavy will not produce the desired effect. Garnet's relatively high specific gravity (4.0) has significant kinetic energy but makes it too heavy for low-pressure blasting.

Lastly, abrasive blasting can be a disruptive and dusty process. Some minerals used as alternative blast media have known associated health risks for the operator and create potential environmental problems on disposal. Because most garnet abrasives probably contain no heavy metals and less than 0.5% free silica, this is beneficial in the abrasives blasting market and has aided in the increased use of garnet blasting media over the past decade.

When properly prepared, the use of almandine–pyrope grains can overcome most of the apparent problems associated with other blasting media. This mineral series is hard enough to meet most needs and durable enough to minimize problems with dust at the blasting site. In North America, where low-cost silica sand is still the most widely used blasting medium, garnet has earned a small share of the market. Higher costs—three to four times more than competing materials—has prevented greater market penetration, so a sophisticated cost/performance analysis must be completed in most cases. Although many blasting contractors do not recognize the value of garnet, in countries where silica sand is banned or restricted, garnet has earned a more significant market share.

Use of andradite and grossular garnet as blasting media is rare. The less durable nature of andradite, because of its crystal structure, causes rapid breakdown and dusty conditions during blasting. It offers little technical advantage over the use of lower-cost media.

Abrasive Grains for Water-Jet Cutting

Water-jet cutting is the process of combining water under ultrahigh pressure with entrained garnet grains to cut a wide range of materials ranging from soft leather and fabric to hard steel, titanium, and other metals. It is possible to carve extremely complex shapes with computer-assisted cutter control. Water is first focused into a tight, restricted stream (usually about 0.010 in. [0.25 mm] in diameter) by passing it through a ruby or diamond orifice. The stream then passes through a mixing chamber and focusing tube. Although garnet is introduced in the mixing chamber where it begins to mix with the water stream, most mixing occurs in the focusing tube. The garnet-laden water stream exits the tube at very high velocity and is directed at the item to be cut. Almandine–pyrope garnet is excellent for this application as it strikes the necessary balance between cutting productivity and equipment wear.

Development of the water-jet market began slowly in the 1980s and early 1990s, but it has grown at a faster rate in the past 15 years. Future growth is expected to remain steady as use of this technology expands in existing areas and enters new applications that require an entrained flow of abrasives (garnet) in the water stream to cut metal, plastics, and glass. Abrasive water-jet cutting provides a tool for manufacturers faced with the task of cutting new materials such as composites and sandwiched materials that presented special machining problems in the past. Water-jet cutting also allows for flexibility and eliminates the need for flame cutting. For example, when cutting fragile materials or intricate patterns in a work piece, abrasive water-jet cutting significantly decreases the amount of distortion or breakage.

High-Density Medium in Water Filtration

Water filtration is the third market segment for loose-grain garnet. In this application, garnet—either almandine–pyrope or andradite–grossular—replaces common sand or gravel in the filter system. Sand filters trap and collect particulate matter in natural, municipal, or process waters. The use of garnet in the system provides a high-density layer that can be maintained after routine system backwashing. The relative high density of garnet allows for more rapid filtration rates and for more efficient backwashing. In addition, the durability of the garnet permits an extended life-span for the filter bed.

Besides its high density, the value of the garnet in water filtration lies in its availability in specially graded gravels, its resistance to chemical attack, and its tenacious nature. The disadvantage of garnet as a filtration medium is its higher installation cost when compared with lower-cost silica sand. Highly cyclical, this market application for garnet is presently considered to be flat. In addition, there is concern that new filtration techniques will erode the future demand for garnet in this market.

Standards for Garnet Applications

Minimum quality and technical standards are established for each garnet application. Although there are no national standards for loose-grain abrasives used in blast cleaning and water-jet cutting, the marketplace efficiently eliminates materials that perform poorly. Efforts to impose narrow screening limits on garnet producers have failed because—unlike manufactured products—mine operators are limited by the nature of the deposits. For example, beach sand deposits cannot provide coarse, angular garnet if none is present in the natural sand deposit.

Nonetheless, the industry has established some specifications and guidelines that affect the producers. Some of these are the following:

- California Air Resources Board—certifies blasting abrasives (CARB, undated)

- MIL-A-22262B—U.S. military abrasive specification (DOD 1996)
- SSPC ABM-1—industry trade group specification (SSPC 1989)
- ANSI B74—U.S. Coated Abrasive Standard (ANSI 1992)
- ISO 9001—International Organization for Standardization quality control protocol (ISO 2000)
- B100-01—American Water Works Association filter standard (AWWA 2001)

Most of these do not prevent a mining company from entering and serving targeted markets. Because of the inherent nature (or geological character) of the deposit, however, some mines are better suited to meet certain specifications. For example, the military specification for blasting abrasives imposes a limit of 1.0% crystalline silica (quartz), but this generally is not a problem for garnet producers.

Table 2 shows the size ranges of the most important garnet grades. Because there are no industry-wide standards, the ranges are subject to the capabilities and interests of individual producers.

PRICING AND FUTURE TRENDS

Over the last decade, garnet prices have declined in all markets. Inflation and increased logistics costs have contributed further to reduced returns for producers. This is the result of at least two economic factors. First and foremost, supply has grown at a much faster rate than has demand. Second, oversupply of fine grades has stimulated discounting in attempts to equalize demand at individual mine sites. As of this writing, this strategy has failed. Pricing in each market varies widely depending on the type of garnet, the grade required, the amount ordered and shipped, and the type of packaging. The estimated values of several key garnet products around the world (in U.S. dollars, free on board [f.o.b.] bagged) are as follows: North America, \$125 to \$600; India, \$60 to \$120; and Australia, \$90 to \$145.

Pricing at the user location is affected further by transportation costs, warehousing and distribution expenses, and premium pricing for small-lot orders. Real price increases, which were forecast in the 1990s, will continue to be delayed until excess capacity is absorbed or a new use for garnet causes a significant change in the pattern of demand.

Demand for garnet in both blasting and water-jet cutting was one such benchmark event. The next possible surge in demand for garnet could come from the tightening of environmental regulations and industrial hygiene requirements in the United States and Canada. Concerned groups in both countries have questioned the widespread use of metallurgical slags as abrasives. Trace metals found in these slags may constitute an environmental and/or health risk. On the other hand, slags continue to be the second largest provider of blasting abrasives in the United States—right behind silica sand. Thus, it is highly unlikely that any legislation of consequence will be passed in the foreseeable future. In addition, some U.S. authorities have considered changing regulations governing the allowable exposure limits for crystalline silica in the workplace. For further discussion on the controversy and regulations pertaining to respirable silica dust, refer to the chapter on Industrial Sand and Sandstone.

With increased defense spending, blast cleaning in shipbuilding and aircraft manufacturing is predicted to increase over the next few years, as is oil-drilling pipe cleaning, the result of more oil-field exploration drilling.

Garnet markets likely will continue to exhibit the basic two-tiered quality classification that has developed over the last 15 years. Applications demanding superior levels of product quality will continue to find material available at premium price levels. Those

Table 2. Size ranges of selected grades of garnet

Use	U.S. Mesh	Micrometers
Blast Media		
X-Coarse	16 × 20	1,200/840
Coarse	20 × 40	840/420
Medium	30 × 60	600/250
Fine	60 × 100	250/150
Jet-Cutting Media		
Coarse—Demolition	40 × 60	420/250
Standard	60 × 80	250/180
Fine	80 × 100	180/150
Filter Media		
Coarse	12 × 20	1,700/840
Fine	40 × 60	420/250
Other Uses		
Grains	36 through 280	
Powders	320 through 1,600	

applications that are less demanding will be served by the lower-cost, less technical products.

ALTERNATIVE MATERIALS AND MINERALS

Garnet is a substitute for other minerals or manufactured products in key areas of application. In abrasive blasting, it is a higher-cost/high-performance substitute for silica sand and slag. Manufactured abrasives such as aluminum oxide and steel grit offer the user alternative media at higher costs, but at levels of cutting productivity superior to those of silica sand and slag or at greatly reduced rates of material consumption through recycling. The user is presented with a wide range—if not confusing array—of choices. In the U.S. market, the mineral staurolite is yet a third choice. Produced as a by-product at titanium mineral mines in northern Florida, fine-grained aluvial staurolite is packaged and marketed aggressively as a low-cost (<US\$100 f.o.b. per ton) alternative to silica sand and slag. The small grain size makes it ideal for preparation of new steel but limits its application in more rigorous maintenance painting programs.

In water filtration, garnet is a substitute for common silica sand and gravel. Its use as a high-density mineral can be mimicked by any mineral having a sufficiently high specific gravity. Other products such as specular hematite, magnetite, ilmenite, plastics, and iron slag are used with varying success.

Almandine-pyrope garnet has proven to be the best choice for use as a water-jet cutting medium. It is hard enough (Mohs hardness of 7.5+) to ensure the efficient cutting of most industrial metals, but not hard enough to cause significant levels of equipment wear. Its specific gravity seems just right for this application while still providing maximum energy transfer. Also, producers have worked hard to meet the specifications for the water-jetting application in providing clean, well-graded products around the world. Nonetheless, research for an effective substitute for garnet is ongoing. Although media such as aluminum oxide or other manufactured “super” abrasives can increase cutting speed greatly, this is more than offset by increased component wear. Materials and forming sciences are working together to seek a superior tube construction that will allow the use of these more aggressive abrasives. If this is accomplished, it will have significant consequences for garnet suppliers.

Garnet's other specialized use as coated abrasives for fine woodworking and finished polishing powders and lapping compounds seems to be a stable, if somewhat mature, market. Quartz

sand, silicon carbide, and fused aluminum oxide are alternatives to garnet in these applications.

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Gilsonite

Bryce T. Tripp and Earl R. White

INTRODUCTION

Gilsonite, a naturally occurring solid hydrocarbon of the asphaltite group, is found in commercial quantities in the Uinta Basin of northeastern Utah, in Uintah and Duchesne counties. Gilsonite occurs in a subparallel set of straight, linearly continuous, vertical veins in a northwest-southeast trending zone approximately 100 km long by 50 km wide (Figure 1). The veins are an integral part of the hydrocarbon-rich Uinta Basin, which also contains oil shale, coal, tar sand, and other solid hydrocarbons, including wurtzilite, tabbyite, and ozokerite.

Definitions

Gilsonite occurs in disseminated blebs and in dikes (veins), sills, and fracture fillings, often in association with oil shale or bituminous deposits (tar sands). Gilsonite has a dull, black, coal-like appearance on weathered surfaces and a shiny, black, obsidian-like appearance (Figure 2) on a fresh, conchoidal to hackly fracture surface. A small amount of Gilsonite in deep parts of some veins is in a semisolid state or in the form of a liquid ooze. Gilsonite solidifies with increased oxidation of its organic compounds and loss of hydrogen (Hunt 1963). Industry at one time defined three major subdivisions of Gilsonite based on appearance and fusing temperature: selects, seconds, and jet. Selects material is very shiny, fuses from 149°C to 168°C, and tends to occur in centers of veins. Seconds are somewhat duller than selects, fuse from 152°C to 183°C, and tend to occur along vein margins, sometimes with a columnar-jointed, “pe ncillated” texture. Pe ncillated texture forms at right angles to vein walls and penetrates about 15 cm into the ore. Gilsonite also has flaky or scaly texture in some localities. A third, unusual variety called *jet Gilsonite* has a brilliantly shiny surface, is bluish black, and fuses from 199°C to 230°C (Abraham 1960). It was found only in the Cowboy vein. Gilsonite is now classified by fusing temperature in to five ranges, which are used in different applications and sell for different prices. Gilsonite from different veins or different parts of veins is sometimes mixed to achieve a product with a specific fusing temperature range.

Gilsonite was named after Samuel H. Gilson. He was not one of the original discoverers of Gilsonite, but became linked to the material through his enthusiastic search for its uses and markets, and local people began referring to the material as Gilsonite rather than by its scientific name, *uintahite* (Kretchman 1957; Covington 1964). The name *Gilsonite* was further solidified in common usage when a mining company adopted and trademarked the name.

In the late 1800s, people were uncertain about the exact nature of Gilsonite and whether it was asphaltum, coal, or mineral wax. Samples were shipped to several scientists during the 1860s to early 1880s for examination. Henry Wurtz (1869) described a sample in the Columbia College School of Mines collection and noted the similarity of this material to the grahamite that occurs in dikes in Ritchie County, West Virginia. Blake (1890) examined this same sample and determined it to be *uintahite*, an asphaltite that he had described in an earlier scientific paper (Blake 1885).

Properties

Physical and chemical characteristics of Gilsonite (Table 1) are important both for differentiating among asphaltites and determining its industrial applications.

Hydrocarbon Classification

Gilsonite is classified as a member of the asphaltite group of hydrocarbon bitumens. A wide range of naturally occurring solid hydrocarbons are somewhat similar in appearance, occurrence, and properties. Scientists began describing these materials and developing schemes to differentiate between them more than 100 years ago. Herbert Abraham (1960) developed a systematic classification scheme for hydrocarbons based on physical and chemical characteristics such as solubility, physical state (solid or liquid), fusibility, and oxygen content. Hunt (1963) slightly modified Abraham’s classification system. King, Goodspeed, and Montgomery (1963) devised a classification scheme starting with the geologic origin of the hydrocarbon. Hunt (1979) combined aspects of the Abraham classification and the King, Goodspeed, and Montgomery classification, deleted petroleum from the scheme, and subdivided some of the hydrocarbons based on their hydrogen-to-carbon ratios (Figure 3). Other proposed variations have been published in Rogers, McAlary, and Bailey (1974), Jacob (1983), Curiale (1986), and Cornelius (1987). Curiale (1986) discounted the predominantly physical/chemical approach and emphasized classification by molecular and bulk maturation data. Jacob (1983) emphasized the use of petrographic data in classifying solid bitumens. Hunt’s (1963) classification scheme is commonly accepted and is easy to apply using basic laboratory test data.

Development History

Crawford (1957) and Remington (1959) carefully summarized the fragmentary early history of Gilsonite discovery and development;

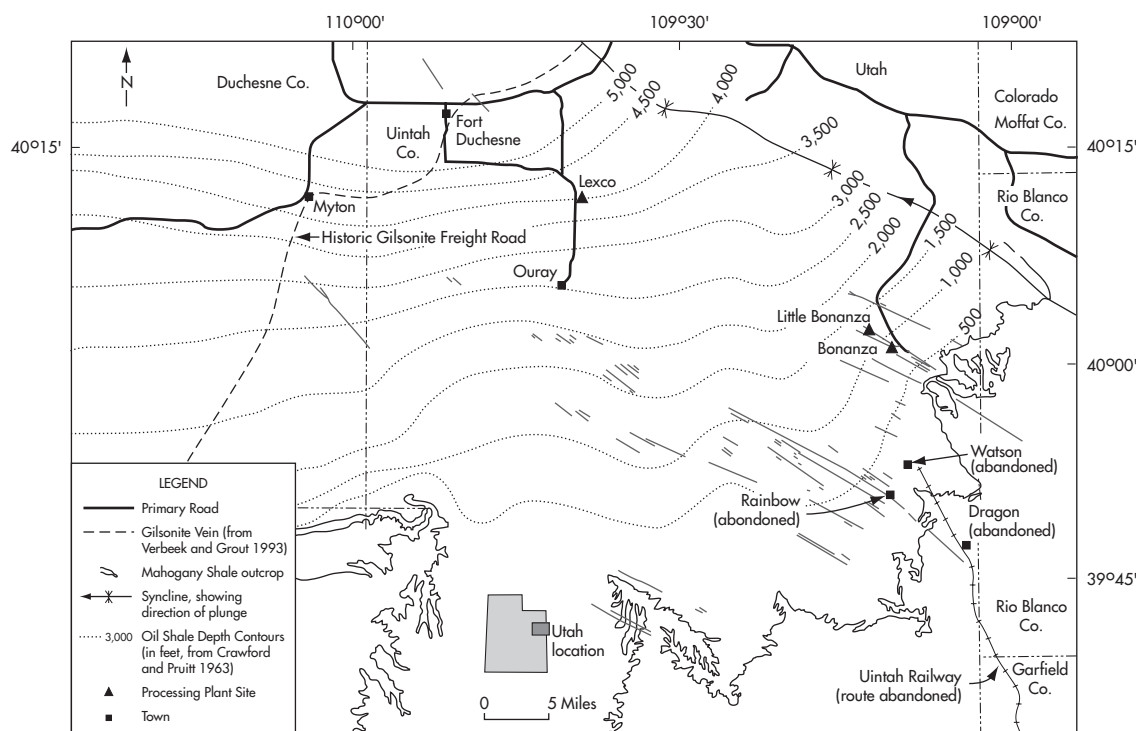
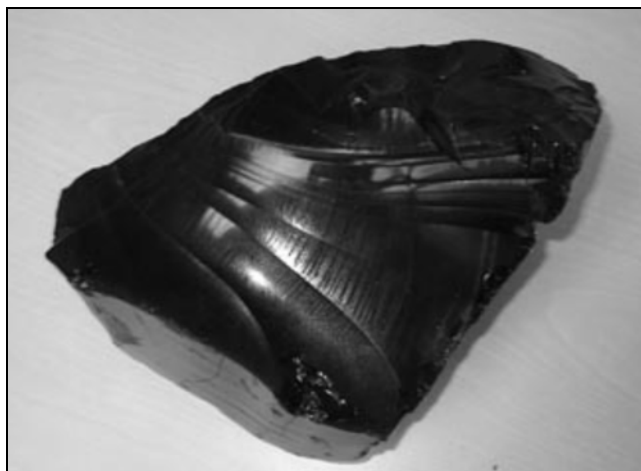


Figure 1. Gilsonite vein locations, industry facilities, and some geologic information for the Gilsonite field, Uinta Basin, Utah



Courtesy of AGC.

Figure 2. Sample showing luster and fracture of an unweathered Gilsonite sample (about 12 cm in diameter)

the following information is largely derived from their reports. Ute and other Native American tribes knew about the Uinta Basin Gilsonite and possibly used this material, but the first documented use of Gilsonite was in 1868 by John Kelly at the U.S. government Whiterocks Indian Agency. Kelly, the agency blacksmith, asked local Native Americans to help him find coal for his forge; the Native Americans collected Gilsonite, probably from the nearby Carbon vein, and brought it to him. When added to the forge, the flaming, molten Gilsonite ran out of the forge and nearly burned down the building (Remington 1959).

Though many prospectors were involved in the early discovery of Gilsonite veins, two individuals deserved the most credit for the early development of a Gilsonite industry. Samuel H. Gilson and Bert Seaboldt independently became interested in Gilsonite in 1885 and 1886, respectively. They formed a partnership in 1886 with other Utah business and mining entrepreneurs, and then incorporated on June 11, 1886, to develop seven mining claims on the Carbon vein that Seaboldt had staked on January 9, 1886. Both Gilson and Seaboldt were enthusiastic promoters of this hydrocarbon material, but Samuel Gilson (a flamboyant sheriff, rancher, horse trader, and inventor) captured the imagination of local residents while promoting the material, so they jokingly called the material Gilsonite. The name *Gilsonite* became even more established when Gilson, as a jest, offered his new partners one dollar if they would name the material and company after him. They agreed and named the company the Gilsonite Manufacturing Company and trademarked the name Gilsonite for the material.

An impediment to further development was that the claims were located on Ute tribal lands and, therefore, were technically invalid. Seaboldt and partners lobbied the U.S. Congress who agreed to remove the Carbon vein from the reservation if the Native Americans would agree to sell the land. In September 1888, the Utes ratified an agreement relinquishing 2,800 ha of land around the Carbon vein in exchange for a payment of \$49/ha. The Gilsonite Manufacturing Company mined and shipped about 2,700 Mt of Gilsonite from the Carbon vein in 1888 that sold for \$88/Mt.

A few years of rapid property consolidation followed, which are well documented by Kretchman (1957) and Crawford (1957). Gilson and partners continued to stake and purchase additional claims. Gilson and Seaboldt also became associated with Charles O. Baxter, a mining engineer from St. Louis, Missouri. Baxter incorporated the St. Louis Gilsonite Company on June 16, 1887,

Table 1. Physical and chemical characteristics of Gilsonite

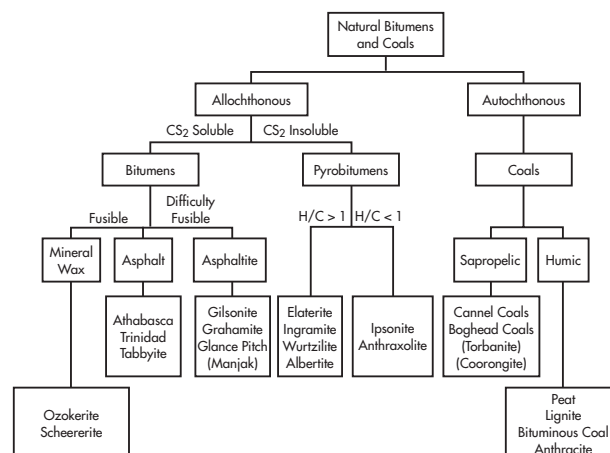
Characteristic	Value	Source
Color*	Black	
Fracture*	Conchoidal to hackly	
Luster*	Bright	
Streak	Brown	Abraham 1960
Hardness, Mohs scale	2	Abraham 1960
Specific gravity, g/cc	1.03–1.10	Abraham 1960
Bulk density, kg/m ³	641	Ziegler† 2004
Solubility in CS ₂ , %	98	Abraham 1960
Solubility in petroleum naphtha, %	10–60	Abraham 1960
Carbon, wt %	85–86	Abraham 1960
Hydrogen, wt %	8.5–10	Abraham 1960
Sulfur, wt %	0.22–0.53	Bell and Hunt 1963
Nitrogen, wt %	2.25–3.29	Bell and Hunt 1963
Oxygen, wt %	1.5	Wen, Chilingarian, and Yen 1978
Refractive index	1.59–1.64	Bell and Hunt 1963
H:C ratio	1.42–1.47	Bell and Hunt 1963
Fusing (softening) point, °C (ring-and-ball method)	161–230	AGC 2004
Moisture content, wt %	0.5	Ziegler 2004
Heating value, J/kg	4.2 × 10 ⁹	Ziegler 2004
Specific heat, 168°C	0.52	Ziegler 2004
Penetration, 28°C	0–3	Ziegler 2004
Porphyrim content, wt % (nickel complex)	0.004–0.03	McGee 1956
Molecular weight	8,130–12,300	Dickie and Yen 1967
Saturated hydrocarbons, wt %	2.4–2.8	AGC 2004
Asphaltenes, wt %	56.7–76.2	AGC 2004
Resins (maltenes, wt %)	21.0–26.7	AGC 2004
Volatile matter, wt %, dry, ash-free basis	75.2–86.5	AGC 2004
Fixed carbon, wt %	13.8–18.6	Hunt 1963
Ash, wt %	0.3–0.7	AGC 2004
Resistivity, ohm-m	1.9 × 10 ¹⁰	Neel 1980
Reflectance, % RM	0.11–0.13	Jacob 1983

* Readily observable characteristic; no source required.

† Ziegler = Ziegler Chemical & Mineral Corporation.

with Samuel Gilson apparently owning an interest in the company. Baxter and Gilson spent part of 1887 and 1888 staking and purchasing Gilsonite properties; Baxter probably spent about \$115,000 for Gilsonite property in the Duchesne area (Kretchman 1957). During this time, Baxter picked up a substantial land position along the Pariette vein. In 1889, the Anheuser-Busch Company bought out Samuel Gilson's share of the St. Louis Gilsonite Company and changed the name of the company to the Gilson Asphaltum Company (Kretchman 1957). Anheuser-Busch was interested in using Gilsonite for lining beer barrels. The Gilson Asphaltum Company also acquired all the assets of the Gilsonite Manufacturing Company for \$100,000 after September 1889, making the Gilson Asphaltum Company the largest Gilsonite company in the Uinta Basin. Baxter retained Seaboldt and other Gilsonite Manufacturing Company employees as mine operators and renamed the development on the Carbon vein the St. Louis mine.

Many other Gilsonite veins had been discovered in the basin and many were located on Ute tribe lands. Gilsonite prospecting,



Source: *Petroleum Geochemistry and Geology* by John M. Hunt. Copyright 1979, 1995 by W.H. Freeman and Company. Used with permission.

Figure 3. Classification scheme for naturally occurring bitumens and coals

among other immigrant infringements on tribal lands, led to armed conflict between Ute tribal members and U.S. Cavalry troops. Company negotiations with the Utes and federal legislation altering tribal land boundaries eventually gave Gilsonite miners clear title to the best Gilsonite veins by 1903 (Kretchman 1957; Covington 1964). The Gilson Asphaltum Company then held the largest Gilsonite resources, a virtual monopoly (Kretchman 1957). Property consolidation and resolution of remaining title conflicts cleared the way for rapid expansion of the industry.

From 1888 to about 1906, Gilsonite mined from the Carbon and Pariette veins was transported 80 to 113 km via horse-drawn wagon over a rough dirt road southwestward to the railroad at Wellington in Carbon County (Covington 1964). The round trip took 10 to 11 days. Freight added \$11 to \$13/Mt (late 1800's dollars) to the total production cost of about \$22/Mt (late 1800's dollars) (Kretchman 1957). The Gilson Asphaltum Company decided to expand production and exploit the much larger veins in the Dragon/Rainbow Area by constructing a narrow-gauge railroad, named the Uintah Railway, from the Dragon mine to the Mack, Colorado, siding on the Denver and Rio Grande Western rail line. Construction of the 85-km-long railroad started on October 5, 1903, and was finished by September 1904 (Kretchman 1957). The railroad traversed rugged country and was noted for steep grades, sharp curves, and many bridges (Bender 1970). The rail line was extended in 1911 to the Rainbow mine and the Watson shipping terminal. The transportation cost of a ton of Gilsonite from Dragon to Mack was \$11/Mt (early 1900's dollars) (Kretchman 1957). The Dragon/Rainbow Area was the major production center for Gilsonite from 1904 to 1935. In 1935 the Gilson Asphaltum Company moved its principal operations north to Bonanza, Utah, and shipped ore by truck via U.S. Highway 40 to the railhead at Craig, Colorado; the Uintah Railway was no longer needed and was abandoned in 1937 (Kretchman 1957). Transportation from Bonanza, Utah, to Craig, Colorado, in 1956 cost \$6/Mt. A plant at Bonanza processed ore primarily from the Bonanza, Cowboy, and other large veins adjacent to the plant. In 1938 the Gilson Asphaltum Company changed its name to Barber Asphalt Company (the predecessor of the Barber Oil Company).

Barber Oil Company sold part ownership in the Gilsonite operation to Standard Oil of California (now ChevronTexaco Corp.) in 1948 (Lewis 1994). The new jointly owned company was named

the American Gilsonite Company (AGC). The new company put renewed effort into a long-term research project to make gasoline and high-purity electrode carbon from Gilsonite (Kretchman 1957). Refinery design problems were solved by 1954, but a lower-cost method to transport the Gilsonite was deemed necessary to make the project feasible. After research and analysis, a 116-km-long slurry pipeline was constructed on the abandoned Uintah Railway right-of-way to a newly built (in August 1957) petroleum refinery at Gilsonite, Colorado (Kretchman 1957). The intended market for gasoline from the refinery was western Colorado, and most of the electrode carbon was intended for the growing aluminum smelting industry of the Pacific Northwest (Henderson 1957). Use of Gilsonite for refinery feedstock greatly expanded production.

In 1957, AGC started mining Gilsonite with water-jet cutters to speed production and prevent Gilsonite dust explosions; Kilborn (1964) describes the hydraulic mining technique in detail. AGC sold the refinery in 1973. Mine production declined from about 360,000 Mtpy to about 54,000 Mtpy because the refinery ceased operation. AGC reemphasized nonfuel uses of Gilsonite, and within 10 years AGC's Gilsonite production expanded to 91,000 Mtpy (Jackson 1985). In 1981, AGC replaced its 30-year-old, 4,500-Mtpm mill. The new \$6-million processing plant was designed to process 9,000 tpm of ore, be more efficient, improve product quality, and meet environmental and safety regulations (Jackson 1985). In January 1981, Chevron bought out Barber Oil's share of the business (Jackson 1985; Hawes 1990). AGC has mined ore from several mines on different veins simultaneously to supply the various grades of Gilsonite specified by customers. Softening or fusing temperature is one of the main criteria in grading Gilsonite. In 1983, AGC mined ore from 11 Gilsonite mines near Bonanza (Shushan 1983). In 1990, AGC operated five mines that yielded ore fusing at 168°C; 183°C; 199°C; 205° to 211°C; and 230°C (Hawes 1990). In 1991, Chevron sold out to Stratford Enterprises Company of Tulsa, Oklahoma (Lewis 1994). AGC is now an independent, publicly held company.

Two smaller companies have recently mined Gilsonite: Ziegler Chemical & Mineral Corporation (Ziegler) and Lexco, Inc. Ziegler, the second-most significant Gilsonite-producing company, was incorporated in 1944 as a New Jersey-based producer of pitches, asphalts, and resins. The company, then known as G.S. Ziegler and Company, purchased Gilsonite from small, independent Gilsonite producers. Ziegler decided to acquire its own Gilsonite properties, and in 1952 purchased the holdings of the Utah Gilsonite Company, which had been in operation since 1920. In 1953, Ziegler purchased some of the property of the American Asphaltum Association (a company formed in 1902 by former stakeholders in the Gilson Asphaltum Company). Ziegler purchased one other independent company during the 1949–1953 period. Ziegler additionally acquired the assets of the Standard Gilsonite Company in 1962 and renamed the combined company the Ziegler Chemical & Mineral Corporation (Lewis 1994; Ziegler 2004). The office and plant of the consolidated operations were located at Little Bonanza, Utah. Ziegler usually had produced less ore than AGC, but in 1994 it produced more than 50% of the Gilsonite mined in the Uinta Basin (Ziegler 2004).

Lexco is a relatively recent entrant into the Gilsonite business. It began operations in 1988. Lexco has a processing plant southeast of Fort Duchesne, in central Uintah County, and has mined Gilsonite from the ITM and Cottonwood mines. As of 2004, Lexco operates the Cottonwood mine, where the vein width averages 91 to 97 cm. It is not currently operating the ITM mine, where the vein width averages 46 cm and was mined in sections as narrow as 36 cm.

RESOURCES AND PRODUCTION

Eldridge (1901) estimated that five major veins in the Uinta Basin contained more than 28 Mt of Gilsonite based on field examination. Dennis (1930) quoted a figure of 45 Mt of original, in-place resource; though he does not indicate a source for this number. Cashion (1964) estimated about 41 Mt of original resource based on his extensive geologic investigations of the Uinta Basin. Neel (1980) estimated that about 4.5 Mt of minable reserves remained in the Uinta Basin, with total remaining resources of 9 to 14 Mt. Some undiscovered, probably smaller veins are likely to be added to the resource base in the future.

Gilsonite production from 1907 to 2002 typically ranged from about 9,000 to 54,000 Mtpy with a spike to 430,000 Mtpy in 1961, during Chevron's Gilsonite mining for refinery feed.

GEOLOGY

Geology of Uinta Basin Gilsonite

Gilsonite veins trend northwest to southeast through fluvial and lacustrine sediments of the Uinta Basin. The veins (Figure 1) are nearly vertical, are subparallel with other veins in the area, and are remarkable for their strike length, vertical extent, and uniformity over long distances. Vein lengths of 5 to 10 km are common. The longest vein, the Black Dragon–Rainbow–Pride of the West vein system, is 39 km long. Vein widths of 0.5 to 1.0 m are common. The widest vein, the Cowboy vein, is up to 5.5 m wide. Vein depths are controlled primarily by the depth to hydrocarbon source beds in the oil-shale zone of the Tertiary middle and upper Green River Formation. The Mahogany zone, a particularly rich part of the oil-shale beds (and a probable source bed for Gilsonite), crops out at the very southeastern end of the Gilsonite vein system, dipping gradually northwestward into the center of the Uinta Basin (Figure 1).

The veins cut across gently dipping strata ranging from early Eocene, primarily fluvial Wasatch Formation to the sequentially overlying fluvial and lacustrine, middle and upper Eocene Green River Formation; the fluvial and lacustrine, late Eocene Uinta Formation; and the fluvial, late Eocene and Oligocene Duchesne River Formation. Some Gilsonite occurs in the Green River Formation below the Mahogany zone and in the underlying Wasatch Formation. Gilsonite extends below the Mahogany at the Cowboy, Black Dragon, and Colorado (also known as the Black Diamond; it is continuous with the Weaver and Wagon Hound) veins at the southeastern end of the Gilsonite field (Pruitt 1961). The Wasatch Formation to Duchesne River Formation stratigraphic section was deposited just before, during, and just after the existence of Lake Uinta in the Uinta Basin. Fluctuations in lake level left a complex record of interfingering fluvial, marginal lacustrine, and open-water lacustrine facies. Oil shale, the petroleum source for the Gilsonite, was deposited in a shallow-water, open-lacustrine depositional setting with abundant algal growth and preservation.

The Uinta Basin is an asymmetrically structural, stratigraphic, and topographic basin. It has a steeply dipping northern flank and a gently dipping southern flank. The Uinta Basin was initiated by west-to-east compressional tectonics of the Cretaceous Sevier Orogeny. The Sevier Orogeny created extensive thrust-related mountains in western Utah and a subsiding foreland basin in eastern Utah. Subsequent early Tertiary Laramide orogenic deformation segmented the Sevier foreland basin into a series of uplifts and basins that included the Uinta Basin. The Uinta Basin is surrounded by the Uinta Mountains to the north, Douglas Creek Arch to the east, Uncompahgre Uplift to the southeast, San Rafael Swell to the southwest, and Wasatch Range to the west.

Origin of Uinta Basin Gilsonite

Geologists have studied and discussed Gilsonite's origin for more than 100 years. Verbeek and Grout (1993) give an interesting summary and critique of the numerous theories. They conclude that Gilsonite is an early derivative from the abundant oil shale in the middle and upper part of the Green River Formation, expelled under the heat and pressure of burial. Studies have demonstrated chemical similarities between oil-shale source beds and Gilsonite (Hunt, Stewart, and Dickey 1954; Hatcher, Meuzelaar, and Urban 1992). Hydrocarbon generation probably created overpressured conditions. Water, expelled under these conditions, hydrofractured the rock in an extensional tectonic setting. Later, viscous Gilsonite generated in the deeper part of the basin was forced upward and laterally along the preexisting fractures, pushing them open.

The idea that the fractures predate Gilsonite emplacement is supported by wall rock mineralization and alteration data. Thin layers of iron oxide and some authigenic quartz crystals commonly coat wall rocks, and iron oxide and chlorite fill wall rock pore space, separating wall rock from the later-emplaced Gilsonite. In some areas, calcite deposits separate wall rock and Gilsonite vein filling (Monson and Parnell 1992). Also, wall rock is often bleached along the veins. Verbeek and Grout (1993) attribute these coatings, pore fillings, and bleaching to the migration of a large volume of water through these fractures before Gilsonite emplacement.

Several types of data support the concept that Gilsonite was forcibly injected. Some Gilsonite occurs as sills, so pressure of emplacement exceeded the lithostatic load. Gilsonite also locally impregnated wall rock typically from a few centimeters up to 1 m in depth (but up to 5.5 m has been reported [Pruitt 1961]), implying high-pressure emplacement. Monson and Parnell (1992) and Verbeek and Grout (1993) studied the structural features of vein walls and found them consistent with emplacement under high pressure rather than passive filling under low pressure.

The idea that Gilsonite was intruded as viscous, plastic material is supported by observed relationships between Gilsonite and wall rock. Most notably, slabs of spalled wall rock often did not fall to the bottom of the vein but were supported in Gilsonite not far below their original point of attachment to the wall rock.

Global Asphaltite Deposits

Large concentrations of high-purity Gilsonite are rare in the earth's crust; the Uinta Basin deposits are by far the most economically significant. Table 2 lists the few other Gilsonite occurrences reported in the literature along with deposits of glance pitch and grahamite, the other two members of the asphaltite group of hydrocarbons. These two other hydrocarbons are listed because they have similar origins; they may occur in the same sedimentary basins; and, in a few applications, glance pitch and grahamite might be blended with Gilsonite or substituted for Gilsonite. Many of the deposits listed in Table 2 are of scientific interest only and have no economic value, or were mined out years ago. Additionally, identification of the asphaltite present at some of these deposits is questionable.

EXPLORATION AND MINING

Exploration and Deposit Evaluation Techniques

All of the veins mined today are considered "old" known veins because they were discovered by prospectors examining and mapping surface exposures. The veins, where exposed, have prominent surface expressions, appear as black straight bands irrespective of topography, and contrast strongly with host rocks of tan sandstone and siltstone. The veins, however, are frequently covered by allu-

vium and colluvium and may be well exposed only on ridges and in drainages, disappearing under valleys, and reappearing on adjacent ridges. Where covered, veins can often be mapped by the presence of weathered Gilsonite flakes, sparse vegetation directly over Gilsonite veins, or evidence of past mining such as the presence of headframes and shafts. The veins are straight and continuous and the regional geology is uncomplicated, making it easy to extrapolate between good exposures. Because Gilsonite is very lightweight, it is easily washed down colluvium-covered slopes, so streaks of Gilsonite float can be offset from actual vein locations by 6 m or more.

Where alluvium or colluvium covering is relatively thick, the usual exploration technique was to project the trend of a vein, and then trench or sink shallow shafts to verify location and determine the extent and quality of the Gilsonite. The current exploration practice involves angle drilling of suspected vein extensions with a truck-mounted drill rig; AGC uses a Longyear 44 rig. Planned mine site locations are core drilled to determine if minable ore exists at various depths. Drilling is important because, in the past, mines had to be abandoned soon after mining started because the ore pinched out. Before a mine begins operations, the shaft location typically is core drilled to various depths; additional drilling generally is completed 122 m along the strike of the vein on both sides of the shaft. Data collected during exploration include mining information such as vein width and wall rock characteristics and also ore quality. Quality characteristics of Gilsonite veins, particularly the melt point, viscosity, and ash content, can change rapidly along strike or with depth. This information is important for mine planning and for determining potential markets for the Gilsonite.

Because Gilsonite veins are almost vertical, it is necessary to position the drill rig at right angles to the trend of the vein and to angle the drill string so that several holes from the same drill pad intersect the vein at various depths. Typical drill intercepts are at vertical depths of 30, 91, 183, and 244 m. The driller completes most exploration drill holes with carbide button bits with a 37/8-in. diameter. When the hole is approximately 15 m from the calculated Gilsonite intercept, the driller switches to a 17/8-in.-diameter core bit to complete the hole. The core is extracted in 1.5-m segments and saved for testing. Drilling several angle holes from the same pad saves time and reduces environmental impacts; the environmental footprint of the site is generally less than 0.1 ha. Minimizing environmental impacts aids the exploration permitting process.

AGC conducted an extensive exploration and development program starting in the early 1970s, which was managed by Chevron geologists. The Rainbow, Little Emma, Eureka, Independent, Bonanza, and Wagon Hound veins were drilled. Almost all drilling was done to verify reserves, which AGC planned to mine five or more years in the future. AGC opened one mine in 2000 on reserves core-drilled in the early 1980s, and then redrilled by AGC in 1998. AGC's current practice is to drill five or six locations per year.

Geochemical and geophysical exploration methods for Gilsonite have yielded mixed results, and so none has become standard procedure. Botbol (1961) collected soil samples along a closely spaced transect across covered extensions of known veins, and then concentrated and measured the Gilsonite in the samples. The data showed that anomalously high Gilsonite content in closely spaced samples matched the expected trend of the veins.

Several questions must be answered to determine whether a Gilsonite vein can be mined:

1. Who has title to the land and minerals? A significant part of the remaining Gilsonite resource is on federal or Native American reservation lands, and leasing can be difficult.

Table 2. Global occurrences of the asphaltites Gilsonite, glance pitch, and grahamite

Country/State	Province/County/ District/Region	Location	Data Source
Gilsonite			
Canada	Northwest Territories	Pine Point mine	Goodarzi and Macqueen 1990
China	Xinjiang Uygur Autonomous Region	Ghost City, Junggar Basin	Parnell et al. 1994
Iran	Southwest Iran	Posteh Ghear Valley	Goodarzi and Williams 1986
Mexico	Veracruz State, Papantla District	Near Talaxa	Abraham 1960
Philippines	Leyte	Balite area	Palacio 1957
Russia	Archangel Province, Ukhta District	na*	Abraham 1960
U.S./Colorado	Rio Blanco County	SW of Meeker	Aurand 1920; Vanderwilt 1947
U.S./Oregon	Crook County	Near Prineville	Abraham 1960; Hodge 1927
	Wheeler County	Near Clarno	Hodge 1927; Abraham 1960
U.S./Utah	Uintah County	Uinta Basin	Verbeek and Grout 1993
Glance Pitch			
Argentina	Neuquen Province	na	Allen 1932; Meyerhoff 1948; Abraham 1960; Parnell and Carey 1995
Barbados	Conset District	Near Groves, Springfield, St. Margaret, Quinty, and Burnt Hill	Abraham 1960
Canada	Northwest Territories	Pine Point mine	Goodarzi and Macqueen 1990
Columbia	Tolima Department	At Chaparral	Abraham 1960
	Bolivar Department	At Simiti	Abraham 1960
Chile	Magallanes Territory	na	Abraham 1960
Cuba	Camaguey Province, Morón District	na	Redfield 1937, 1949
	Morón District	na	Abraham 1960
	Santa Clara Province, Sancti Spiritus District	na	Abraham 1960
	Pinar del Rio Province, Mariel District	Near Banos	Redfield 1949; Abraham 1960
El Salvador	San Miguel Department	Near Quebrada Granda	Abraham 1960
Estonia	Gulf of Finland	Near Port Kunda	Abraham 1960
Haiti	na	Near Azua	Abraham 1960
Iraq	na	Near Abu Gir	Abraham 1960
Mexico	Vera Cruz State, Papantla District	Near Talaxca	Abraham 1960
	Vera Cruz State, Chapapote District	na	Abraham 1960
Nicaragua	Chontales Department	Near Santo Tomas	Abraham 1960
Palestine/Israel	na	At Masada, and Seil-el-Modschib	Abraham 1960
Russia	Ufa Province	Near Sadinsk and Ufa	Abraham 1960
Syria	na	Near Hasbaya	Abraham 1960
U.S./Utah	Emery County	Temple Mountain	Abraham 1960
		Flat Top Mountain	Abraham 1960
Grahamite			
Argentina	Neuquen Province	na	Meyerhoff 1948; Abraham 1960
	Mendoza Province	na	Abraham 1960
Canada	Northwest Territories	Pine Point mine	Goodarzi and Macqueen 1990
Cuba	Pinar del Rio Province, Mariel District	na	Redfield 1937, 1949
	Havana Province	na	Abraham 1960
	Santa Clara Province	na	Abraham 1960
Mexico	Vera Cruz State	na	Eldridge 1901
	Papantla District	na	Abraham 1960
	San Luis Potosi State, Tamazunchale District	na	Abraham 1960
	Tamaulipas State	Near city of Victoria	Abraham 1960
Peru	Junin Department, Tarma Province	Near Huari	Abraham 1960
Trinidad	na	Near San Fernando	Abraham 1960
U.S./Colorado	Grand County	na	Kirkpatrick 1928; Abraham 1960
U.S./Oklahoma	Pushmataha, Atoka, and LeFlore counties	na	Taff 1909; Kirkpatrick 1928; Redfield 1949; Ham 1956

(Table continued next page)

Table 2. Global occurrences of the asphaltites Gilsonite, glance pitch, and grahamite (continued)

Country/State	Province/County/ District/Region	Location	Data Source
Grahamite (continued)			
U.S./Texas	Fayette County	Near Lagrange	Taff 1909; Kirkpatrick 1928; Redfield 1949; Ham 1956
	Webb County	Near Laredo	Taff 1909; Kirkpatrick 1928; Redfield 1949; Ham 1956
U.S./West Virginia	Ritchie County	na	Eldridge 1901; Redfield 1949; Abraham 1960
Unclassified Asphaltites			
Germany	Northwest Germany	Bentheim mine	Abraham 1960; Parnell et al. 1996
Turkey	Southeast Turkey	na	Lebkuchner, Orhun, and Wolf 1972; Heavy Oiler 1989
U.S./California	na	Near Santa Maria, Santa Barbara, and Asphalto	Eldridge 1901, 1903
U.S./Colorado	Costilla County	Near San Luis	Vanderwilt 1947
	Garfield County	na	Vanderwilt 1947
	na	5 miles north of Rabbit Ears Pass in the Green River Basin	Vanderwilt 1947
	na	Middle Park area	Eldridge 1901; Aurand 1920; Vanderwilt 1947
U.S./Oklahoma	na	Newark Group basins	Parnell and Monson 1995
	Latimer, LeFlore, Pittsburgh counties	na	Howell and Lyons 1959; USFS 2004

Adapted from Abraham 1960.

* na = not available.

2. Is the deposit accessible? Some unmined portions of veins are located in very remote parts of the region with concomitant high transportation costs. Additional road construction and improvements may be needed (with associated permitting costs). Trucking costs from mine to processing plant can be high.
3. Is the Gilsonite vein thick enough? The average width of veins mined to date is about 1.8 m, but veins from 46 to 51 cm wide have been mined recently (veins as narrow as 36 cm have been explored).
4. Does the Gilsonite meet minimum grade requirements? The fusing temperature of Gilsonite ore is critical.
5. Is the Gilsonite contaminated with broken wall rock? In some cases, excessive wall rock contamination prevents the mining of some of the vein.

Mining and Transportation

Three companies produced Gilsonite in 2004. AGC produced from six mines on four veins (two on the Eureka, two on the Wagon Hound, one on the Independent, and one on the Bonanza). Multiple mines operate simultaneously to yield material for various uses. Gilsonite from certain mines may meet requirements for specific uses, or different grades of Gilsonite from two or more mines may be blended to meet customer specifications. Mine planning is completed for each year based on business forecasts for four major markets: oil-field uses, foundry applications, asphalt, and inks. Ziegler produced from mines on several veins, and Leeco produced from the Cottonwood mine on the Cottonwood vein.

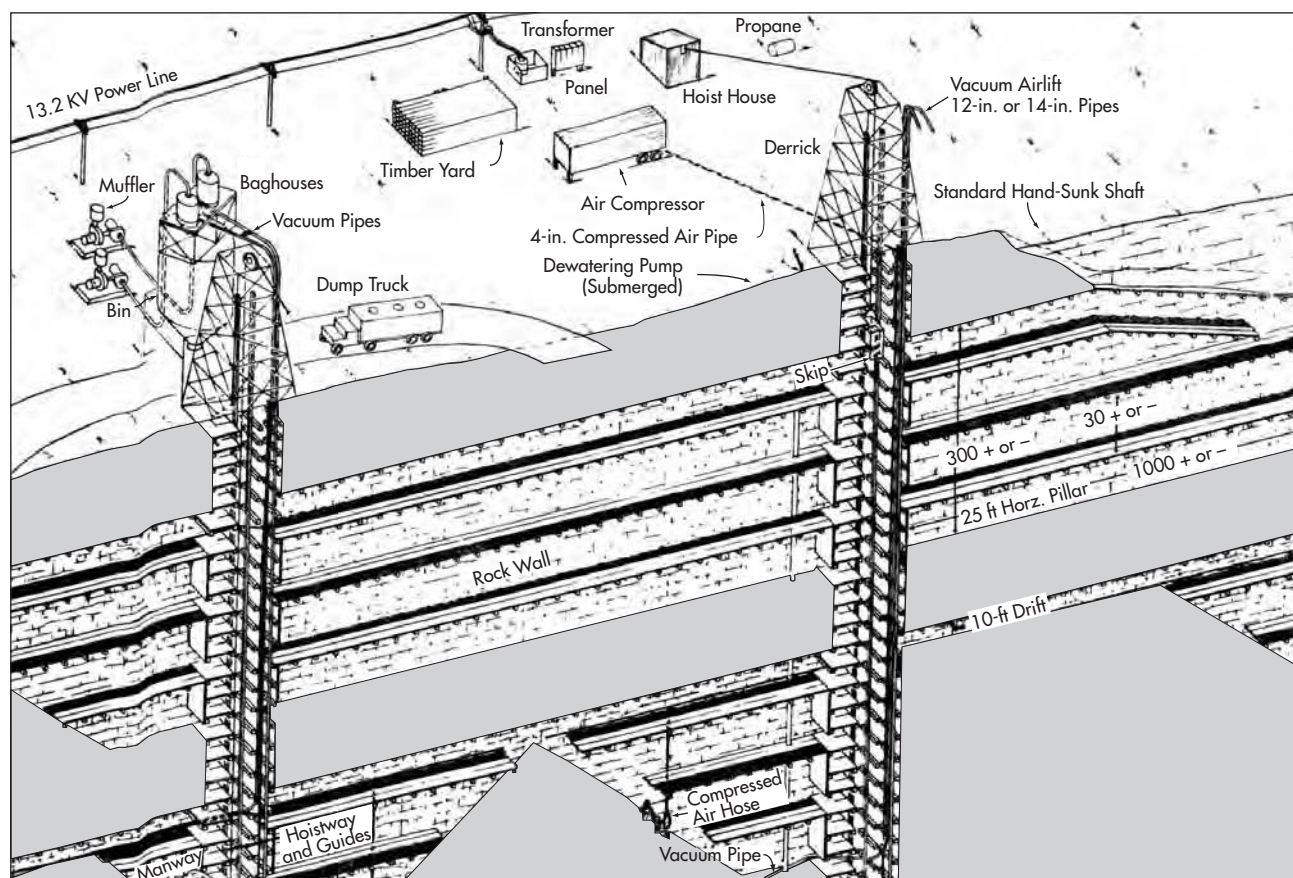
Early mining consisted of deep trenching along veins by hand using sharp picks, bagging the broken ore in 90-kg cloth bags, and hoisting the ore to the surface using a wooden headframe and horse power or, later, tractor power. Explosives commonly were not used because of the risk of explosion from Gilsonite dust. All Gilsonite produced today from the Uinta Basin is collected by underground mining methods (Figure 4). Mining consists of two major phases: shafts are sunk at regular intervals along the veins, and drifts and

slopes are then extended laterally from the shafts. The surface Gilsonite of the vein is not mined; a surface pillar with a minimum thickness of 9 m is left between shafts.

Mining begins with main shaft development either by hand sinking directly into the ore or by drilling the shaft with a Teton drill rig that has a large-diameter (2.1-m) bit. The method selected depends on the width of the vein at the surface and at depth. Hand sinking is preferred if the vein is at least 0.6 m wide at the surface because it yields saleable Gilsonite. Shaft drilling contaminates the Gilsonite with wall rock; it is, however, sometimes necessary on veins that, on outcrop, are too narrow for hand mining but widen at depth. The Eureka vein outcrops usually are narrow, but the vein widens with depth; therefore, the large-diameter drill is used to develop a shaft down to the depth where the vein is at least 1.2 m wide. Once this width has been encountered, shaft sinking continues by hand. Drilled sections of shafts are usually about 67 m deep. Shafts developed in the ore body are typically 8 m long. All the shaft support equipment, including landings and guide rails, is installed in conjunction with hand sinking. The shaft contains three compartments: two outside compartments contain pipes for the air-lift and compressed air, and a central compartment contains a skip for miners.

Once the main shaft has been developed to a depth where the ore is wide enough for mining and is at least 9 m below the surface, a drift is started in one or both directions from the shaft. These drifts extend 152 to 213 m from the shaft and serve as the escapeway drifts for the initial phase of mining. When the initial drifts are complete, a small escapeway shaft is raised to the surface or is drilled if the distance from the surface to the escapeway drift is more than 15 m. Where the ore width is insufficient to conduct shaft raising or sinking in the vein, an escapeway shaft is drilled to intersect the escapeway drift.

Recently, AGC changed its mining methods by sinking the main shaft to the bottom of the ore deposit, and then developed the initial drifts at this lower level, extracting ore from the bottom to the top of the mine. The major benefit of this method is reduced



Courtesy of AGC.

Figure 4. Schematic cross section through a typical vein Gilsonite mine showing development of underground workings and typical surface facilities

maintenance of the shaft and escapeway. After the ore has been extracted from the lower levels, those portions of the drifts and shaft no longer need to be maintained. If mining is conducted from the top of the mine to the bottom, all drifts and shafts must be maintained for the life of the mine.

In 1963, AGC began using a 1.5-m-diameter drill rig to drill shafts on Gilsonite veins. This prototype reverse-circulation rig used water as a drilling fluid, featured reversible rotation direction, and had an average drilling rate of 9 m/hr in Gilsonite and 0.9 to 1.2 m/hr in sandstone wall rock (Kilborn 1964). AGC currently uses a similar rig with a 2.1-m-diameter bit and an airlift system to remove drill cuttings through the drill stem.

Gilsonite slope mining usually is initiated by developing two drifts, 30 vertical m apart, from the main shaft to the escapeway shafts. Development can take place along strike in both directions from the shaft. Once these drifts are completed, mining begins on the floor of the upper drift downward, creating a 45° slope angle. This slope is extended along the upper drift until the bottom of the slope reaches the lower drift, creating a slope in the ore body, which is approximately 43 m long. Mining progresses from the bottom of the slope, which is the lower drift, to the top of the slope, which is the upper drift. A miner using a chipping hammer cuts a 1.2-m-high bench on the bottom of the slope. The miner then cuts this bench up the 45° incline to the top of the slope. As the ore is cut with the chipping hammer, it slides down the slope and is directed into the

airlift that conveys the ore to the surface. In a 1.5-m-wide vein, each bench mined up slope yields 79 Mt of production. These benches are mined until the slope reaches the escapeway shaft. The remaining triangle of ore is mined from the top to the bottom of the slope so that a straight face of ore is left.

The Gilsonite ore usually is mined using industrial pneumatic chipping hammers that weigh approximately 5.4 kg and are equipped with 30.5-cm-long, hardened steel moils. Compressed air for the chipping hammers comes from a 112-kW air compressor on the surface via a 7.6-cm-diameter steel pipe down the shaft to the working face (Jackson 1985). On occasion, permissible explosives will be used if the ore is particularly hard to mine.

The nearly vertical attitude of Gilsonite veins requires setting mine timbers in the following manner. Mine timbers are placed on 1.5-m centers to provide ground support in Gilsonite mines. The timbers used in the shaft and on working floors are "hitched" into holes approximately 5 cm deep and slightly larger than the diameter of the timber and are locked into these hinges with wooden wedges. With the support resting on the 5-cm-wide rock ledge of the hitch, the timber will remain in place regardless of shrinkage. Timbers that are set only to control the wall rock are not hitched but are placed on 5 × 25 × 30 cm cap boards on each end and then wedged tightly into place.

AGC conveys the mined ore from the shaft, drift, or slope by means of an airlift system (made possible because of the relatively

low density of Gilsonite). Each system usually is equipped with three centrifugal fans, each powered by a 75-kW electric motor. The Sprout Waldron centrifugal fans are arranged in series and together develop a vacuum of 140 in. of water gauge. The fans are connected to a 30-cm-diameter, steel airlift pipe, which is connected to a baghouse and bin arrangement. The airlift pipe extends from the baghouse into the mine. The capacity of the airlift system partially controls depth of workings and distance between shafts. The airlift system can efficiently transport Gilsonite in 335-m-deep shafts with 213-m-long drifts, but performance decreases if these distances are exceeded. The airlift system performs three additional functions: (1) it ventilates the mine; (2) it breaks the ore into smaller fragments (Gilsonite fractures easily during mining and transport); and (3) it removes the small amount of water that percolates into the mine. Occasionally, large inflows of water require pumping by 37-kW, staged pumps. Although the airlift system is expensive to operate, it is a versatile and proven technology.

Additional mechanization of Gilsonite mining has been limited by the following:

- Lack of equipment designed to operate in narrow veins
- The highly explosive nature of Gilsonite dust that complicates use of explosives and diesel-, gas-, and electric-powered equipment
- The need to prevent contamination by wall rock fragments, which favors careful hand mining of the ore

Despite these constraints, AGC experimented with several mechanical mining systems. During the 1950s and 1960s, AGC tried two methods of hydraulic mining and the use of a tunnel-boring machine (Kilborn 1964; Dewey 1965). Pneumatically powered "jet-cutting cars" mined horizontal benches underground using 13,800-kPa water jets to fracture the ore, which was then pumped from a sump to the surface. AGC later tried vertical hydraulic mining. Pilot holes were drilled vertically through the vein to intersect a drift at depth. A water-jet cutting bit was attached to the end of the drill string in the mine drift and the drill rig then reamed upward along the pilot hole, breaking the Gilsonite, which then fell to the drift below (Kilborn 1964; Dewey 1965). Neither hydraulic method has been used recently, in part because AGC no longer transports ore via a slurry pipeline. Drying the wet ore at the processing plant obviously is costly. AGC also experimented briefly with a tunnel-boring machine that drilled a 340-m-long tunnel in the Cowboy vein. It could mine Gilsonite at about 4.6 m/hr.

In September 2003, AGC contracted with a machine manufacturing company in Mt. Storm, West Virginia, to build a continuous mining machine. The unit is powered by a hydraulic power pack at the surface. A pressure hose and a return hose are threaded down the shaft and through the drift to the machine's location. The machine has a cone-type cutting head fitted with carbide-tipped bits and generally rides over the top of the 30-cm airlift pipe. Controls are similar to those of a normal backhoe. The unit is trammed forward or backward by activating hydraulic motors attached to steel tracks. A cutting drum is attached to a boom, which has horizontal and vertical movement along with boom extension. The cutting drum also is fitted with an additional hydraulic ram that allows the drum to move vertically. The machine was delivered in February 2004 and was immediately installed in the Eureka vein on drift development. This piece of equipment has doubled productivity.

PROCESSING AND PACKAGING

AGC hauls mined ore to a processing facility in Bonanza, Utah. The plant was rebuilt in 1981, effectively expanding its capacity to 109,000 Mtpy (Lewis 1994); the basic design, however, has not changed. Ziegler processes ore at its plant in Little Bonanza,

Utah, and Lexco processes Gilsonite at its plant southeast of Fort Duchesne, Utah.

Gilsonite from the AGC mines is hauled to the plant by 15-t dump trucks and is discharged into specific bunkers for each mine. Front-end loaders move the material from these bunkers into one of three bins. A drag conveyor moves the Gilsonite from the bottom of the bins onto a 1/4-in. screen where rock and mine debris is removed. Gilsonite is very friable, and 99% of the ore is broken to 1/4 in. by mining and transport. A drag conveyor moves the Gilsonite from the screen to a fluid-bed dryer where the coarse fraction (+65 mesh) and fines (-65 mesh) are separated. The plant was designed with five 1,400-t concrete silos that hold specific products such as oil-field products and foundry-grade material. The fines and coarse fraction are delivered to specific silos by pneumatic conveyance and by drag conveyors, respectively. About 15% to 20% of the Gilsonite is pulverized for use by the oil-field, ink, and foundry industries.

Gilsonite is withdrawn from the bottoms of the silos and discharged into one of two packaging bins. These bins serve two 23-kg paper-sack packers, two bulk-bag packers, and the bulk ore bin. Products are packaged, palletized, and shipped or warehoused according to customer specifications. Currently (2004), about 15% of the Gilsonite is shipped in bulk and 85% is packaged. About half the packaged material is in 23-kg paper sacks and half is in 907-kg supersacks. A small amount is packaged in smaller bags. Quality assurance testing is performed at the Bonanza plant, and a certificate of analysis is included with all orders. AGC ships all the products produced at Bonanza by common truck carriers.

Additional processing at the Bonanza plant includes blending different grades of Gilsonite; adding surfactants and dispersants to some specialty products (such as Bore-Plate); and solvent extraction, filtering, refining, and flaking of a refined resin product (ER Resin) for the printing ink industry. Users can also process the Gilsonite during product manufacture (e.g., filtering out grit during the manufacture of ink).

MARKETING

Uses

Gilsonite has an extremely wide range of uses; these uses have changed over time with new technology and industrial needs. Kemmerer (1934), Carey and Roberts (1949), Davis (1951), Kretchman (1957), and Remington (1959) give good summaries of past Gilsonite uses, and current uses are discussed in the following subsections.

Oil Well Drilling Mud Additive

For many years, Gilsonite has been added to drilling fluids to stabilize boreholes through shaly stratigraphic intervals, preventing borehole enlargement. Gilsonite plugs microfractures, bedding plane voids, and pore spaces and forms a thin film on the borehole wall. Gilsonite is added at about 1 to 3 kg per barrel of drilling mud (Davis and Tooman 1989). Gilsonite also reduces drill string torque and drag, and thus reduces the likelihood of stuck drill strings (J & J Specialty Products Inc. 2003). Bore-Plate, a specialty product for this application, is a mixture of Gilsonite grades (75% to 85% of the formula), surfactants, and dispersants designed for use in water-based oil well drilling fluids (AGC 2004).

Oil Well Cementing

Gilsonite is added to oil well cement for use in primary cementing of lost-circulation zones in surface, intermediate, and production pipe. It also is used for secondary cementing such as squeezing, recementing above inadequate fill-up, and plugging back to reestablish drilling fluid circulation (Slagle and Carter 1959). Gilsonite is used because of its low density, low water absorption, chemical inertness,

mechanical strength, granular nature, and minor deformation under high pressure. These properties allow Gilsonite to effectively enter, bridge, and seal lost-circulation zones. Typically 11 to 23 kg of Gilsonite is used per sack of cement (AGC 2004).

Asphalt Pavement Binder Modifier

Powdered Gilsonite is added to asphalt paving mixes to improve pavement performance. Gilsonite (1) increases stiffness and viscosity of the binder; (2) improves load-bearing capacity and reduces highway rutting; (3) improves ductility and resistance to low-temperature cracking; (4) increases durability of the pavement; and (5) improves workability of the mixture during paving. Typically 5% to 15 % Gilsonite is added to the mixture's binder (Asphalt Associates Limited 2003).

Asphalt Driveway Coater/Sealer

Asphalt preparations of Gilsonite, solvents, and other additives are used to coat weathered asphalt driveways, playgrounds, and other asphalt surfaces to improve appearance, reduce water infiltration, and slow deterioration of the asphalt pavement (Tamko Roofing Products 2003).

Built-up Roofing Component

Gilsonite is added to roofing asphalts. The compound acts as a waterproofing agent and as an adhesive that binds layers of roofing felt together.

Foundry Sand Additive

Gilsonite is an additive in sand mixtures used to make molds for casting gray iron and pig iron. Adding Gilsonite makes a better mold that imparts a smoother finish to the cast piece and is easier to remove from the cast item (AGC 2004).

Paint Component

Gilsonite is added to bitumen-based paints to increase hardness, adhesion, UV stability, and water and chemical resistance. Gilsonite paint formulations are often used on automobile frames and radiators. Gilsonite is also an ingredient in wood stains (AGC 2004).

Ink Component

Gilsonite and Gilsonite resin, derived by solvent extraction of raw Gilsonite, are used as carbon black wetting agents for black news ink and heatset and gravure ink. In addition to wetting and dispersing the carbon black pigment, Gilsonite or Gilsonite resin binds the pigment to the paper, yielding high-gloss print that resists rubbing off. Gilsonite can be mixed with other natural and synthetic oils, resins, and other additives to yield ink suitable for different types of printing presses and printing applications. Gilsonite typically comprises 2% to 5% of ink formulations. Refined Gilsonite resin is used in offset printing ink in concentrations of 15% or more to replace more expensive resins (AGC 2004).

Miscellaneous Applications

Gilsonite is used as an organic fuel in fireworks; for manufacture of high-purity carbon electrodes in the nuclear industry; as a binder in metallurgical additives and refractories; and in manufacture of contact and hot-melt adhesives, friction products, and pipe coatings (AGC 2004).

Geographic Distribution of Users

Locations of sales agents and distributors for AGC and Ziegler Gilsonite illustrate the global market distribution (AGC 2004; Ziegler 2004). Company-owned sales offices typically handle dis-

tribution in North America. The following list tabulates distributors by region:

	AGC	Ziegler
Asia/Middle East/Oceania	20	9
Europe	16	8
Central/South America	9	3
Africa	1	1

Product Pricing

The price of Gilsonite products depends on customer specifications, quantity ordered, type of packaging, sizing of material, chemical modifications of Gilsonite, industrial demand, competitor pricing, substitution of other materials in Gilsonite applications, and government regulatory mandates. Price ranges by application for 2004 were as follows (AGC 2004):

Industry Sector	Price Range, \$/Mt
Foundry molds	275–440
Oil well drilling and cementing	330–2,000 (Bore-Plate)
Asphalt and paving	500–660
Chemical products	550–1,000
Inks and paints	1,700 (ER Resin)

The most highly modified, value-added Gilsonite products are ER Resin and Bore-Plate. ER Resin is derived from raw Gilsonite by solvent extraction and refining, and sells for several times more than raw Gilsonite. Bore-Plate is a mixture of Gilsonite grades with added surfactants and dispersants designed for use in water-based oil-well drilling fluids to stabilize shale intervals in wells and to seal loss zones (AGC 2004). Bagging and pulverizing add about \$110/Mt and \$44/Mt, respectively, to each Gilsonite grade.

OPERATING COSTS

The costs to mine, process, package, and ship Gilsonite range from \$88 to \$770/Mt. These costs are directly related to mining conditions (vein width, ground control, royalty payments, and other factors); beneficiation requirements (adding special chemicals or other minerals to Gilsonite, sizing, blending, pulverization, and other requirements); and packaging requests (such as packaging into special types of bags).

LEASING, PERMITTING, AND RECLAMATION

Gilsonite producers rely on access to Gilsonite deposits on private, state, and federal lands. Before 1920, Gilsonite was considered a locatable mineral. Mining claims could be filed on federal lands (including lands that were surveyed and later transferred to the state), and patents were issued if mineral discovery requirements were met. For Gilsonite, these claims were issued for land 150 ft on either side of the vein and 1,500 ft long along the strike of the vein.

The Mineral Leasing Act of 1920 terminated the locatable mineral status of Gilsonite on federal land. Gilsonite on state lands has been by lease only since the land was surveyed and transferred to the state from the federal government. All leasing is done on a bid basis, and the successful bidder must pay annual production royalties of 10% of the sales price on both state and federal lands. Operators are allowed to deduct some beneficiation costs from the sales price to determine an adjusted sales price for calculation of the federal royalty. The federal government also charges an annual rental of \$1.24/ha. The Utah School and Institutional Trust Lands Administration (SITLA) manages the bulk of Utah state lands. SITLA charges a minimum annual rental of \$2.47/ha, but it can be higher and advanced minimum royalties can be imposed. All annual rentals and annual minimum advanced royalties can be

deducted from annual production royalties for the year in which they accrue. The leased lands are typically described by $\frac{1}{4}$, $\frac{1}{4}$ sections; in some cases, however, these 40-acre parcels are placed contiguously to describe larger lease areas. Those wishing to obtain a Gilsonite lease from SITLA must nominate the desired parcel for inclusion in SITLA's quarterly, competitive lease sale. Lessees are required to submit quarterly production reports.

The Utah Division of Oil, Gas and Mining (UDOGM) regulates exploration and mining on state, federal, and private lands. Exploration and mining plans must be approved by UDOGM and the federal or state agency that has jurisdiction over those lands. As of 2002, a UDOGM exploration permit requires a flat application fee and a reclamation bond based on the estimated number of acres disturbed during exploration. An annual exploration report is required at the end of the project or year's end, whichever comes first. Mine permit applications have two sets of rules based on estimated surface area to be disturbed; large mine permits govern disturbances of more than 5 acres and small mine permits govern disturbances of less than 5 acres. A small mine permit requires a flat application fee, a minimal permit application form, and a reclamation bond, but does not require a detailed reclamation plan. It also requires an annual report and an annual fee that is paid on a fiscal-year basis. A large mine permit requires a flat application fee, a more extensive mine permit application that includes a mine plan, and a detailed reclamation plan and bond. It also requires an annual report and an annual fee paid by fiscal year.

The U.S. Bureau of Land Management (BLM) manages exploration, leasing, and mine permitting on federal leases. There are two ways to initiate a lease through BLM:

1. In known Gilsonite resource areas, an applicant can obtain an exploration license. This requires (1) an exploration plan, (2) a fee, (3) a published invitation to others to participate in the exploration (applicants negotiate their own financial arrangements), and (4) a report at the end of the exploration. Applicants may then request that the land be competitively leased. On known Gilsonite resource areas, applicants also may request that the BLM competitively lease the land without first having an exploration license.
2. On land with no known Gilsonite resource, an applicant can request a prospecting permit; if valuable minerals are found, the applicant can apply for a preference rights lease that is good for 2 years. A report is required at the end of prospecting.

Once the applicant obtains a lease, several conditions must be met. The applicant must (1) file a mining and reclamation plan, (2) post a reclamation bond, (3) pay production royalties of 10% less some deductions, and (4) submit a quarterly production report listing ore mined and ore sold. Any exploration, construction, or mining requires an "impact assessment" to meet the requirements of the National Environmental Policy Act. The Antiquities Act, the Endangered Species Act, and other environmental impacts are addressed in the impact assessment. AGC, for example, uses 1.5 to 2 years as a rule of thumb for the time required to permit a mine.

HEALTH AND SAFETY

Gilsonite, as a finely powdered dust, is flammable and explosive but has no other serious safety, health, or environmental issues. There have been several serious mine explosions, and mine and plant fires in the 116-year history of the industry. Most accidents occurred long ago and in most cases probably involved obvious human error such as the use of open flames underground or improper blasting procedures. The last serious fire was in 1994 at Ziegler's Little Bonanza plant when plant maintenance sparked a

surface fire that injured two workers, destroyed some facilities, and burned 1,800 Mt of mined Gilsonite (Gomez 1994).

Gilsonite is nontoxic, noncarcinogenic, and nonmutagenic as classified in the U.S. Occupational Safety and Health Administration's material safety data sheets and the U.S. Food and Drug Administration Section 175.300, part 3, subpart (iv) (Ziegler 2004). FDA permits Gilsonite to be used in coatings that come in contact with food. Gilsonite dust presents no special respiratory hazards in mining or processing, although producers recommend wearing a respirator in very heavy dust environments.

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Glaucanite

John H. Dooley

Glaucanite is a group of dioctahedral, potassium, iron-rich, compositionally heterogeneous, phyllosilicate (clay) minerals. In sufficient amounts, glaucanite imparts an olive green to greenish black color to sediment. Glaucanite-rich sediment is informally referred to as greensand, green earth, greensand marl, clay marl, sand marl, lime sand marl, or simply marl, as it is known in New Jersey. The term *greensand* as a rock name for glaucanite-bearing sediment is more appropriate than greensand marl or marl, terms that have been doggedly perpetuated in the literature. Marl, as currently used, is restricted to limey sediments, and therefore glaucanite sand in a limey, earthy sediment may be appropriately termed a greensand marl. Terms such as black marl, ash marl, poison marl, and acid marl have been used to describe greensands having strongly acidic properties (Tedrow 2002).

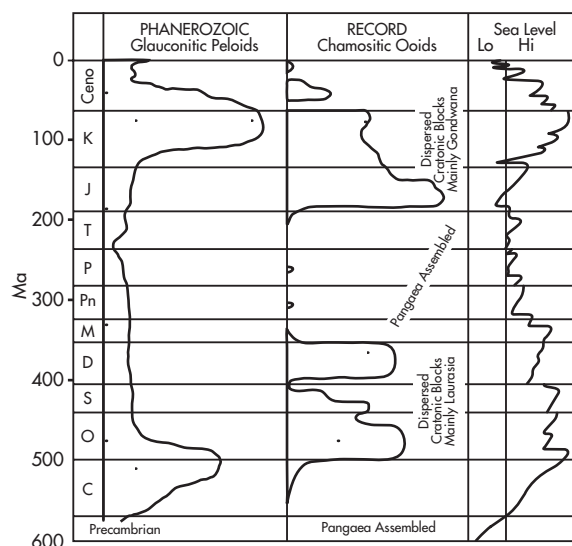
Because of its potash and phosphate content, greensand was mined and marketed as a natural fertilizer and soil conditioner for more than 100 years. The advent of manufactured fertilizers with adjustable nutrient ratios led to a decline in the use of greensand in agriculture. The material has since been recognized as useful in water treatment. Unfortunately, despite large reserves and worldwide distribution, glaucanite has not been used to any significant commercial extent because no major application has been found for a substance with its chemical composition and properties. This is due mostly to a paucity of research on its potential commercial uses.

Extraction of potash received considerable attention during and just after World War I. Because of relatively high extraction costs and a generally low potash content (less than 8%), glaucanite lost its appeal as a source of this commodity.

GEOLOGY

Glaucanitic greensands are unconsolidated sandy, silty, or clayey sediments of marine origin found in formations ranging in age from Precambrian to Recent (Figure 1). Although greensands are generally moderately sorted because of the presence of fine matrix, the glaucanite fraction of these sediments is usually well sorted because glaucanite pellets are remarkably uniform in size when autochthonous, although reworked (allochthonous) glaucanitic sediments can be poorly sorted (Amorosi 1997).

In the geologic strata, the contacts with overlying and underlying sediments are either gradational or unconformable. Primary sedimentary structures are generally lacking, but cross bedding, massive bedding, and bioturbation have been reported.



Source: Reprinted from *Earth Science Reviews*, Volume 20. F.B. Van Houten and M.E. Purucker. Glaucanite peloids and chamositic ooids—favorable factors, constraints, and problems, pages 211–243. Copyright (1984) with permission from Elsevier.

Figure 1. Comparative record of the relative abundance of glaucanitic peloids and chamositic ooids in the Phanerozoic

The clay (phyllosilicate) fraction in the greensand matrix consists of mainly illite/smectite, illite, micas, ferri illite, kaolinite, and chlorite (Bell and Goodell 1967; Seed 1968; Bremner and Willis 1993; Gibson, Bybell, and Mason 2000; Wiewióra et al. 2001).

Most greensand deposits contain, in addition to glaucanite, minerals such as quartz, mica, pyrite, some heavy minerals, and calcium carbonate in the form of shell or cement derived from marine organisms. Iron oxides, phosphatic nodules, fecal pellets, and foraminifera are locally common, and skeletal remains of marine vertebrates are occasionally found. Color photographs of glaucanitic cores from New Jersey are shown in Miller et al. (2004).

MINERALOGY

Glaucanite grains range from 1 mm (coarse sand) to the submicrometer (clay) and develop different shapes (Figures 2–5). The

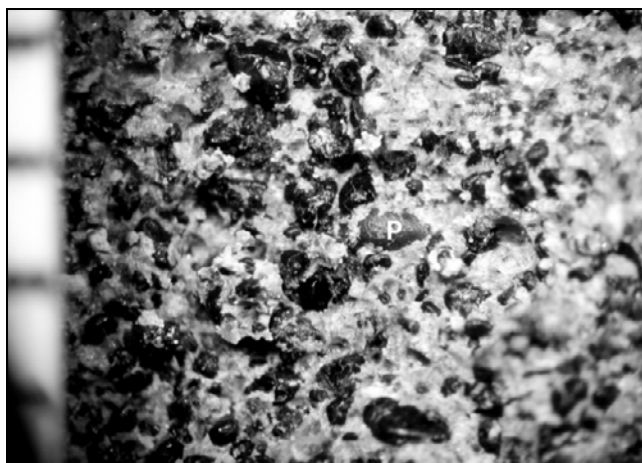


Figure 2. Glauconite sand peloids (black) in a clay/silt carbonate matrix of the Navesink Formation from 1,013 ft depth in the Millville (New Jersey) corehole. An apatite (fecal?) pellet (P) is in the center of the photo. Note that in this particular core sample, the glauconite peloids are not in grain-to-grain contact but are supported by the clay/silt matrix. This is an example of a greensand marl. Scale on left side has 1-mm gradations.

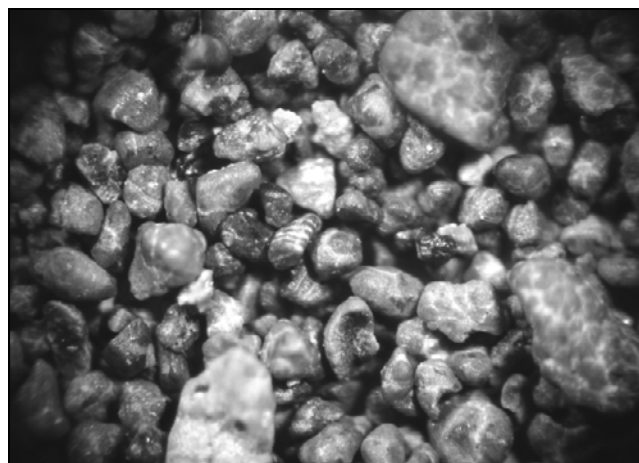


Figure 4. Photomicrograph of glauconite sand peloids in the Upper Shark River Formation (New Jersey) from 631.6 ft depth in the Millville corehole. Morphologically, the peloids are smoother and less sutured (suturing obscured slightly) than those from the Navesink Formation (Figure 3). The Shark River glauconite may have been transported. The vermiform (banded) pellet in the center is likely glauconitized fecal matter (~47× magnification).

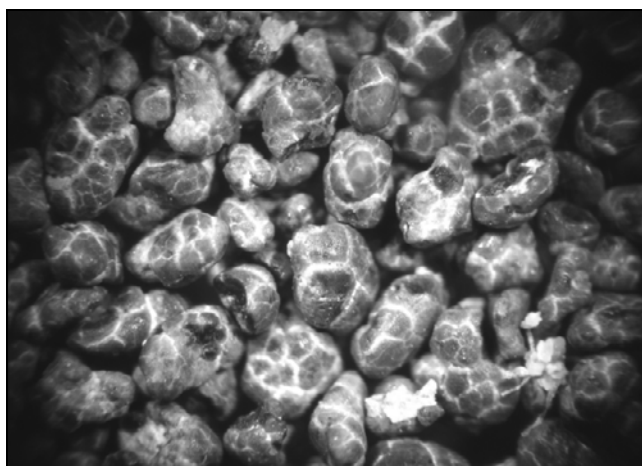


Figure 3. Photomicrograph of the typical morphology of glauconite sand peloids in the Navesink Formation from 1,013 ft depth in the Millville corehole. The peloids are highly sutured—typical of most evolved glauconite—with carbonate minerals filling the sutures (~35× magnification).

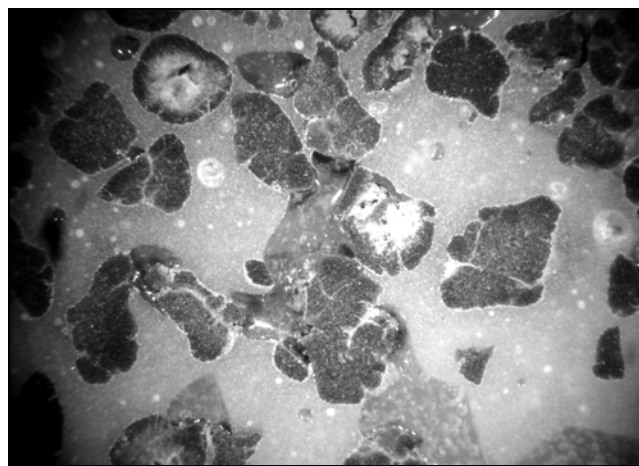


Figure 5. Photomicrograph of the cross section of polished glauconite sand peloids embedded in epoxy resin. Note the peloid to the right of center which has a void filled with a much lighter green mineral. Most peloids lack zonation (i.e. visually homogeneous from core to rim). Fractures, often infilled with minerals, are the characteristic sutures of mature glauconite.

largest percentage by weight is 0.49 to 0.125 mm (medium to fine sand). Grains are usually sutured or smooth and peloidal. Glauconite occasionally fills the interstices of coarse-grained sediments. Authigenic glauconite may form the cement or matrix.

Glauconite is a group of hydrous, iron, potassium phyllosilicates with a compositional range between glauconitic smectite and glauconitic mica (glauconite *sensu stricto*) end members (Odin and Matter 1981). Because of this range in end-member composition, glauconite has varying concentrations of the major constituent elements—aluminum, calcium, magnesium, and sodium—and many trace elements, for example, arsenic, lead, nickel, uranium, vanadium, and zinc. Its empirical chemical formula is

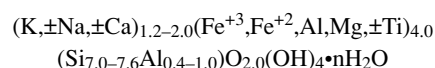


Table 1 shows the chemical composition of glauconite from New Jersey.

The chemical composition of glauconite was investigated by Foster (1969), who computed atomic ratios and layer charges for 32 samples from 12 countries. Table 2 shows the compositional range of these glauconites. Table 3 lists greensand analyses from 10 localities in the United States.

In the structure of mica, two silica tetrahedral sheets face one central octahedral sheet (Grim 1968). The tips of the tetrahedra

Table 1. Comprehensive chemistry of New Jersey glauconite (glauconite isolates from glauconitic geologic formations) on an "as received" basis*

Analyte	Mer1242	Mer1228	Marshall	RedBank	USharkR	Navesink	Horners	Navesink	Mt. Laurel
SiO ₂	46.86	49.73	48.39	50.83	49.76	50.38	50.70	44.90	34.90
TiO ₂	0.24	0.05	0.11	0.11	0.14	0.07	0.074	0.061	1.001
Al ₂ O ₃	9.57	8.75	8.02	8.78	8.44	7.92	6.73	6.55	10.80
Fe ₂ O ₃	24.73	20.86	19.00	17.68	20.88	18.13	21.40	19.10	32.30
MgO	2.67	3.09	3.78	4.02	3.73	4.42	4.45	4.11	2.72
CaO	0.53	8.75	8.02	8.78	8.44	7.92	1.09	6.08	2.33
Na ₂ O	0.07	0.05	0.05	0.05	0.04	0.05	0.11	0.12	0.10
K ₂ O	7.16	7.71	7.67	6.22	7.02	7.08	8.54	7.93	5.40
P ₂ O ₅	0.16	0.79	1.81	0.55	0.23	1.01	0.54	3.19	1.17
LOI†	7.50	7.20	7.40	9.40	8.50	7.80	5.15	5.60	7.60
Total	99.49	99.78	99.41	99.15	99.44	99.43	98.78	97.64	98.32
As	53	23	15	13	19	8	7	17	136
B	N.A.‡	N.A.	N.A.	N.A.	N.A.	N.A.	569	584	487
Ba	37	24	21	17	13	13	31	48	120
Be	5	5	5	5	6	5	10.5	7.8	9.8
Bi	0.2	0.1	0.1	0.1	0.1	0.1	<0.5	<0.5	<0.5
Br	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	<1	<1	<1
Cd	<1	<1	<1	<1	<1	<1	<0.2	<0.2	<0.2
Cl	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	<50	<50	53
Co	17.6	16	17.8	19.8	3.8	10.9	11	10	31
Cr	137	58	88	116	162	90	351	121	1150
Cs	2.5	2.4	2.3	2.9	4	2.2	<3	<3	<3
Cu	8	11.2	6.8	12.8	3.1	7.1	2.8	3.4	3.9
Ga	16	17	16	19	14	18	12	13	10
Ge	0.9	1	1.3	1	1.5	1.5	<10	<10	<10
Hf	1.3	0.6	0.7	0.9	1.3	0.5	3	<1	<1
Hg	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	0.007	0.027	0.013
In	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	<0.5	<0.5	<0.5
Li	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	39	51	33
Mo	<2	<2	<2	4	<2	2	<1	<1	<1
Nb	6.8	2.4	3.5	2.2	3.6	1.5	3	2	24
Ni	25	29	24	31	19	23	33	21	71
Pb	9	215	12	222	4	163	5	9	16
Rb	264	293	288	210	282	220	263	212	150
S	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	100	3600	800
Sb	0.5	0.7	0.6	0.7	0.4	0.7	1.3	1.2	5.2
Sc	16	10	8	13	11	5	6.7	2.8	8.8
Se	N.A.	N.A.	N.A.	N.A.	N.A.	N.A.	<5	<5	<5
Sn	3	4	4	3	2	2	N.A.	N.A.	N.A.
Sr	78	89	167	123	54	126	63.4	213	107
Ta	0.4	0.1	0.2	0.2	0.2	<0.1	<1	<1	<1
Th	12.4	2.06	4.11	3.49	3.43	1.45	<0.5	<0.5	10.6
Tl	0.07	0.07	0.10	0.30	0.09	0.10	<0.10	<0.10	<0.10
U	2.45	1.72	5.31	2.54	1.78	2.98	<0.5	4.7	8
V	433	167	131	106	157	73	115	78	685
W	0.9	<0.2	<0.2	<0.2	<0.2	2.0	<4	<4	6
Y	12.5	30.9	54.3	22.7	9	18.5	22	39	42
Zn	105	65.9	72.6	127	118	76.5	113	96.6	221
Zr	45	29	25	32	38	17	29	22	64

* Oxides are in weight percent and others are in ppm (mg/kg).

† LOI = Loss on ignition.

‡ N.A. = not analyzed.

Table 2. Compositional range of glauconite, wt %

SiO ₂	46.9–52.9	CaO	Trace–1.9
Al ₂ O ₃	5.8–15.2	Na ₂ O	Trace–1.6
Fe ₂ O ₃	9.3–24.1	K ₂ O	5.1–9.3
FeO	1.0–6.3	TiO ₂	0–1.8
MgO	2.3–4.6	H ₂ O	4.3–7.2

Source: Foster 1969.

Table 3. Greensand analyses of 10 greensands, wt %

	1	2	3	4	5	6	7	8	9	10 [*]
SiO ₂	51.83	46.28	63.55	77.93	77.80	73.00	35.18	52.61	30.00	36.44
Al ₂ O ₃	6.23	5.42	4.41	7.48	7.86	9.60	5.30	9.56	14.11	29.02
Fe ₂ O ₃	20.08	23.64	15.74	3.54	5.42	7.20	17.35	23.04	25.09	13.36
CaO	0.52	1.10	0.48	2.39	2.12	2.88	16.00	1.39	10.80	2.72
MgO	3.66	3.57	2.35	1.01	0.82	1.55	trace	2.87	3.46	1.88
K ₂ O	6.60	7.50	6.24	2.30	3.60	3.30	1.69	3.49	0.80	na [†]
Na ₂ O	0.76	0.83	0.03	0.12	na	na	1.39	0.42	4.41	na
P ₂ O ₅	0.31	0.52	0.19	0.22	na	na	3.30	na	0.44	na
Carbonic acid	N.A. [‡]	N.A.	N.A.	N.A.	N.A.	N.A.	8.00	N.A.	N.A.	N.A.
LOI	10.34	10.75	6.91	4.83	2.26	2.40	10.10	5.96	N.A.	15.59

Source: Markewicz and Lodding 1983.

* Numbers 1–10 correspond to the following locations and references.

1. Hornerstown greensand, Sewell, New Jersey (unpublished file, New Jersey Geological Survey).
2. Navesink greensand, Sewell, New Jersey (unpublished file, New Jersey Geological Survey).
3. Nanjemoy Formation, Maryland (Grim 1968).
4. Aquia Formation, Maryland (Glaser 1971).
5. Aquia Formation, Hop Yard, Rappahannock River, Virginia (Clark 1912; Gildersleeve 1942).
6. Nanjemoy Formation, Woodstock, Virginia (Clark 1912; Gildersleeve 1942).
7. Lower Eocene greensand, Gas Ridge anticline, Texas (Jones 1936).
8. Glauconite, McNairy County, Tennessee.
9. Weches Formation, Houston County, Texas (Fisher 1965).
10. Winona Formation, Montgomery County, Mississippi.

† na = not available.

‡ N.A. = not analyzed.

point toward the central unit, and the three sheets are combined into a single layer, with a suitable replacement of OH and O. As much as 25% of the silicon may be replaced by aluminum, and the resulting charge deficiency is balanced by interlayer potassium ions. In glauconite, aluminum can substitute for 4.2% to 17.5% of the silicon in tetrahedral sheets. Some of the charge deficiency is balanced by Fe⁺² and Mg⁺² ions replacing Fe⁺³ and Al⁺³ ions in the octahedral sheet. Most glauconite is not a pure dioctahedral phyllosilicate but rather a mixture of 10Å and 14Å expandable-lattice phyllosilicates (Burst 1958; Cimbalnikova 1971).

Like other layer silicates, glauconite absorbs ions from solution. Its exchangeable sites are on the outside of the silica-aluminum lattice, and the exchange reaction generally does not affect the glauconite structure. Both cations and anions are exchangeable, but not much information is available on the latter. Ion exchange is important in chemical separations, water softening, and the properties of soil for both agriculture and engineering. It is usually expressed in milliequivalents (meq) per 100 g, and a typical cation-exchange capacity (CEC) for glauconite is 20 meq/100 g.

The ternary plot by Yoder and Eugster (1955) shown as Figure 6 illustrates the compositional relationship between glauconite and other phyllosilicate minerals. Synonym (s) and varietal (v) terms for merly or erroneously used for glauconite include chloro-

rophanerite, mang anglaconite (v), marsjatskite, marsyatskite (manganoglaconite), sk olite (s), and soda glauconite (v) (Rieder et al. 1998). Pholidoide is a term used in Turkey for a group of aluminous glauconite.

MODE OF OCCURRENCE AND ORIGIN

Glauconite is found in rocks ranging in age from Precambrian to Recent (Figure 1); however, when the term *glauconite greensand* or greensand is used, a Tertiary or Cretaceous age is generally implied. The term greensand denotes an unconsolidated glauconite-rich sand. Glauconite frequently forms the major constituent in many sandy, silty, or even clayey formations of Tertiary and Cretaceous age. Greensand can be present as a solid massive bed, as disseminated grains, as glauconite-rich masses and aggregates, or as fillings in fossil worm tubes or foraminifera. Brown to grayish, ovoid, phosphatic (carbonate fluorapatite—francolite) fecal pellets can be accessory grains in greensand deposits (Figure 2). Fresh glauconite is typically olive green to dark green and has a polylobate to round or tabular shape.

The genesis of glauconite has been debated for decades. Three hypotheses have been proposed to explain its formation. The layer-lattice hypothesis (Burst 1958; Hower 1961) invokes the transformation under reducing conditions of degraded, detrital micaceous

minerals into a neoformed iron- and potassium-rich illite-group mineral. This process supposes a substitution of iron for aluminum in the octahedral sites, its balancing of the concomitant charge increase by potassium incorporation in the interlayer, thereby resulting in the synchronous fixation of iron and potassium within the lattice. Odin and Matter (1981) argue that the layer-lattice hypothesis is incompatible with several observations attendant with glauconitization.

The epigenetic substitution hypothesis (Ehlmann, Hulings, and Glover 1963) proposes that glauconite layers develop through solution of preexisting minerals with seawater furnishing the requisite ions.

The precipitation-dissolution-recrystallization (pdr) hypothesis (Odin and Matter 1981; Ireland, Curtis and Whiteman 1983) proposes that glauconite minerals result from neoformation of dissolved matter precipitated in pores in a progressively altered and replaced substrate. A precipitate forms as crystallites of green and (potassium-poor) glauconitic smectite, or as a silicic ferruginous gel, which transforms diagenetically to a glauconitic smectite in a slightly reducing microenvironment. The glauconitic smectite presumably ages to a better-ordered micaceous mineral (glauconite) as potassium is supplied from seawater at the sediment-seawater interface (known as the benthic boundary layer). Though the epigenetic substitution hypothesis supposes neoformation processes similar to those implied by the pdr hypothesis, the latter implies independence between the nature of the substrate and the neoformed iron-rich phyllosilicate.

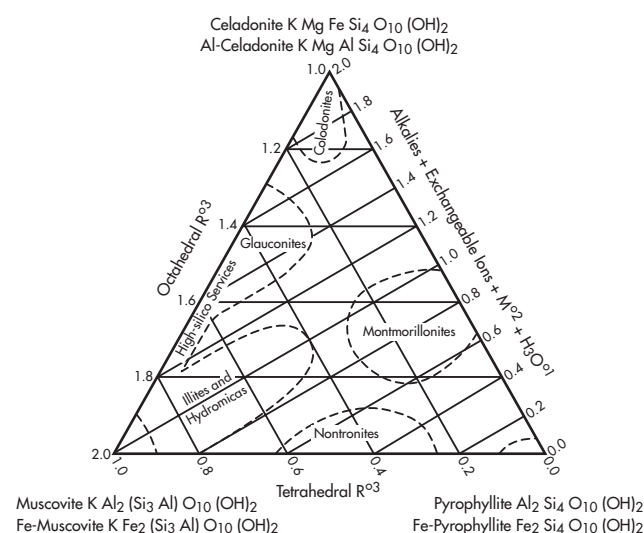
A detailed Mössbauer investigation yields insight into one of several possible processes of glauconite formation (McConchie et al. 1979). Apparently, authigenesis starts with the defective or degraded phyllosilicate structure of an authigenic or detrital mineral decomposed in part by marine biogenic activity. The structure is highly charged but is temporarily neutralized by potassium, sodium, calcium, and particularly magnesium cations. Iron enters the structure as ferrous iron, replacing neutralized cations, and is partially oxidized to octahedral ferric iron. Ferrous iron continues entering the structure while the system proceeds toward equilibrium.

Based on principally strontium isotopic data for some glauconitic pellets, Stille and Clauer (1994) presented a two-stage evolutionary model for glauconite. The initial stage involves the dissolution of clay precursors and simultaneous crystallization in equilibrium with the precursor-dominated chemical environment until 4.5 wt % K_2O is achieved. The second stage consists of crystal maturation with increased potassium contents in equilibrium with the marine depositional environment.

Laboratory synthesis of glauconitic minerals under essentially "natural" conditions (Harder 1980, p. 221) demonstrates that "glauconite may form by the precipitation of iron hydroxides and adsorption of silica and K from dilute solutions...." He concludes that iron and aluminum in detrital minerals dissolve in reducing microenvironments and precipitate in more oxidizing ones in a variety of sediment substrates.

Scientific evidence for glauconitization favors dissolution-recrystallization processes rather than a progressive transformation of 2:1 phyllosilicates (Odin and Matter 1981; Stille and Clauer 1994). Despite the evidence, the transformation of detrital phyllosilicates could apply to specific cases of glauconitization. Research continues to focus on whether these hypotheses can adequately explain the formation of glauconite in a marine environment and the accumulation of greensand strata of considerable thickness and extent.

Glauconite forms widely in surface sediments deposited on continental shelves and topographic highs of all oceans except in



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Figure 6. The relationships of dioctahedral phyllosilicate minerals, with fields indicated in which natural clay mineral compositions lie

extremely cold regions. It commonly forms in water depths of 50 to 500 m, with the highest abundance developing between 150 and 300 m, that is, at the shelf-slope transition. Glauconite authigenesis occurs at the sediment-seawater interface in areas characterized by low to negative sedimentation rates. Most glauconite deposits are associated with hiatuses and are used as a diagnostic feature of transgressive cycles in sequence stratigraphy.

Most glauconite peloids are cryptocrystalline in thin section, and their texture changes with progressive glauconitization. Texturally, authigenic glauconite peloids in their initial stage of formation often consist of tiny, ill-defined globules with diameters less than 0.5 μm . These coalesce, forming 2- to 3- μm rod-like or "caterpillar" crystallites. As authigenesis proceeds, 4- to 5- μm bladed aggregates form rosettes. Most evolved glauconite peloids consist of well-developed, slightly sinuous, subparallel, lamellae structures.

DISTRIBUTION OF MAJOR DEPOSITS

United States

The most important greensands are developed in the Mid-Atlantic Coastal Plain. Glauconite is found as an accessory mineral in many coastal plain sediments of New Jersey, Delaware, and Maryland, but highly glauconitic greensand is best developed in Upper Cretaceous and Early Paleocene formations.

Greensand crops out in a narrow belt that trends northeast-southwest across New Jersey, Delaware, Maryland, and beyond, but in general the glauconite content and thickness of the strata and the potash content of glauconite in them decrease southward. Table 1 shows the comprehensive chemistry of glauconite from New Jersey.

The Marshalltown Formation of Late Cretaceous age is composed of dark greenish gray, fine- to medium-grained, massive, highly glauconitic sand and silty fine quartz sand. Its thickness ranges from 3 m to more than 10 m.

The Hornerstown Formation of Early Paleocene age is a dark gray to dusky green, fine- to medium-grained glauconitic sand locally containing bright-green clay matrix and a little quartz sand.

Locally it contains a few thin, brown to reddish brown, clayey or indurated goethitic bands. Its thickness ranges from 1.5 to 7 m.

The Na vesink Formation of Late Cretaceous age is a dark greenish gray, medium-grained, massive, extensively bioturbated, poorly sorted, glauconitic sand containing varying amounts of quartz. It contains calcareous clay (marl) toward the top and goethitic bands or masses locally. Its thickness ranges from 3 to 7.5 m.

The Aquia Formation is composed of fine- to medium-grained, highly glauconitic sand with calcite-cemented layers. Its maximum thickness exceeds 35 m.

Other Countries

Glauconitic greensands are developed on all continents and have been geologically mapped in many countries. At some locations, glauconite is the most abundant constituent of the formation. In most cases, however, it is present in relatively small amounts or as a minor component of the sediment.

Australia

North of Perth in Western Australia, three glauconitic formations have a cumulative thickness of 90 m—the Molecap Greensand at the base, the Gingin Chalk, and the Poison Hill Greensand at the top. In some beds, the glauconite content reaches 50% of the sediment (McLeod 1965). The entire sequence is Late Cretaceous age (Brown, Campbell, and Crook 1968).

The Paleoproterozoic (c. 1800 Ma) Earaheedy Basin in Western Australia contains widespread glauconite in clastic units of the Chiall and Wongawall formations of the Minningarra Subgroup (Pirajno and Adamides 2000). Glauconite-rich strata of the Chiall Formation are interbedded with stratiform iron-manganese oxides, typical of passive continental shelf environments.

Brazil

The upper rhythmite of the Proterozoic Paranoá Group in the region of Cabeceiras in Brazil contains three glauconitic sandstones. Glauconite concentration ranges from less than 10% in the white sandstone to more than 50% in the green-reddish sandstone (Guimaraes et al. 2000).

Egypt

In the Western Desert of Egypt, the upper part of the Nubian Sandstone is composed of a 380-m-thick sequence of gray-green, very glauconitic shale, alternating with sandstone. It is Early Cretaceous age (Said 1962).

England

The Upper Greensand Formation is composed of highly glauconitic siltstones and sandstones and is developed in the southern and southeastern parts of England. The formation is well exposed at Ballard Cliff (Bennison and Wright 1969).

Hungary

The Lower Cretaceous age Nana Formation in the Transdanubian region is composed of highly glauconitic marls. The largest concentration of glauconite is in the lower part of the formation.

In the southern part of the Buda Mountains, clays and sands rich in glauconite are well developed in the Torokbalint Formation of Oligocene age.

Israel

The Cretaceous-age glauconitic sediments in the Negev Area of Israel first appear in the Hatira Formation and continue for several

meters into the overlying Hazera Formation. In some beds, glauconite makes up 80% of the rock (Bentor 1966).

The Pliocene-age Abu Hareira Sandstone is a hard, cross-bedded, glauconite-rich sandstone. The formation is best developed between Gaza and Beersheba (Picard and Solomonica 1936), with a maximum thickness of 30 m.

Lithuania

According to Smith et al. (1996, p. 2883), in their evaluation of the sorption of heavy metals by Lithuanian glauconite, "Several hundred million metric tonnes [are] reportedly accessible (i.e., at or near the surface) in Lithuania."

New Zealand

All major glauconitic deposits in New Zealand are found on South Island.

The Iron Creek Greensand is a highly glauconitic, massive sand in the Iron Creek Area. The formation reaches as much as 250 m in thickness and is of Late Cretaceous to Eocene age (Gage 1970).

The Waipara Greensand, which is of Paleocene–Eocene age, consists of alternating soft and hard, green, richly glauconitic sandstones. It is exposed in banks of the Waipara River and the south branch of the Waipara River.

The Kokoamu Greensand is pure, highly glauconitic sand. The formation is of Late Oligocene age and is developed and exposed in the Duntroon Area.

The Gee Green sand is exposed in the coastal Kakanui Area. The formation shows distinct stratification and is very glauconite rich. It is at least 15 m thick and is of Oligocene–Early Miocene age (Gage 1957).

Pakistan

The lower member of the Chichali Formation in Pakistan in the western Salt Ranges, Trans-Indus Ranges, and parts of Kohat is composed of sandy glauconitic shale that passes upward into dark green glauconitic and fossiliferous sandstone (Danilchik and Shah 1967).

South Africa

One of the most extensive glauconite (and phosphorite) deposits in the world mantles the southern African west coast and the Agulhas Bank continental shelf sediments (Coles et al. 2002). The major part of the Igoda Formation, which is of Late Cretaceous age, is composed of highly glauconitic sandy limestone and glauconitic calcareous sandstones. The formation is exposed in cliffs on the southwestern side of the Igoda River (Klinger and Lock 1978).

Switzerland

The Altmann Schist of Early Cretaceous age contains highly glauconitic layers, reaches a maximum thickness of 40 m, and is best developed in the Helvetic Alps, especially near Santis and Pilatus in Switzerland (Funk 1971).

Thailand

The green sandstones of the Phra Vihan Formation of Thailand are rich in glauconite. The formation is of Early Jurassic age and is well developed on the Khorat Plateau (Ward and Bunnag 1964).

Former U.S.S.R.

Glauconitic sandstone is widespread in the northwestern region of the European former U.S.S.R. It occurs in Ukraine, in the Volga

region, on the eastern slope of the Ural Mountains, in Kazakhstan and in Uzbekistan, and also in the Far East. These glauconitic deposits are mainly in Jurassic, Cretaceous, and Paleocene sands and sandstones. Their glauconite content commonly reaches 50% to 80%.

Venezuela

The Cogollo Group in Venezuela includes a sequence of sediments containing as much as 80% glauconite. The group reaches 610 m in thickness, is of Early–Late Cretaceous age, and is well developed in the central Lake Maracaibo Area (Bartok, Reijers, and Juhasz 1981).

West New Guinea (Irian Jaya)

The Kembelangan Formation, which is Jurassic to Paleocene in age, is well developed in the Vogelkop region of West New Guinea. Its Upper Cretaceous age portion is very glauconitic. Glauconite usually makes up more than 50% of the rock.

PROPERTIES

Magnetic Susceptibility

Glauconite has a variable paramagnetic susceptibility. Magnetic separation is, therefore, a commonly used method for separating it from impurities. With a Frantz Isodynamic magnetic separator, the following settings generally give a clean separation of glauconite from quartz, coprolites, pyrite, and calcite grains:

Side slope	20°
Forward slope	15°
Current	0.50 A (ampere)
Mass magnetic susceptibility	$(K_m) = 25 \pm 5 \times 10^{-6}$

Three steps of medium-intensity magnetic separation, preceded by washing and removal of +0.59- and -0.074-mm fractions, result in purified glauconite. The purified glauconite then can be effectively separated into differently evolved fractions by incrementally decreasing the current. This results from increasing magnetic susceptibility (and specific gravity) as glauconite evolves from glauconitic smectite to glauconitic mica.

Specific Gravity

The specific gravity of glauconites ranges widely depending on the abundance of mixed-layer minerals and K_2O , the degree of substitution in the tetrahedral and octahedral sites, and the extent of weathering. Shutov et al. (1972) reported the results of careful fractionation of purified glauconites by means of a density column, which permitted separation in heavy liquids in steps of $0.020 \pm 0.001 \text{ g/cm}^3$. The specific gravity of glauconite of various geologic ages and provenances ranged between 2.32 and 2.92. Odin and Matter (1981) report the specific gravity of glauconite to range between 2.2 and 2.9.

The wide range in specific gravity of glauconite limits the effectiveness of heavy liquid separation as a purification method. It can be used on some greensands with good results to separate mixtures of glauconite of different provenances and different stages of diagenesis.

Thermal Characteristics

Thermal curves for glauconites show weight losses between 80° and 255°C and between 520° and 825°C. The first temperature range corresponds to dehydration, the second to actual decomposition of the mineral (Smykatz-Kloss 1974). Prolonged heating at 1,000°C results in the formation of maghemite, which inverts into hematite (Spoljaric and Crawford 1980).

TECHNOLOGY

Exploration

Standard exploration procedures consist of outcrop examination, trenching, split-spoon and auger drilling, and sampling. Drilling is essential for determining the extent of a deposit and its thickness. Exploration data are used to construct geologic, isopach, isograde, and other maps; to calculate the volume of a deposit; and to determine minable reserves. Field examination commonly involves only the determination of color, grain-size range, and clay matrix content to make certain that the deposit meets required criteria.

Evaluation of Deposits

Whether a deposit of glauconitic greensand is suitable for commercial exploitation is determined largely by the physical and chemical properties of the glauconite itself. Both field and laboratory tests are employed in this determination. Important physical properties include color, grain size, degree of sorting, and the amount of glauconite in the unconsolidated or poorly indurated sediment. Economically acceptable greensands contain at least 90% sand-size glauconite. For use in filters, glauconite must be green, dark green to almost black, and must be present in sand-size pellets. Deposits should contain not more than 2% to 3% clay matrix and must show no evidence of weathering.

Chemical properties are determined by analytical means and include analyses for major elements (Si, Al, Fe, Mg, Ca, Na, K, and P) as well as some trace elements. Chemical composition is especially important for greensand used in agriculture. Most important are the K content, which should be at least 6% (as K_2O) and devoid of pyrite. Agricultural greensand deposits must be fine-grained, preferably clayey. Once a glauconitic greensand is determined to be of commercial quality, the reserves available in the deposit must satisfy the producer's production requirements.

Mining

Most Cretaceous and younger greensand deposits are unconsolidated sediments. Various methods of open-pit extraction have been used, ranging from pick and shovel in the earliest days to power shovels, draglines, and hydraulic mining. Inversand Company's operation at Sewell, New Jersey, which is currently the only commercial greensand producer in the United States, uses hydraulic mining methods in the Hornerstown and underlying Navesink formations. The pit has been opened to a depth greater than 15 m. Overburden, consisting of sandy units of the Kirkwood Formation, is about 7.5 m thick and is removed before greensand extraction. The lower part of the Hornerstown Formation, which constitutes the upper part of the deposit, is 5 to 6 m thick and overlies 3 to 4.5 m of nearly pure glauconite belonging to the Navesink Formation. After the beds are slurried by a jet of high-pressure water, the greensand is pumped from a sump through a pipeline to a tank at the nearby processing plant.

Agrolith A/S, a wholly owned subsidiary of Mineral Development International A/S (Birkeroed, Denmark), is the sole commercial producer of glauconite in Europe.

Processing and Purification

Processing at Sewell, New Jersey, involves first the screening of crude, mine-run greensand. Approximately two thirds of the crude is recovered as -1.0- to +0.25-mm feed for the production of manganese greensand. The remaining one third consists of -0.25- mm material that is too fine for use as a water filtration medium. The -0.25- to +0.088-mm fraction is stockpiled and sold as a soil conditioner and natural fertilizer, and the -0.088-mm fraction is pumped as waste to settling ponds. Agrolith A/S supplies glauconite with a

Table 4. Greensand in water softening

Porosity, %	2 to 3
Effective size, mm	0.30 to 0.33
Uniformity coefficient	1.40 to 1.55
Screen analysis, mm	1.0 to 0.25
Attrition loss per annum, %	2
Weight per cubic meter, air-dried, kg	1,360
Recommended pH operating range	6.6 to 8.3
Maximum permissible temperature of raw water, °C	46
Maximum permissible turbidity in raw water, ppm	10
Maximum permissible iron in raw water as Fe, ppm	2.5
Bed expansion during backwash, %	30 to 35
Exchange capacity as CaCO ₃ , kg/m ³	6.4 to 6.9
Salt requirement, kg/m ³	22.4
Time required for regeneration in water softener, min	40
Recommended maximum softening rate, L/m per m ² bed area	204
Recommended wash rate, L/m per m ² bed area	285
Recommended minimum bed depth, m	0.75
Recommended maximum bed depth, m	1.85

Courtesy of New Jersey Geological Survey.

grain-size distribution having 98 % less than 0.25 mm and 10 % less than 0.10 mm (Coles et al. 2002).

After screening, the -1.0- to +0.25-mm fraction is washed for 2 hr with clean water to remove silt and clay. This is followed by several chemical treatments. Treatment with each chemical solution is followed by a fresh water rinse before the next chemical is used. The treatments each take between 0.5 and 1.75 hr. The first four treatments are with solutions of sodium aluminate, sodium silicate (twice), and aluminum sulfate. These chemicals harden the glauconite particles. The next eight treatments use manganese sulfate and potassium permanganate to build a manganese dioxide coating on the glauconite. This coating is the active agent in removal of iron, manganese, heavy metals, hydrogen sulfide, and radium from water.

The total time required for all chemical treatments is approximately 14 hr. Afterward, the material is slurry-pumped to a drying building, drained of most of its free water in holding pans, and dried in gas-fired ovens. The drying time for each batch is approximately 20 hr. The material is then packed in 0.03-m³ bags or 1-t supersacks and is palletized and stretch wrapped for shipment.

PRODUCTION

Historical Background

Greensand was used as a fertilizer in New Jersey in the latter part of the 1700s. During the early 1800s, its use became more common; applications of as much as 22.5 kg/m² were sometimes made, although recommendations for agricultural use suggested 4.5 to 11 kg/m² (Tedrow 1957). Many crops, especially the forage type, were said to improve with greensand application; because of its slow release of potash, however, large quantities were required. Certain greensands that contain sulfur and sulfide minerals are harmful to plant growth, and these were classified as poison, burning, or black marls. The availability of higher-grade potash salts from other mineral sources and the manufacture of prepared fertilizers displaced the agricultural use of greensand during the latter 1800s.

During the mid-1800s, the greensand industry, centered in a small section of the eastern United States, grossed more than \$500,000 per year. Toward the end of the century, however, annual

production dwindled to less than \$100,000. By 1910, only six or eight greensand producers were grossing less than \$5,000 per year each (Tyler 1934). The U.S. industry revived briefly during World War I because of the curtailment of foreign potash, especially from Germany.

During the latter 1940s and early 1950s, greensand was again recommended as a food nutrient for plants and farm crops. Agronomic studies discussed its potential as a soil additive that gradually releases potash and many trace element nutrients essential for plant growth (Tedrow 1957). Greensand was sold with the idea that it would condition soil and absorb and hold water while its base-exchange properties released trace elements.

For a short time, glauconite was used in certain parts of New Jersey as a binding additive in the brick industry. In the 1800s, it was used for making green glass (Cook 1868).

In the early 1900s, the base-exchange properties of glauconite were recognized for water treatment and the mineral gained acceptance as a water softener. Mansfield (1922) does not mention base exchange, even though this phenomenon was known in 1916 or earlier. From 1916 through 1922, several patents for the use of glauconite as a water-softening agent were granted. A method was also patented for treating greensand to improve it for water softening and ready regeneration with common sodium chloride brine (Borrowman 1920; Spencer 1924; Kriegsheim and Vaughan 1930).

Treated glauconite, on contact with water containing magnesium or lime, takes up magnesium or calcium ions and releases sodium ions. This exchange is limited to the outer surface of glauconite grains, and when all the surfaces have absorbed their capacity, the grains must be regenerated. Regeneration, simply stated, consists of treating or backwashing the glauconite with a sodium chloride solution, which replaces the hard-water elements with sodium, thus reviving the glauconite. The process has become more sophisticated because of competition among companies in the water-softening business.

Greensand products for water softening generally consisted of several different grades distinguished by the particular treatment the glauconite was given during processing. The standard greensand water softener was produced from natural glauconite that was only washed and classified. Table 4 gives its characteristics for water softening.

To increase its water-softening capacity, glauconite was treated by a process that made it more porous. Although most of the specifications remained the same as those for the washed greensand shown in Table 4, the porosity changed from 2%–3% to 11%–13%, and the exchange capacity (as CaCO₃) increased from 6.4–6.9 kg/m³ to 8.6–10.2 kg/m³. Maximum permissible raw water turbidity dropped from 10 ppm to 5–7 ppm, and the maximum permissible iron in raw water decreased from 2.5 to 1.5 ppm. By increasing the porosity of glauconite even more, the exchange capacity was also further increased, with a corresponding change in some of the other specifications. This special porosity process increased the salt requirement for regeneration, for example, from 22.4 kg/m³ to 40 kg/m³. Another method of processing greensand involved heating it to approximately 200° to 400°C to drive off water. After cooling, it was treated with salt brine, which made the greensand product more efficient because softened water did not become cloudy.

During the latter 1940s, greensand was displaced as a water-softening agent by phenol formaldehyde resin, which has twice the softening capacity, is not affected by water temperatures above 45°C, and requires the same amount of salt for regeneration. After 1950, phenol formaldehyde resin was displaced by styrene resins, which have an even higher water-softening capacity but require no more salt for regeneration.

In the late 1860s, almost a million tons of green sand were mined each year for use as fertilizer. In 1855, greensand brought \$0.07/bushel (\$2.00/m³), and in 1877 it was selling for \$0.65/t at the pit. Reports indicate that production was principally from New Jersey. By the 1870s, annual production had dropped to less than 100 ktpy. Toward the turn of the century, demand for greensand improved, but in 1908 fewer than 10,000 t were produced, for a total value of only \$3,500. The number of producers dropped from 13 in 1908 to 4 in 1912. The use of greensand for water softening in the early 1920s revived the industry. Table 5 shows the tonnage produced in New Jersey from 1922 through 1971.

In 1926, Inversand Co. started operations near Sewell in Gloucester County, New Jersey. In the late 1940s, National Soil Conservation Co. started operations at Medford in Burlington County, New Jersey, and produced greensand at that location until the early 1960s. Table 6 shows the production of New Jersey greensand for water treatment and agricultural uses from 1959 to 1963.

USES

Present-day use of glauconite is limited to two applications—water treatment and soil conditioning. Production is concentrated in the coastal plain of New Jersey, where greensand is extracted from Cretaceous and Paleocene age sediments. A small amount of greensand for soil conditioning was once mined in Maryland (closed in 1970) and Virginia, leaving New Jersey as the sole producer in the United States.

Inversand Co., a Division of Hungerford & Terry, Inc., produces processed greensand, also called manganese greensand, in the United States. In water treatment it is used as a filter medium for removing soluble iron or manganese salts and hydrogen sulfide from well water. It is employed in vertical and horizontal pressure filters and open-gravity filter systems by almost all water-conditioning equipment manufacturers. Purple to almost black manganese greensand is used in two water treatment processes. In the older, intermittent regeneration (IR) process, it is regenerated intermittently with a weak solution of potassium permanganate (KMnO₄).

A newer process, developed and patented by Hungerford & Terry around 1960, has replaced the older one and is called continuous regeneration (CR). Potassium permanganate is injected directly into the raw water upstream of the unit containing manganese greensand and may be preceded by chlorine injection. In this process the greensand does not require intermittent regeneration, only an occasional wash. The CR process uses potassium permanganate more efficiently than does the IR process and has gained favor because of its ability to reduce very high iron levels in water to extremely minute amounts, frequently to less than 10 ppb. When a well water supply contains very little iron but significant quantities of manganese, then the older IR process is more appropriately used.

For home and garden use, greensand is recommended as a mulch, top dressing, and conditioning additive to soil for gardens, potted plants, and vegetable starting plots. It slowly releases nutrients, loosens clayey soil, is nonburning, holds moisture, and gradually contributes potassium to plants to stimulate photosynthesis. The usual application is 0.05 to 0.49 kg/m², although larger amounts may be applied depending on the nature of the soil.

A number of other uses have been suggested or tried locally. Finely ground glauconite has been used as a green paint pigment, but its low refractive index and tendency to weather to red iron oxide inhibit its suitability for this application. This niche market has been resurrected, however, by the marketing of glauconite from the Baltic states as “natural earth pigments” to painters of Russian religious icons. For variations in color and texture of the pigment, greensands (not necessarily glauconite) used by icon painters were

Table 5. Greensand production in New Jersey

Years	Tons	Value, \$
1922–1923	16,780	188,000
1924–1925	24,490	330,000
1926–1927	21,770	337,000
1928–1929	22,680	460,000
1930	11,520	225,000
1947–1951	27,884	na*
1967–1971, average	3,118	na

Courtesy of New Jersey Geological Survey and U.S. Bureau of Mines.

* na = not available.

Table 6. Greensand production in New Jersey by use, t

Year	Water Treatment	Agricultural Use
1959	1,815	4,175
1960	1,725	3,400
1961	1,360	2,630
1962	1,725	2,040
1963	1,815	Not reported

Courtesy of New Jersey Geological Survey.

mined from such diverse sources as celadonite from Monte Baldo near Verona, Italy, in 1574; chlorite from Cornwall in England; and greenish bentonite from northern Bohemia (Hradil et al. 2003). Greensands were mined also from the Baltic states, Cypress, France, Poland, Saxony, and Mendip Hills of England.

Pure glauconite has been used to a limited extent as a glass-polishing agent. Glauconite from the Weches Formation in Texas contains clayey beds that were formerly cut or sawed and dried to form a tough, reasonably durable building stone (Jones 1936; Fisher 1965).

FUTURE TRENDS

Potential New Uses

In light of declining demand for greensand, efforts have been made recently to develop new uses. Glauconite's catalytic properties have been investigated in some detail in the United States, the former U.S.S.R., Japan, Germany, and France (Hartough and Kosak 1947; Kvirikashvili 1962, 1964; Gornak 1963). Acylating reaction, dehydration of cyclohexane to benzene, condensation of aldehydes, and oxidation and dehydrogenation of alcohols have been carried out with glauconite-based catalysts. The relationship between catalytic activity and CEC has encouraged efforts to enhance the former by increasing the latter through heat treatment and chemical methods. Because CEC increases with the amount of mixed-layer component present, these efforts also have focused on replacing more of the potassium in the glauconite structure with hydroxyl ions. Heating of glauconite in a reducing atmosphere leads to the formation of metaglauconite, the sorptive properties of which are being studied.

An entirely different approach is the destructive dissolution of glauconite and recovery of at least three marketable products, high-purity silica, potash, and iron oxides. Turrentine (1925) first proposed this process. Efforts are under way to prove its economic feasibility with the help of modern chemical engineering practice.

Some extensive greensand deposits are situated near population centers, so glauconite's capacity to absorb hazardous waste fluids is being investigated. Recent studies in Germany and the

United States suggest that glauconite can be used as a filter for radioactive wastes (Kohler 1976) and heavy metals from landfill leachates and industrial effluents (Spoljaric and Crawford 1978, 1979). The efficacy of using manganese greensand to remove arsenic from water and hazardous waste liquids has been studied (Subramanian et al. 1997; Hanson et al. 1999). An increasing demand for this mineral in solving pressing pollution problems can therefore be anticipated. Food shortages in several parts of the world may also bring about renewed interest in glauconite as an inexpensive fertilizer and soil conditioner.

ECONOMIC FACTORS

Pricing

The list prices effective March 2004 for manganese greensand sold by Inversand Co. ranged from \$915 to \$990/m³, depending on the quantity purchased (R. Biegenwald, personal communication). All prices were free on board (f.o.b.) from the point of shipment in New Jersey. Agrolith A/S sold glauconite sand, consisting of about 95% glauconite, 2% quartz, and 3% "clay," for \$450/m³ ("300US\$ per tonne," according to Coles et al. 2002). Standard packaging consists of 0.028-m³ bags stretch-wrapped on pallets holding 25 bags each, an octagonal box strapped to a pallet and holding 0.71 m³ of product, or supersacks holding 1 t each.

Marketing and Distribution

The two avenues of distribution for manganese greensand are dealers and original equipment manufacturers. Dealers are primarily small- to medium-size water treatment companies that resell tanks, chemicals, and so forth, and provide service for domestic and other small water systems. Original equipment manufacturers design and manufacture equipment for large-scale municipal and industrial installations, and smaller commercial and domestic systems, and provide service for these water treatment facilities. They receive a small price incentive for making large single orders and promote the product. Many dealers are located in the midwestern United States. Large dealers in Europe distribute greensand from ports of entry in Sweden and Italy. Inversand Co. has also shipped greensand to Indonesia, South Korea, Trinidad, Chile, and Thailand in past years. A large manganese greensand water treatment system, possibly the largest ever, was built in Saudi Arabia in the late 1980s.

Alternate Materials

Low pH commonly causes unacceptably high concentrations of dissolved iron in water. This problem can be corrected with a neutralizing calcite filter, a water softener, raising the pH to a minimum of 6.7, or oxidation with chlorine bleach followed by filtration. Manganese can be removed from water by reverse osmosis and by oxidation with chlorine bleach followed by filtration. Small concentrations of manganese can be removed with a water softener. Hydrogen sulfide in concentrations greater than 6 ppm is treated with constant chlorination followed by filtration/dechlorination (McGowan 1984; Anon. 1978).

GOVERNMENTAL FACTORS

Zoning and Land Use

The area of southern New Jersey where glauconitic greensand is produced is heavily populated. It is likely, therefore, that any new mining permits or changes to present land use zoning to accommodate expansion of the greensand mine will be difficult to obtain. Inversand Co. reserves are proprietary data, although their reserves are sufficient to meet current or increased demand for many more years (R. Biegenwald, personal communication).

Environmental Regulation

Inversand Co. is required to comply with a number of environmental regulations and to operate a wastewater treatment plant under the jurisdiction of the New Jersey Department of Environmental Protection (New Jersey Pollutant Discharge Elimination System, or NJPDES). The company must have permits for both surface water discharge and groundwater discharge. Its operations are inspected periodically by the Mine Safety and Health Administration (MSHA), which checks workers for exposure to crystalline silica dust and enforces regulations regarding safety practices.

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Graphite

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INTRODUCTION

This chapter will be restricted mostly to elemental carbon in the form of natural (mined) graphite. Elemental carbon also takes the form of diamonds and fullerenes, both with different crystal structures than graphite. Graphite also can be synthesized by bringing a carbonaceous material to the temperature of graphitization; most commonly, petroleum coke is used. Either graphite shapes (i.e., electrodes) or powder can be made in this manner. Synthetic (artificial) graphite powder and natural graphite are often substituted for each other, or mixtures containing both kinds are prepared for customers.

History

Prehistoric man used graphite to make drawings on cave walls and the Egyptians used it to decorate pottery. As early as 1400 AD, graphite crucibles were made in the Haffnerzell district of Bavaria.

Through the Middle Ages, graphite was confused with other minerals, especially galena and molybdenite. Two common names that are still used for the mineral are plumbago—meaning lead-silver—and black lead. The latter implies that graphite is either composed of lead or contains a large percentage of it. C. von Gessner is credited with having recognized it as a separate mineral in 1565, but its composition was not determined until 1779 when C. Scheele demonstrated that graphite oxidized to carbon dioxide, thus proving it to be a form of carbon. In 1789, A. Werner named it *graphite*, from the Greek word *graphein*, meaning “to write.”

The United States has long relied on imports for its graphite supply because of the lack of suitable domestic graphite reserves. Sri Lankan graphites were imported as early as 1820, and Madagascar graphites were imported following the opening of mines there about 100 years later. Mexico has long supplied the United States with most of its amorphous graphite requirements.

Classification and Industry Structure

Natural graphite can be divided into three classes: disseminated flake, crystalline vein (fibrous or columnar), and amorphous. Flake graphite is a lamellar form found in metamorphic rocks, such as marble, gneiss, and schist. Each flake is separate, having crystallized as such in the rock. Crystalline vein graphite (also called lump or high crystalline graphite) is found in well-defined veins or pocket accumulations along intrusive contacts of pegmatites with limestones. The graphite in these deposits is of two types, foliated and columnar. The Sri Lankan graphite deposits are vein type.

Amorphous graphite commonly is found as minute, microcrystalline particles fairly uniformly distributed in weakly metamorphosed rocks, such as slates, or in beds consisting almost entirely of graphite. The latter usually are metamorphosed coal seams with as much as 80% to 85% graphitic carbon, whereas the former are altered carbonaceous sediments, commonly ranging from 25% to 60% carbon. The graphite content of amorphous graphite deposits is dependent on the amount of carbon present in the original sediments; there is no evidence of enrichment by intrusive rocks. Certain amorphous graphite deposits undoubtedly were formed by contact (thermal) metamorphism, while others are probably the result of dynamic (regional) metamorphism.

Synthetic (artificial) graphite is manufactured in electric furnaces from petroleum coke.

Terms and Definitions

Graphite has been marketed as graphite, plumbago, or black lead. Industrial usage of such terms tends to be confusing to one not immersed in the industry. For example, the two main commercial categories of natural graphite are crystalline and amorphous; but all graphite is really crystalline and the commercial distinction is actually one of crystal size. Thus the term *amorphous*, although widely used, is a misnomer.

Amorphous can also refer to very fine particles of crystalline flake graphite that can only be sold for low-value uses, such as foundry facings. This very fine flake also is called crystalline dust. Fine-grained varieties of lump graphite easily reduced by grinding to fine particle size are called amorphous lump, distinguishing them from tough, platy, and acicular varieties (known as crystalline lump), which may be reduced in particle size only with difficulty.

Crystalline flake graphite is well defined in paragraph 213 of the Tariff Act of 1930 as follows:

The term “crystalline flake” means graphite or plumbago which occurs disseminated as a relatively thin flake throughout its containing rock, decomposed or not, and which may be or has been separated therefrom by ordinary crushing, pulverizing, screening, or mechanical concentration process, such flake being made up of a number of parallel laminae, which may be separated by mechanical means.

Under this definition, finely divided particles of crystalline flake graphite would be classified as crystalline graphite. But the

Table 1. Salient natural graphite statistics

Year	Unit	1998	1999	2000	2001	2002
United States						
Production						
Apparent consumption*	Tons	33,600	26,400	39,000	28,200	23,600
Exports	Tons	28,000	29,400	21,800	23,900	21,600
Value	Thousands	\$14,100†	\$15,200	\$12,500	\$16,900	\$19,200
Imports for consumption	Tons	61,600	55,800	60,800	52,100	45,100
Value	Thousands	\$34,800	\$34,700	\$32,500	\$23,300	\$22,300
World						
Production	Tons	651,000	682,000	846,000	797,650‡	759,000§

Source: U.S. Geological Survey 2004.

* Domestic production plus imports minus exports.

† All values in U.S. dollars.

‡ Preliminary.

§ Estimated.

U.S. Court of Customs and Patent Appeals has repeatedly held that commercial designations, not scientific terms, must govern classification and that when a commercial meaning differs from the technical meaning, the commercial designation has precedence. Thus, large quantities of fine-crystalline flake graphite are imported as amorphous graphite.

PRODUCTION, TRADE, AND RESOURCES

Salient Graphite Statistics

Table 1 shows the salient statistics for natural graphite in the United States and for total world production. There is no graphite mined in the United States. The statistics for apparent consumption is understated because the export numbers include natural-synthetic graphite mixtures. World graphite production statistics are usually preliminary for several years because many nations report figures very slowly; the statistics for some nations (e.g., India) are overstated because they are reported on an as-mined basis. The U.S. Geological Survey (USGS 2004) updates these statistics periodically and posts the data on its Web site (<http://minerals.usgs.gov/minerals>).

U.S. Graphite Consumption and Imports

There are almost no published statistics on U.S. consumption of natural graphite, by end use, because so much of USGS survey data are company proprietary. In addition, the numbers for amorphous graphite include natural-synthetic mixtures. In 2002, USGS data showed that 17,500 t crystalline graphite worth US\$16.8 million was consumed in the United States, compared to 15,000 t worth US\$15.8 million in 2001. In 2002, 21,900 t of amorphous graphite and mixes worth US\$18.4 million were consumed, compared to 18,800 t worth US\$14.7 million in 2001.

The U.S. import statistics shown by the USGS indicate that the major sources of graphite are China, which supplied 18,500 t worth \$6.55 million in 2002; followed by Mexico with 9,920 t worth US\$1.15 million; Canada with 8,360 t worth US\$4.31 million; Brazil with 4,190 t worth US\$3.67 million; and Madagascar with 2,030 t worth US\$0.97 million.

World Graphite Production and Resources

Table 2 shows that natural graphite is produced by 21 nations, led by China. China sets world prices, has a rapidly growing domestic market for graphite, and is a huge exporter. Brazil is a significant

exporter worldwide, and Mexico and Canada export mainly to the United States.

Table 3 shows graphite reserves and resources for a number of major graphite-producing nations.

GEOLOGY

Mineralogy, Crystallography, and Ore Impurities

Graphite is found in laminated, flaky aggregates disseminated in schistose rocks. It also occurs in veins and exhibits a foliated or fibrous structure. Graphite is a black lustrous mineral that crystallizes in the hexagonal system, with rhombohedral symmetry. The crystals are six-sided and tabular in form; the faces commonly are striated. The flakes have perfect basal cleavage and are opaque. When well-crystallized, flakes have a black metallic luster, whereas amorphous material is black and earthy with a microcrystalline compactness. The flakes feel greasy.

Physical and Chemical Properties

Graphite is an excellent conductor of heat and electricity. It melts at approximately 3,550°C at a triple point under 88 kg/cm². It sublimates between 3,300°C and 3,500°C at 1.033 kg/cm². At 3,726°C, a second triple point occurs at approximately 10,000 atmospheres. Thermal oxidation in the presence of oxygen begins at 300°C, and the rate increases with temperature. Graphite is used in lubricants and brake linings because of its lubricity (slipperiness) and in refractories because it is a good heat conductor while keeping its shape at high temperatures and does not react with molten metals.

The three forms of carbon (charcoal, graphite, and diamond) are distinguished by chemical and physical tests. The specific gravity of charcoal is 1.3 to 1.9; of graphite 2.266 g/cc (crystal density); and of diamond 3.5. Graphite has a hardness of 1 to 2 (Mohs scale).

Graphite has a meager chemistry and resists chemical attack by most reagents and is infusible in most common fluxes. It will form intercalation compounds with alkali metal vapors, mostly with potassium, rubidium, and cesium, where the metal ions fit between the planar carbon networks of the crystals, and the graphite structure is retained. Graphite will react with concentrated sulfuric acid to form graphite sulfate, but the reaction is easily reversed by merely adding water. Graphite oxide, a yellow substance known since 1859, is stable over a limited range around 200°C (392°F). It

Table 2. Graphite: World production, by country, t*

Country	1998	1999	2000	2001†	2002‡
Austria	10,738	2,635	669	116	0
Brazil (marketable)§	61,369	53,503	71,208	70,091	60,922
Canada†	25,000	25,000	25,000	20,000	15,000
China†	224,000	300,000	430,000	450,000	450,000
Czech Republic	28,000	22,000	23,000	17,000	16,000
Germany	270	300	300‡	300	300
India (mine)** ††	143,333	145,000	140,000	140,000	130,000
Korea, North	35,000	33,000	30,000	25,000	25,000
Korea, Republic of	62	62	65	65	65
Madagascar	20,629	16,137	40,328	2,013	1,000
Mexico					
Amorphous	42,893	27,781	30,330	21,442	14,065
Crystalline flake	568				
Mozambique	5,889	4,007			
Norway‡	2,600	2,500	2,500	2,500	2,500
Romania	1,951	1,041	1,251	1,176	1,200
Russia†	6,000	6,000	6,000	6,000	6,000
Sri Lanka	5,910	4,592	5,902	6,585	3,619
Sweden	3,011	4,500	5,108	963	900
Turkey (mine)‡	15,000	15,000	15,000	15,000	15,000
Ukraine	5,104	7,461	7,431	7,500	7,500
Uzbekistan†	60	60	60	60	60
Zimbabwe	13,806	11,405	11,838	11,836	9,912
Total	651,193	681,984	845,990	797,647	759,043

Source: U.S. Geological Survey 2004.

* Table includes data available through May 13, 2003.

† Preliminary.

‡ Estimated.

§ Does not include the following quantities sold directly without beneficiation, in tons: 1998—10,747; 1999—10,700; 2000–2002—not available.

** Reported figure.

†† Indian marketable production is 10% to 20% of mine production.

converts into black pyrographitic acid below, or usually explodes above that temperature. Graphite fluoride is formed by exposing graphite to fluorine and hydrogen fluoride, and is of some interest as a high-temperature lubricant.

Origin and Mode of Geologic Occurrence

Graphite is widely distributed throughout the world, occurring in many types of igneous, sedimentary, and metamorphic rocks. Many occurrences, however, are of little economic importance. The more important occurrences are those found in metasomatic-hydrothermal deposits and in sedimentary rocks that have been subjected to regional or contact metamorphism.

Most, if not all, of the world's deposits of flake and crystalline graphite occur in metamorphic rocks of Precambrian age. Marble, gneiss, and schist are the most common types of rock in which economic deposits of flake graphite occur. In many cases, pegmatitic veins have intruded the rocks. Vein graphite is normally found in rocks similar to these, but the enclosing wall rock is not necessarily graphitic. This type of deposit assumes the character of a true lode.

Economic deposits of graphite include five main geological types:

1. Flake graphite disseminated in metamorphosed, silica-rich sedimentary rocks

2. Flake graphite disseminated in marble
3. Amorphous deposits formed by metamorphism of coal or carbon-rich sediments
4. Veins filling fractures, fissures, and cavities in country rock
5. Contact metasomatic or hydrothermal deposits in metamorphosed, calcareous, sedimentary rocks

Natural graphite in these deposits varies widely in physical appearance. Klar (1958) classified graphite occurrences on the basis of crystal characteristics into microcrystalline dense graphites and macrocrystalline silvery-bright graphites. Microcrystalline graphite occurs in deposits of high carbon content as exceptionally small crystals discernable only by high-powered microscopes, whereas the macrocrystalline type generally occurs in lower concentrations and in larger crystal form.

Each type is described in more detail in the sections that follow.

Flake Graphite Disseminated in Metamorphosed Silica-Rich Sedimentary Rocks

A large part of total world production of graphite is derived from rocks such as quartz-mica schist, feldspathic or micaceous quartzite, and gneiss. The graphite flakes in these rocks are oriented parallel to the plane of foliation. The graphite varies widely in physical appearance and characteristics. The flakes range in size from a fraction of

Table 3. World graphite resources (recoverable flake or crystalline concentrates or of amorphous graphite, kt)

Country	Type	Reserves	Reserve Base*	Inferred Reserve Base
Austria	Amorphous	50	50	1,100
Brazil	Flake	500	1,000	2,800
Canada	Flake	1,500	2,700	3,000
China	Amorphous	58,000	200,000	0
	Flake	6,000	20,000	4,000
Commonwealth of Independent States (with Ukraine)	Amorphous	1,000	21,000	540,000
Czech Republic	Flake	900	2,300	11,000
Germany	Flake	130	220	600
India	Flake	735	3,800	10,400
Korea, North	Amorphous	1,000	11,000	20,000
	Flake	700	1,000	1,100
Korea, Republic of	Amorphous	20	90	2,000
	Flake	6	20	60
Madagascar	Flake	940	980	180,000
Mexico	Amorphous	3,000	3,000	10,000
	Flake	106	106	320
Norway	Flake	200	200	40
Romania	Amorphous	300	300	0
Sri Lanka	crystalline†	50	50	150
	Flake	1,800	3,800	5,000
United States‡	Amorphous	0	850	5,000
	Flake	0	60	100
Zimbabwe	Flake	600	600	1,200
Other	Flake	280	300	900
Total amorphous		63,400	236,300	578,100
Total flake		14,400	37,100	220,500
Total crystalline		50	50	150

Source: Adapted from U.S. Geological Survey 2004.

* The reserve base includes reserves; the inferred reserve base does not include the reserve base.

† Known as high crystalline or lump, comprising crystalline lump and amorphous lump.

‡ Reserve base is Alabama only; inferred base is Alaska plus New York.

a millimeter to an average of 40 cm, and may vary by deposit in thickness, toughness, density, and shape.

The principal deposits of flake graphite are in lenses or layers as much as 33 m thick and some thousands of meters long. The lenses have variable graphite content, both within themselves and from one lens to another. The content of an average deposit is about 10%–12% carbon, but some deposits containing as little as 2% graphite have been mined. In Madagascar one rich lens contains 60% graphite. Crystals in each deposit vary in size, usually reflecting the grain size in the parent rock. In an above-average deposit, crystals as large as 4 cm across are common.

Deposits of this type of graphite are described by location in the sections that follow.

Alabama. The deposits of northeastern Alabama, in Chilton, Coosa, and Clay counties, occur in two northeast-trending belts, 1–3 km wide, with a combined length of about 90 km. Worked intermittently since the late 1800s, the mines reached their peak production during World War I. The deposits, called *leads*, are groups of parallel layers and lenses in the Ashland quartz-mica schist that contain 1%–5% disseminated flake graphite. The mined leads range from 6 m to more than 35 m in thickness, dip gently to

Table 4. Sample assay results

Size	Kilograms of Flake per Ton of Ore
+50 mesh	3.0–7.0
–50 +100 mesh	3.5–19.0
–100 mesh	4.0–35.0
Total flake	17.5–65.0

steeply, and have been traced up to 1,200 m long strike. Some are essentially constant in strike and dip over long distances; others are folded, faulted, or both. The deposits are weathered to depths as great as 35 m. In general, the flake ranges from less than 1.25 mm to 5.00 mm in diameter, but most are less than 1.25 mm in diameter. Assays of samples from 32 properties in the northeastern belt by the U.S. Bureau of Mines gave the results shown in Table 4.

Most of the graphite produced in Alabama during and after World War II was formerly stockpiled, but Alabama graphite has been marketed for most common graphite uses.

Texas. The flake graphite deposits of Texas occur in the Precambrian Packsaddle Schist in Llano and Burnet counties. The deposits show a wide range of graphite content and flake size. The most important deposit was one in Burnet County, which was operated by the Southwestern Graphite Company.

Canada. The Lac Knife graphite deposit at Fermont, Quebec, has unusually rich ore; quite atypical of other commercially important Canadian deposits. The graphite deposit and its surrounding host rock, a quartz-feldspar (biotite) gneiss, usually migmatized, represent the southern extension of the Menihek shales and argillites of the Churchill Province into the Grenville Province. Garnet, kyanite, and pyrrhotite are associated minerals. The graphite is uniformly disseminated when the ore has less than 10% graphite. Graphite blebs appear in ever-increasing size as the ore increases in richness above 10%. When the ore is above 25% graphite, veins and massive zones of graphite are observed. The graphite occurs as independent grains, specifically medium to coarse flakes or masses of fine grains, or as inclusions in other minerals, including graphite interlain with mica.

Germany. Deposits east of Passau, Bavaria, near the Austrian border, were known to prehistoric man and have been worked since the Middle Ages. They consist of crystalline graphite in seams, lenses, and disseminated flakes in gneiss and schist. Individual seams and lenses up to 10 m in thickness are mined for a few hundred meters. At Kropfmühl, the only mine now operating, a very heavily folded bed of graphite is mined at eight successive depths in some places. This bed of graphite is interbedded with marble and micaceous gneiss in a zone that is 130 m in stratigraphic thickness. Exposures 0.5–1.0 m thick are mined. Graphite forms 10%–30% of the lenses. Associated minerals are mainly feldspar and calcite, and less quartz, pyrrhotite, pyrite, biotite, hornblende, sphalerite, and galena. Both weathered and unweathered rocks have been mined. Two grades of crucible flake (92%–97%), three of pencil flake (96%–97%), and five grades of fines are produced. The deposits are syngenetic and formed by metamorphism of organic carbonaceous sediments.

Madagascar. Probably the largest resources of high-grade, crystalline flake graphite in the world are on the island of Madagascar. The deposits occur in belts of micaceous gneiss and schist over a distance of more than 800 km in the eastern half of the island from the latitude of the city of Tamatave to the southern end of the island. The principal producing area extends about 110 km along the east coast from Tamatave to Marovintsy. Individual deposits are graphite-rich layers that range from 3.0 m to more than 35.0 m in thickness; some can be followed for a few thousand meters. The graphite content reportedly ranges up to 60%, but ore averaging 4%–11% disseminated graphite has been worked in recent years. Operations are confined to the weathered upper parts of the deposits, and reserves of weathered ore are considered ample for many years at current rates of production. Flake graphite from Madagascar is noted for its high proportion of coarse flake, uniform thickness, toughness, and cleanness, and for the care with which it is graded for export. It sets the world standard for high-quality flake.

Norway. In Europe the principal productive graphite deposits of Norway, Germany (Bavaria), and the Czech Republic consist of flake graphite disseminated in mica schist or mica gneiss or are closely associated with these rocks. The productive deposits of Norway (A/S Skaland Grafittverk) are on Senja Island in northern Norway (latitude, 60°39'N; longitude, 17°E), and are lenses of graphitic rock enclosed in mica schists. The richest ore contains 25%–30% graphite. The ore is hard and must be crushed to recover the graphite.

Flake Graphite Disseminated in Marble

Flake graphite disseminated in marble probably originated from carbonaceous impurities. Graphite commonly is less than 1% of the rock, although in some localities it is as much as 10%. Deposits of this type are structurally complex and exhibit much variation in grade and kinds of accessory minerals over short distances. Their contribution to world production is consequently much less than that from deposits in schists and gneisses.

The most significant graphite deposit of this type in the world is the Lac-des-Iles crystalline flake graphite deposit in Canada. The host rock is a jumble of Grenville biotite-garnet gneiss, quartzite, and graphite-containing marble. Although most of the graphite is found in the higher-grade marble core of a gneissic body, some larger-flake graphite is found in the quartzite ring surrounding the core. The entire sequence is cut by gabbro-diorite dikes and pegmatite bodies and is extensively folded and faulted.

Amorphous Deposits Formed by Metamorphism of Coal or Carbon-Rich Sediments

The graphite in deposits formed by the metamorphism of coal or carbon-rich sediments is almost invariably the microcrystalline variety known to the trade as amorphous graphite. A substantial part of world production of amorphous graphite is from such deposits. The graphite occurs in seams, often distorted by folding and faulting, and is commonly intimately mixed with nongraphitized material. The ratio of graphite to nongraphitized material can vary widely. For example, some high-grade Mexican varieties contain as much as 95% graphite, whereas low-grade Korean graphites are commonly burned for fuel because of high non-graphitic carbon content.

Deposits of this type of graphite are described by location in the sections that follow.

Austria. In southeastern Austria, large resources of graphite are present in a 50-km-long belt of folded metasediments extending from the towns of Leoben to Rottenmann in the Styrian Alps. There are two producing mines. At Kaisereberg, the principal mine, a series of graphitic beds with an aggregate thickness of 12 m are enclosed in graphitic schists and quartzites. Crude ore contains 30%–80% carbon and averages 50%–60%. Refined graphites ranging from 66%–95% carbon are produced by grinding and flotation. The products are amorphous graphite and are used for foundry facings, pencils, paint lacquer pigments, and lubricants.

Mexico. The most important deposits of amorphous graphite in the western hemisphere occur in the state of Sonora, Mexico, in an area 30 km long by 15 km wide, approximately 60 km southeast of Hermosillo. The deposits were discovered in 1867. Six beds of graphite are reported, the thickest averaging 3.0 m, but folding causes local swelling to 7.0 m. They were earlier described as beds of coal interlain with sandstone, folded, and then intruded by granite; the coal thereby converted to graphite. Recent detailed examinations, however, reveal the deposits at the Moradillas mine to be hydrothermal veins; no evidence has been found to indicate that they are metamorphosed coal beds. The veins are said to occupy fissures that cross the bedding of the country rocks at low angles. In the district as a whole, the graphite deposits are reported to be steeply dipping and are said to range from mere stringers to seams that are locally 4–5 m wide. High-grade Mexican graphite averages 80% carbon, but some contains as much as 95%.

The mineral suite for amorphous ore includes mica, clay minerals, tourmaline, and hematite with occasional pyrite and gypsum locally. The ore is prepared for shipment by hand-sorting out the

admixed rock from the hanging walls; then it is crushed, screened, and dried.

South Korea. The amorphous graphite deposits of South Korea, which have yielded about 2 Mt, occur as irregular lenses parallel to the structure of enclosing schists and as phyllites of sedimentary origin. In the Kyeong-Sang district, three seams having minable widths of 24, 6, and 15 m, respectively, have been reported. Deposits formed by dynamic and contact metamorphism of coal beds occur in southern Korea, but Overstreet (1947) reports that these are impure.

United States. In the United States, coals in the Narragansett Basin of Rhode Island have locally been metamorphosed to graphitic anthracite.

Veins Filling Fractures and Cavities

Veins of graphite are typically filled fractures or cavities in the country rock. In thinner veins, graphite occurs as crust or layers of closely packed, coarse, elongate plates (needle lump) oriented perpendicular to the vein walls. Plates vary in length with vein thickness and may be as long as 10 cm. Central portions of thicker veins may consist of platy layers with the crystals parallel to the vein walls.

The origin of graphite vein deposits is uncertain. Winchell (1916) discussed various hypotheses and concluded that the most probable mode of origin involved reduction of oxides of carbon.

The deposits of this type of graphite are described by location in the sections that follow.

Mexico. The most important deposits of amorphous graphite in the western hemisphere occur in the state of Sonora, Mexico, in an area south and east of Hermosillo and south and east of Navajoa. In addition to these strictly amorphous deposits, there are a few deposits such as the one at the Lourdes mine that have supplied vein graphite. Substantially more than half of the total state production formerly came from the Lourdes mine at Moradillas, now closed. These vein deposits, interlain with sandstone, consist of steeply dipping, north-south striking graphite veins ranging from small stringers to seams that average 3–4 m wide at depth. Some veins more than 6 m wide were mined. The graphite content averaged 85%–90%.

Sri Lanka. The graphite vein deposits of Sri Lanka have been worked systematically for more than 140 years, yielding more than 1.2 Mt of graphite since 1880. The main deposits are in Southern, Western, and Sabaragamuwa provinces. The deposits occur in a complex series of Archean granulites, quartzites, garnet-sillimanite gneisses, and marbles in narrow, structurally controlled belts that persist for many miles along the strike. The productive deposits range from simple fissure veins to branching veins or stockworks. Veins commonly are a few millimeters to almost a meter thick. Some of the larger deposits are tabular bodies parallel to the foliation of enclosing rocks. Graphite-filled vugs as long as 24 m and 2 m × 1 m in cross section are reported. The highest grades of Sri Lanka graphite carry 97%–98% carbon. A variety of minerals, chiefly quartz, pyrite, calcite, apatite, and pyroxene, and lesser rutile, allanite, magnetite, and various lime-magnesia silicates, have been reported to be associated with graphite in the veins, but it is not clear whether these minerals were deposited with the graphite or merely minerals of the wall rocks accidentally enclosed in the veins. Resources of graphite in Sri Lanka are probably very large.

United States. Deposits of this type at Sturbridge, Massachusetts, were mined in the 1640s, the first graphite mining in the United States. The only sizeable domestic vein deposits, however, are those at the Crystal Graphite mine near Dillon, Montana. There, graphite fills networks of fractures in gneiss and pegmatite around the northwesterly plunging nose of an isoclinal fold, a structure that

involves granite gneiss, schist, marble, and quartzite of the Precambrian Cherry Creek Series. The veins are a few millimeters to 60 cm thick and 1–15 m long. The formation of the veins has been related to the development of the pegmatites, but Ford (1954) later showed that fracturing and vein formation took place after the formation of these rocks.

India. Vein deposits have also been reported from southern India (e.g., in Tamil Nadu).

Contact Metasomatic or Hydrothermal Deposits in Marble

Concentrations of graphite occur in various parts of the world in silicified carbonate rocks. Some are clearly contact metasomatic; others show gradations to typical hydrothermal deposits. As a group, they are characterized by variability in deposit size (generally small), variability in flake size and content, and irregularity of form. The average grade of most deposits is low, and, consequently, they have accounted for only a minor part of total world production.

Distribution of Major Deposits

Africa. Zimbabwe's only producer is the Lynx mine near Karoi, although there are other deposits nearby. It is operated by its parent-owner, a subsidiary of Graphitwerk Kropfmühl A.G. of Germany. The ore is mined underground from a lenticular ore body running 20%–35% crystalline flake graphite. The ore is beneficiated by flotation to make products containing 80%–83% and 90%–94% graphite.

Graphites de Ancuabe Ltda. operated a sizeable mine and plant in Mozambique from 1994 to 1999, and Tanzanian graphite was mined near Merelani for a few years in the 1990s.

Australia and New Zealand. There are some medium-sized deposits in Australia. Several occurrences are also reported in New Zealand.

Austria. The graphite deposits in Styria are thought to have originated by the metamorphism of carboniferous and bituminous substances under high pressure and temperature, during deformation. The deposits, therefore, occur in comparatively small lenses and, with one exception, must be mined underground.

The major mines in Styria, some of the two centuries old, are near Kaiserberg and Triben. Geologically, these Alpine deposits are embedded in a zone of fine-grained, scaly schists in lenses and individual beds as much as 10 m thick. The ore is black, soft, fine-grained, and dense, with a carbon content of 40%–88%. It is low in sulfur (0.2%–0.3%) and iron and practically free of carbonate and phosphate.

The first and only flotation plant for amorphous graphite is at Kaiserberg. The process was developed in the laboratories of Franz Mayr-Melnhof & Company's subsidiary Grafitbergbau Kaisersberg, where fine (2 µm average particle size) graphite with 92% carbon is produced, suitable for lubrication, pencils, pigment, and drilling mud.

Brazil. The three major crystalline flake graphite mines are in the state of Minas Gerais, and belong to Nacional de Grafite Ltda. The mines are at Itapeceira, near Belo Horizonte, Pedra Azul, about 16 km from the Minas Gerais–Bahia boundary, and Salto da Divisa, 50 km from Pedra Azul. Pedra Azul is by far the largest producer of the three. The ores mined are graphite-containing soils, the results of very extensive weathering of the original host rock. Therefore, no blasting is required before the ore is removed by front-end loader or shovel. The ore at Itapeceira averages 20% graphite and occurs in numerous small pockets spread over an area of 130 sq km. Usually only a small number of these pockets are mined at one time. The ore at Pedra Azul averages 5%–12% graphite, is mined at a number of faces, and usually

blended to a mill feed running 6%–7% graphite. Beneficiation plants at the three locations use flotation to make a final product. A chemical leaching plant that produces high-purity (99.6%) graphite is located at Itapecerica.

A handful of very small mines located in the states of Minas Gerais and Bahia produce unbeneficiated product sold as is.

China. Graphite is produced in a number of provinces in China, of which two are by far the most significant. Shandong Province is a major flake graphite producer, and its major mines are the Nan Shu, Bai Shu, and Dong Guan. Bai Shu also has an exfoliated graphite plant. Heilongjiang Province is the other major producer, with three mines east of Harbin at Jixi: the Liumao (the largest flake producer), Lin, and Moshuan mines. Inner Mongolia produces graphite, mostly from the Xing Ho mine. Shanxi Province produces graphite from the Guodian and Deisheng mines. Hunan, at the Lutang mine, and Guandong provinces also produce graphite. China has very low production costs, which has allowed it to establish a major niche in the world market in the 1980s; however, domestic consumption of graphite has increased rapidly and infrastructure problems have appeared.

Commonwealth of Independent States and Ukraine. Graphite occurs in a number of places in the Urals, Siberia, Uzbekistan, and particularly the Ukraine. Reliable sources indicate that 75%–90% of the graphite produced is crystalline flake, almost all fine flake. Until the early 1980s this region was a significant exporter to most world markets, including the United States.

The biggest producer, probably accounting for 75% of total production or 60 kt, is the Zavalyevsky complex in the Ukraine, near Gayvorgan. The mine is an open-pit operation on steeply dipping ore bodies that range from 3 m to 35 m thick and produces ore grading from 3% to 7% crystalline flake graphite. The beneficiation plant also produces colloidal graphite products, lubricants, and high-purity graphite containing between 99% and 99.9% graphite.

Czech Republic. Graphite is mined in two areas, one in Bohemia near the Austrian border and one in Moravia near the Polish border. Both mine fine-grained crystalline flake or, more usually, crystalline dust from metamorphic host rocks, mostly gneiss or schist. In Bohemia, the ore contains 15% graphite; its beneficiation by flotation creates a product containing 80%–96% graphite, and a final leaching yields a 99.99% graphite product. In Moravia, the ore contains 30%–40% graphite.

Germany. The Passau district (Bavaria) has long produced flake graphite suitable for crucibles. Historical documents frequently refer to this graphite, which probably furnished the graphite in the Middle Ages for alchemists' crucibles. The graphite-bearing country rock is a part of the "kristallines Grundgebirge," the old gneissic and schistose rock of the Bohemian massif; the gneissic rocks are believed to have been metamorphosed during the Carboniferous period.

Today, Graphitwerk Kropfmühl A.G. produces flake graphite exceeding 96%–97% graphitic carbon suitable for crucibles, pencil leads, and lubricants. This company also chemically purifies graphite to +99.9% carbon in several size grades. The company mines one graphite bed (1.5 m thick) that is so tightly and heavily folded that it can be intersected eight different times in depth at many locations. Thicker layers occur in places because of folding. The ore runs 20%–25% graphitic carbon. It is beneficiated and processed by flotation, grinding, and screening.

India. The major graphite-producing Indian states are Orissa and Rajasthan, but Andhra Pradesh, Bihar, Gujarat, and Tamil Nadu also produce graphite. Orissa usually accounts for 65%–75% of all Indian production. Major companies include Agrawal Graphite

Industries, with mines near Ganjaudar and Temrimal in Orissa State, and TP Minerals Pvt. Ltd., with mines near Phulbani, Madagudarf, and Sargipali, all in Orissa State. Both companies produce a variety of crystalline flake and powder graphites, which mostly go to a wide variety of domestic end uses. The most important Indian end uses are in crucibles and foundries.

Indian graphite deposits usually occur in garnet-sillimanite-muscovite gneisses of the Khondalite group. Of the total reserves of recoverable graphite, 35% are located in Kerala State, 31% in Bihar State, 13% in Orissa State, and the balance elsewhere.

Madagascar. The African island of Madagascar is an important producer of graphite because of the size and quality of its flake. Occurrences are widespread along the eastern coast near Tamatave, in the central section near Tananarive, and in a southern section between Betroka and Bekily. Current production comes from the deposits along the eastern coast. The main producers are Societe Miniere de la Grande Ile and Establishments Galois. Each company markets its own graphite; graphites from different deposits are not blended.

The deposits are in a region where lateritic deposits of iron and bauxite also are found. The graphite occurs in highly metamorphosed schists and gneisses that have weathered deeply to soft, ferruginous clays. The graphitic content of the original rock has been raised through the natural leaching process. The graphite, being resistant to weathering, is found among the weathered residue.

The crude ore contains 3%–10% graphite, of which about two-thirds is large flake and one third is fine flake. Commercial interest is primarily in the large flake; it is strong, flexible, and is the best graphite for refractories. It is also favored for crucibles. The pyrometric cone equivalent of the ash is cone 16 to 20 and is higher than the ash of other flake graphites.

The nongraphitic portion of the flake product is uniform and consists (after oxidizing) chiefly of a clayey residue with some quartz and a sprinkle of accessory minerals such as mica, zircon, rutile, and epidote. Sulfur compounds are absent and iron is low.

Mexico. Sonora contains extensive deposits of amorphous graphite, and most Mexican graphite mines and mills are located here. The Sonoran deposits are homogeneous and contain about 80% graphitic carbon. They were discovered in 1867, and exploitation began in 1891. There are said to be as many as seven distinct beds of graphite within alternating layers of metamorphosed andalusite-bearing Triassic rocks.

The operating mines are located about 400 km southeast of the U.S. border in the region of Moradillas. This region is arid, and water for operation is scarce. Other amorphous graphite deposits are reported in the states of Baja California del Norte and Coahuila in northern Mexico, and Hidalgo and Guerrero in central Mexico.

Several crystalline flake deposits are known in Oaxaca; one of these has been worked at Teixtlahuaca. The owner, Grafito de Mexico SA de CV, beneficiated the ore nearby by flotation.

Norway. A/S Skaland Grafitverk has been the only operating graphite mine in Norway. Currently closed, it is expected to reopen. The deposit is on Senja Island in northern Norway. Flotation brings the carbon content up to 80%–93%.

Republic of Korea. The Republic of Korea is a minor producer of natural graphite and has produced both amorphous and flake products. The principal mining areas are in the provinces of Chung Nam, Kyong Gi, L yung Pak, and Kang Won, near Seoul. Almost all the deposits are in the vicinity of anthracite coal mines, lending support to the idea that the amorphous graphite is derived from coal.

Sri Lanka. Sri Lanka contains the largest known deposits of vein graphite. Very large deposits are located in the western and southwestern sections of the island. The extent of the deposits has inspired significant study, and although the resulting literature is extensive, little is known about the origin of the vein graphite. According to Wadia (1943)

The vein graphite deposits are believed (by some) to have been formed by reduction, at high temperatures and pressures, of carbon dioxide liberated during the assimilation of limestones and dolomites by charnockitic and related igneous magmas.

The structures of these ore bodies contrast markedly with those of other forms of graphite and are typical of vein, dike, pegmatitic, or pneumatolytic ore deposits.

Almost all high-quality vein graphite comes from Sri Lanka. Despite rising labor costs, most of the production is still done by hand cobbing and hand sorting to satisfy buyers who still retain a preference for lump grades. Because most graphites are used in industry as a powder, the current operators anticipate a trend toward supplying the powder directly from the mine to the importer, thus reducing hand sorting.

Sri Lankan graphite is highly graphitized; the best grades are completely graphitized. It is favored for lubrication, pencils, electromotive brushes, and other uses requiring high-quality graphite. A subsidiary of Kropfmuhl A.G., Bogala Graphite, is the producer.

Sweden. Woxna Graphite AB produced graphite briefly from a deposit near Edsbyn.

United States and Canada. Graphite is no longer produced in the United States. The lone flake producer, Southwestern Graphite Company in Burnet, Texas, closed its mine operation in 1980. The graphite plants in the United States process imported graphites that are beneficiated, ground, and blended as required to maintain individual company specifications.

Flake graphite deposits in both Alabama and Pennsylvania have been worked intermittently; the last Alabama mine closed in 1953 and the last Pennsylvania mine in 1961. Rhode Island stopped producing amorphous graphite in 1959. An amorphous graphite-like material was produced in Montana in the 1980s.

Deposits of this type occur at a number of places in the Grenville Series in northern New York, southwestern Quebec, and southeastern Ontario. Small deposits west and northwest of Ticonderoga, New York, were worked between 1850 and 1900. They consist of fine-to-coarse flake graphite irregularly concentrated in silicified marble adjacent to bodies of pegmatite.

Canada is endowed with a sizeable number of flake graphite deposits, most in Quebec or Ontario. These deposits are associated with Grenville Series marbles and gneisses. The largest producer is the mine and plant of Timcal Ltd. (formerly Stratmin, Inc.) at Lac-des-Iles, Quebec. Sequoia Minerals Inc. (formerly Mazarin, Inc.) has a good deposit at Fermont, Quebec, currently undeveloped.

Timcal Ltd. operates an open-pit mine on reserves totaling 23.7 Mt averaging 7.5% graphite. With this feed, the company produces as much as 25 kt of concentrate with 92%–98% graphite. Stratmin operated the Asbury Graphite Inc. mine and mill nearby for several years before closure. In November 1988, Stratmin leased the Asbury Graphite operation and contracted to supply Asbury with at least 10 kt of graphite each year for 5 years.

Sequoia (as Mazarin) extensively drilled its Fermont deposit and estimates that its reserves for the first 20 years of mining will total 3 Mt, averaging 17% graphite. Additional reserves total 5.8 Mt, averaging 14.2% graphite. The deposit has good access and is near the railroad running to the iron ore towns of Quebec from Sept Iles.

TECHNOLOGY

Exploration, Drilling, and Testing

Prospecting consists primarily of outcrop examination, trenching, and sampling, usually followed by drilling. A local non-technical person usually makes the initial discovery. In Mexico, a cowboy, shepherd, or local farmer may have found a showing of amorphous graphite. Any associated coal may even have been crudely mined and used locally as a fuel. In Madagascar or Brazil, a local hunter or palm-tapper may have come across a showing of crystalline flake graphite, which is not difficult in Madagascar where almost one-third of that huge island is underlain by graphitic rock or soil. Sri Lankan lump graphite has been known far back into history. Because of the high electrical conductivity of graphite, geophysical methods such as resistivity and self-potential have been used in the search for deposits in certain countries. Occasionally, the initial discovery was made by a government geologist doing routine field work. The Lac Knife deposit was discovered by a Quebec government geologist doing field work in 1959. When serious interest developed, Mazarin started trenching by shovel in 1987, stripped by bulldozer in 1988, and systematically diamond drilled more than 99 holes in 1989. This exploration, drilling, and testing of the Lac Knife crystalline flake graphite deposit is a good example of what the norm will be in the future, displacing the local non-technical person finding a graphite showing.

Mining Methods and Haulage

From 1890 to 1920, underground mining of graphite was practiced in New York and Pennsylvania. From 1942 until the end of World War II, only the open-pit methods were used, because working weathered rock was relatively easy. Graphite was mined underground at Dillon, Montana, during World War II, but shortly thereafter mining ceased because it was too costly to compete with Sri Lankan graphite.

Madagascar operations are entirely open pit, but in Bavaria, Korea, Mexico, and Sri Lanka, because of the depth and physical characteristics of the deposits, underground mining is practiced.

Mexican underground mining operations are 100–400 m below the surface, measured on the angle of the vein. Some of the older mines in Sri Lanka reached depths in excess of 450 m on a vertical plane. For many years, mining operations in Sri Lanka were primitive and ore extraction was slow and cumbersome. The mines were mechanized after World War II.

Madagascar operations also were primitive because low labor costs prohibited mechanization. After 1938 the mines began to use mechanical equipment to remove the overburden, and bulldozers and tractors easily removed the graphite-bearing schists.

Processing and Beneficiation

In Sri Lanka, graphite ore is extracted in lumps and hand-cobbed on a sorting patio to remove quartz inclusions. The finished product is graded as (1) large lump, 97%–99% carbon; (2) ordinary lump, 94%–96% carbon; (3) ordinary lump, 90% carbon; (4) chips, 85%–90% carbon; and (5) chippy dust, 80% carbon. The chippy dust and flying dust grade, however, are not produced in any quantity today.

In Madagascar the crude ore averages 10%–12% carbon. It is crushed by a primary crusher and then conveyed to a series of roll crushers and classifiers to remove the oversized and gangue material. The –6.35-mm product is then passed to flotation rougher cells, which separate the graphite flakes from the clay and sand. The product of the rougher cells passes to the finishing cells where each particle of graphite is recovered by means of a pine oil frothing process. This yields an 80%–84% carbon concentrate, which is dried; an y

residual pine oil is volatilized. The run-of-mill product is upgraded by mechanical means, such as rod mill grinding, to 0.3 mm sieve with 85%–90% carbon. Re grinding and flotation obtain higher carbon concentrates (up to 95%).

At the mill of Graphitwerk Kropfmühl S.A., in Bavaria, crude ores carrying 15%–20% carbon are crushed, passed through a grinding system, and then a rod mill, which reduces the ore to 40 mesh. This product is fed to a series of flotation and grinding steps, and the graphite concentrate is filtered and kiln dried with the final product averaging 90%–93% carbon. For further refinement, this product is milled and screened, producing grades with 95%–97% carbon.

These operations are fairly typical of those found in other countries. Some companies make high-purity graphite by leaching concentrate with strong acids or alkalis.

MARKETING

Graphite is used commercially in a number of applications, described in the sections that follow.

Batteries

Battery makers aggressively compete for available sources of natural graphite, synthetic graphite powder, and other forms of carbon. Carbon, not graphite, is almost always used in older batteries. Alkaline batteries will usually use some kind of graphite. The lightweight, rechargeable lithium ion batteries, typically used in cell phones and digital cameras, use a specialized graphite or a high-tech mesocarbon. Fuel cells are not included here but are in the section on Outlook that follows with other potential uses.

Bearings

Graphite is used extensively in bearings, and varies depending on the type of bearings being produced. This is a small-use market with limited growth potential.

Brake Linings

Graphite consumption as an asbestos substitute increased greatly in the 1980s when the dangers of asbestos were recognized. Graphite is particularly useful in brake linings for heavy-duty vehicles as opposed to passenger vehicles. As long as organic friction materials impregnated with graphite are used and accepted as satisfactory, graphite consumption should increase gradually in accordance with the increased number of vehicles on the road.

Carbon Brushes and Other Electrical Uses

Natural graphite encounters considerable competition from artificial graphite for this use. Wherever artificial graphite has advantages, it has already captured the market. For example, in the production of sliding contacts, the ash content variation in natural graphite has proved unacceptable; now artificial graphite in which the abrasive materials can be controlled is being used.

Crucibles

Crystalline flake graphite consumption to make crucibles has been steadily declining in market share over the last decade. Advances in crucible manufacturing technology now allow much greater flexibility in type and flake size of the graphite utilized.

Expanded Graphite

This use has been growing rapidly until fairly recently. Expanded graphite is used to make high performance gasket material for use at high temperatures or pressures and with radioactive or corrosive fluids. Expanded graphite can be made into a foil laminate that is

used in valve packings and as a gasket material. Foil can also be made into a heat sink for high-tech computer and communication products. Expanded graphite is being used as a hot topping compound to insulate hot ingots and decrease heat loss. Expanded graphite is made from crystalline flake graphite by treating it initially with chromic acid, followed by sulfuric acid, to weaken the bonds between the graphite flakes. The graphite is then heated to drive off the water, causing expansion, creating a product with properties similar to vermiculite.

Foundries

Foundries are one of the largest consumers of graphite. Graphite has a number of uses in foundries, but the largest single use is as a foundry facing or mold wash that allows the metal casting to be easily removed from the mold on cooling. Another significant use is as a carbon raiser, when a carbonaceous material is added to hot metal to raise its carbon content. Graphite is also used to lubricate extrusion dies before hot metal is reshaped to form other products.

Lubricants

This market is tremendously complex because of the variety of lubricating jobs that must be done and the myriad lubricant types that are available. Graphite has been an important lubricant and probably will continue to be, but competition is stiff. Graphite added to a soapy lubricant is considered to be a good die lubricant, particularly for galvanized wire, though the discoloration it produces is not desirable. Natural graphite is a good antiseize agent in steel mill and railroad applications because it creates a solid lubricant film that retains its properties under pressure and high temperature. In this particular use, the customer specifies the graphite content empirically, so its use may not be based on some theoretical factor(s). Natural graphite is used in applications in which the siliceous portion of the natural graphite is overshadowed by the background contamination of dirt and sand, for example, gear lubrication for mining machinery.

Graphite of colloidal size dispersed in kerosene, oil, or another carrier is used when a quick-drying film is desired in high-temperature lubricating jobs (i.e., conveyors passing through ovens).

Packings

Fine flake graphite performs well with oils or greases because it resists temperatures up to 310°C. Closely controlled particle size is less important for packing use. Graphite use will tend to remain relatively steady, but may decline in more modern equipment that no longer uses older style packings. Very small quantities of molybdenum also offer excellent lubricating qualities.

Pencils

Low-cost improvements in the pencil industry have led to greater jetness, higher carbon content, smaller particle sizes, and more unctuousness and opaqueness in the graphite. However, technology improvements must not add to the cost of graphite for the pencil manufacturer. Imported pencil leads from China now have most of the pencil market.

Refractories

Graphite is used in both plastic (castable) refractories, principally in ramming and gunning mixes, and shaped refractories, principally carbon-magnesite brick and alumina-graphite continuous casting ware. For the last 20 years, graphite-containing refractories have increased their market share against other refractories as the demand for high-performance ware has grown, principally for

products that resist high temperature, thermal shock, and corrosion. The steel industry consumes around 70% of refractories worldwide.

Gunning and ramming mixes, used where the refractory must be deformable or flexible, commonly use amorphous graphite. Carbon-magnesite mixes are made from crystalline flake graphite.

Carbon-magnesite brick is used to line basic oxygen converters, in the slag lines and water-cooled sidewalls of electric arc furnaces, and to make steel ladles. Graphite consumption in the former two uses grew rapidly in the 1980s, and consumption in the latter use grew more in later years. Use in basic oxygen converters is still growing in some countries.

Continuous casting wears made of alumina graphite includes items such as shrouds, subentry tubes, and stopper rods.

Graphite Grades and Specifications

As described earlier, the two main categories of natural graphite are known commercially as crystalline and amorphous, even though all graphite is truly crystalline and the distinction is only one of crystal size. "Amorphous," as applied to graphite, has been further complicated by longstanding industrial application of the term to very fine particles of crystalline flake graphite that can be sold only for low-value uses, such as foundry facings. This very fine flake is also called crystalline dust. Fine-grained varieties of lump graphite that can be reduced easily to fine particle size by grinding are called amorphous lump. This distinguishes them from tough, platy, and acicular varieties, known as crystalline lump, that can be reduced in particle size with difficulty. Thus, large quantities of fine-crystalline flake graphite are imported under the amorphous classification.

Sri Lankan lump graphite is classified either as amorphous or crystalline. Each type is divided into a number of grades, depending on the particle size (lump, ranging from the size of walnuts to that of peas; chip, from the size of peas to about that of wheat grains; dust, finer than 60 mesh), graphite carbon content, and degree of consolidation.

Amorphous graphite is graded primarily on graphitic carbon content. Commercial products contain about 50%–94% carbon, depending on their source.

Crystalline flake graphite from Madagascar is divided into two main grades, flake (coarse flake) and fines (fine flake). Madagascar crucible flake must have a minimum of 85% carbon and be in the size range –8 to +60 mesh. Other crystalline flake graphite is graded according to graphitic carbon content and particle size.

The synthetic graphites generally are classified as electrodes, anodes, molded shapes, and powders or scrap, and they are made from petroleum coke and pitch. Graphite fiber is made from textile threads or extruded pitch fibers.

Graphite Prices and Pricing

Graphite pricing behavior is rather complex, mostly because graphite is not traded on any commodity exchange. Graphite prices are subject to negotiation between buyer and seller, and depend on carbon content, flake size and distribution (for crystalline flake), and the identity and nature of any impurities. The product is usually customized for the individual consumer. China has been the world price setter for the last 20 to 30 years, sometimes competing with other nations and at times through interprovincial competition within the country itself.

Three price series for natural graphite are detailed here: (1) crystalline flake, which has become the major competitor in the last decade or so; (2) Mexican amorphous, which is currently in a long-term decline in importance because low-tech end uses are becoming obsolete; and (3) Sri Lankan lump graphite, which is a specialty product because its relatively high price results in a low demand.

Crystalline flake of various sorts is the most important natural graphite and accounts for 80%–90% of the value of U.S. imports. There are posted prices that have not changed for many years. The USGS price for crystalline flake was US\$615 per ton in 2000, US\$520 per ton in 2001, US\$565 per ton in 2002, and US\$560 per ton in 2003; the price for Sri Lankan lump and chip was US\$1,250 per ton in 2000, US\$1,360 per ton in 2001, US\$1,220 per ton in 2002, and US\$1,200 per ton in 2003; the price for amorphous was US\$130 per ton in 2000, US\$131 per ton in 2001, US\$115 per ton in 2002, and US\$120 per ton in 2003. Industry observers have said that even the USGS prices have been subject to substantial discounting in the 2000–2003 period of collapsing demand.

Substitutes for Graphite

The most common substitutes for graphite are other forms of carbon. In steelmaking, petroleum coke, anthracite, and used (synthetic) graphite electrode scrap can be used as a carbon raiser instead of natural graphite. Calcined coke and other carbons can be used in certain foundry core and mold washes instead of natural graphite. Synthetic graphite powders are often substituted for natural graphite, depending on relative price.

Noncarbon substitutes for natural graphite include molybdenum disulfide for lubricant use. Graphite is substituted for asbestos in automotive brake linings and is being substituted for by certain organic nongraphite compositions. Alternate nongraphite refractory compositions, such as silicon-carbide or chrome-containing compositions, can substitute for carbon-magnesite bricks, alumina-graphite shapes, and crucibles.

Packaging and Shipping

The cost of shipping graphite is a major cost consideration for the customer. Because graphite is messy, it must travel bagged or in closed containers. The most common form of packaging is 1-ton "supersacks"; of lesser importance are 25-kg bags of paper or plastic. Burlap bags were commonly used in the past but are now rarely used. Supersacks are made of woven polypropylene and measure 88.9 cm × 88.9 cm × 190.5 cm. For example, amorphous graphite coming from Mexico as lumps commonly were shipped in covered hopper rail cars; fines were transported in bags. Most of the graphite imports now come by ocean freighter as a large shipment with other bulk materials, or as general freight if the shipment is small. Inside the United States, graphite is transported by barge, truck, or rail, depending on port of origin and final destination.

ECONOMIC OR COMPETITIVE FACTORS

Import Duties

U.S. imports of natural graphite as of December 31, 2003, are duty-free for HTS (Harmonized Tariff Schedule) categories 2504.10.1000 and 2504.90.0000. This applies to all nations except Cuba and North Korea.

Graphite By-products or Coproducts

Graphite deposits have been mined exclusively for their graphite content and that practice will continue. In the past, proposals to recover graphite and coproduct mica from a graphite-mica schist and another to recover graphite and gold were considered; however, neither proved to be economically viable.

Depletion Allowance, Costs, and Timing

The U.S. depletion allowance for tax purposes is 22% for domestic lump and amorphous graphite, and 14% on domestic crystalline flake. Because the United States has no domestic reserves and only

small, low-grade resources, there is almost no likelihood of any domestic producer starting production and claiming this allowance. Similarly, questions of costs and timing of domestic production are not likely to arise.

Regulatory and Environmental Considerations

The environmental requirements for natural graphite, which is an inert, nontoxic substance, are limited to dust control and control of organic vapors that may arise in making certain graphite products from imported graphite. Given the current and future absence of graphite mining, no other requirements will be applicable.

OUTLOOK AND FUTURE TRENDS

In the last 4 to 5 years, graphite has lost the majority of its most important market in the United States—refractory use. The 2004 outlook was primarily based on the *Graphite Advocate News* Web site (www.basicsmines.com/graphite), which is updated frequently, and the USGS Web site (<http://minerals.usgs.gov/minerals/>), which is updated two times per year. After several negative years, the positive 2004 outlook reflected a strong U.S. metal-using economy and strongly expanding Chinese domestic natural graphite demand, mostly from the Chinese steel industry. China is poised to become a net importer of natural graphite and will slow down or stop exporting altogether, but this could be temporary or sporadic because Chinese reserves would easily support new mines and additional production. The Chinese steel industry is growing rapidly; Chinese steel production in 1999 was 124 Mt and rose to 200 Mt in 2003. Overall, U.S. graphite sales in 2003 were flat, down 2% from 2002. Graphite sales in 2004 were up 2%–5% from 2003.

Long-Term Shift in Consumption by End Use

Major shifts in U.S. consumption of natural graphite by end use are under way. Graphite consumption in refractories was 11,000 t in 2000 (the latest full set of end-use data) but has dropped to a fraction of former consumption because many U.S. refractory plants have closed, carbon-magnesite bricks have been replaced with monolithics, and U.S. carbon-magnesite brick has been replaced by Chinese imports. Consumption in brake linings was 6,600 t in 2000 but will erode because of new nongraphite-containing (nonasbestos organic or NAO) brake lining formulations. Consumption in expanded graphite/foil/packings was 5,000 t in 2000, which might grow in a few submarkets but otherwise should not grow. Consumption in batteries was 4,000 t in 2000 but should be able to maintain itself in spite of fierce competition from other natural and synthetic carbon materials. Consumption in foundry uses, mostly mold washes, was 3,000 t in 2000 and depends on the future of the foundry industry as other material-shaping techniques come in to use. Graphite use in lubricants was 1,600 t in 2000 and should be stable or maintain slow growth at that level. High-volume use in fuel cells may occur in the longer term. Graphite foil use in heat sinks may become significant.

Short-Term Outlook

Graphite-Based Refractories

Natural graphite (mostly flake) is used in carbon-magnesite brick and in alumina-graphite shapes, with smaller amounts in crucibles, gunning and ramming mixes, and other kinds of refractories. The bricks are used to line basic oxygen steel converters and electric-arc furnaces to withstand extreme conditions (temperature, corrosion, etc.). The shapes are used as continuous casting ware usually in the form of nozzles to guide molten steel from ladle to mold. Consumption for refractories in 2003 dropped 10% from 2002; major

graphite suppliers have left this market. Future demand for carbon-magnesite bricks will most likely be met by imports from China.

Fuel Cells and Heat Sinks

These are potential high-growth, large-volume graphite (natural and synthetic) end uses, but are currently a very small part of consumption. Large volumes of graphite will not be consumed in these end uses for many years.

Brake Linings

Natural graphite (amorphous and fine flake) is used as a substitute for asbestos in brake linings for heavier (nonautomotive) vehicles. The 2003 consumption was up about 2%–3% from 2002.

Graphite Powder (Synthetic)

Graphite powder is mostly used as a carbon-containing additive put in molten steel to raise the carbon content in brake linings, and in packings, seals, batteries, and other minor uses. Synthetic graphite powder production in 2001 was 95,000 t (latest USGS data). USGS data show that imports run 25,000–30,000 t and exports 60,000–70,000 t. The demand for powder in 2003 increased 20% from 2002 in volume.

Lesser End Uses

Lesser applications include use in lubricants, powdered metals, foundry facings, plastics, rubber, and pencils. The growth markets in this category are in rubber and in plastics (including styrofoam coatings). The weakest market for graphite is in pencils, which has almost disappeared; pencil leads now are imported directly from China.

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Gypsum and Anhydrite

Roger Sharpe and Greg Cork

INTRODUCTION

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is a versatile mineral with hundreds of uses. The predominant use of gypsum since ancient times has been as a construction material. According to Schroeder (1970), gypsum was used as a mortar in the Egyptian pyramids in 3000 BC, and Pressler (1985) indicated that at the burning or calcining of gypsum was described by the early Greeks. Gypsum mortar was used in Egypt during construction of the Pyramid of Cheops in the 18th Dynasty (1580–1350 BC). Hydraulic gypsum mortar was used in medieval times in castles and fortresses in what today is Germany. Remnants of walls constructed with hydraulic gypsum mortar have existed for centuries in the Hartz Mountain region of Germany (Wilder 1918).

The development of gypsum plasters is difficult to trace; by the late 1800s, however, a commercial process had been developed to slow the setting time, thereby allowing widespread use of finishing plaster. Prefabricated wallboard panels were developed in 1918 (Adams 1991) but were not widely used until the great construction boom after World War II. Before that time, plastered walls were more common in residential and commercial construction.

Worldwide, the predominant use of gypsum is in the manufacture of construction plasters and portland cement (anhydrite, most commonly used in the manufacture of portland cement, is often sold as a mixture of impure gypsum and anhydrite). The predominant use of gypsum in North America, however, is in various types of wallboard panels. In 2003, about 90% of the total gypsum produced in the United States was used in wallboard and construction plasters.

Gypsum has been used in agriculture as a soil amendment since the middle of the eighteenth century. The earliest accounts of gypsum's agricultural applications were published in Switzerland in 1768. George Washington and Benjamin Franklin were proponents of the use of gypsum in agriculture in the United States in the late 1700s. Benjamin Franklin promoted the use of gypsum by applying ground gypsum, commonly known as "land plaster," to a field of clover in a pattern forming the phrase "Land Plaster Used Here" (Wilder 1918). The clover grew thicker and greener in the areas where gypsum was applied.

Specialized methods of calcination of gypsum and for mulation with additives allow for manufacturing of more than 400 products. Uses vary from simple ground gypsum in agriculture to specialized plaster products in art and statuary; medical applications; intricate cast architectural detail; and fast-setting, high-strength construction products. There is no recognized commodity

value of a ton of raw gypsum. Although mining costs are relatively low, the energy-intensive postmining processing and ultimate end use add significant value to the products made from the gypsum. Freight costs are a significant factor in marketability of a gypsum deposit.

Synthetic gypsum, derived primarily from environmental controls on coal-fired power plants by a process known as flue gas desulfurization (FGD), has become a significant raw material resource used in the manufacture of gypsum wallboard products. Demand for synthetic gypsum has steadily grown since the 1980s, and in 2003 about 26% of the total gypsum used for manufacturing wallboard in the United States was synthetic. Originally thought of as a waste product from the environmental controls on coal-fired power plants requiring disposal in landfills, technological improvements allowed synthetic gypsum to become a marketable coproduct. Many of the wallboard plants in the United States built since the late 1990s use only synthetic gypsum as a raw material.

Gypsum deposits are distributed throughout much of the world, and gypsum is produced in more than 90 countries (USGS 2004). The value of a deposit of gypsum depends on geological, mining, engineering, and other factors in order to be used economically.

The utility and value of a gypsum deposit can change over time as technological innovations in mining and manufacturing occur and new products are developed. Factors that must be considered when evaluating a gypsum resource for potential development, mining, manufacturing, and marketing include the following:

- Proximity to market area—because gypsum has a low unit value, an ideal deposit of gypsum would be located within the heart of a growing metropolitan area
- Transportation—shipment of raw and finished materials by truck, train, ship, or barge; import of paper used in wallboard manufacturing; transportation of finished products to jobsites, distributors, and retail outlets; potential for backhauls of raw materials or finished products
- Fuel and utilities—wallboard manufacturing is highly energy intensive and requires an infrastructure of electrical service and a source of fuel for calcination and drying of wallboard panels
- Water—the availability of process water is essential for the manufacturing of wallboard products but not for plaster, portland cement rock, or agricultural gypsum

Table 1. World gypsum production, 2002–2003

Country	Production, kt	
	2002	2003*
United States	15,700	16,000
Iran	11,500	11,500
Canada	8,850	9,000
Spain	7,500	7,500
China	6,850	6,900
Mexico	6,500	6,800
Thailand	6,330	6,500
Japan	5,900	5,700
Australia	4,000	4,000
France	3,500	3,500
India	2,300	2,300
Egypt	2,000	2,000
Brazil	1,510	1,650
United Kingdom	1,500	1,500
Italy	1,300	1,200
Uruguay	1,130	1,100
Poland	1,100	1,100
Austria	1,000	1,000
Other countries	12,500	12,500
World production (rounded)	101,000	102,000

Source: Olson 2004.

* Estimated.

Table 2. Sources of gypsum imported to the United States in 2003

Country	Total Imports	
	t	%
Canada	5,700,000	68.7
Mexico	1,820,000	21.9
Spain	710,000	8.6
Dominican Republic	67,900	0.8
Total imports	8,300,000	100.0

Source: USGS 2004.

PRODUCTION AND TRADE

The United States is both the largest producer of gypsum (Table 1) and the largest consumer of products manufactured from gypsum in the world. Canada and Mexico are significant producers, and the majority of their production is exported to the United States. Thailand and Spain are also significant exporters of gypsum. Almost two thirds (63%) of the total world production of gypsum in 2003 came from seven countries: United States (15.7%), Iran (11.3%), Canada (8.8%), Spain (7.4%), China (6.8%), Mexico (6.7%), and Thailand (6.4%).

United States

Gypsum wallboard manufacturers in the United States shipped 2.93 billion m² of wallboard products in 2003. The wallboard manufacturing industry is cyclical. Production in the United States and Canada peaked in 1999, declined in 2000, and increased from 2001 to 2003.

The total amount of gypsum consumed in the United States in 2003 was 33 Mt. Mining of natural gypsum amounted to 16 Mt.

Approximately 28.8% of the total gypsum demand, 9.5 Mt, was supplied by synthetic gypsum. Imports of foreign gypsum totaled 8.3 Mt, with Canada supplying almost 69% (Table 2). Manufacturing of gypsum wallboard and plaster products accounted for about 90% of the total amount of gypsum consumed in 2003. About 2.62 Mt were used in portland cement production. Agricultural applications accounted for about 1.0 Mt.

Iran

Iran is the second largest producer of gypsum products in the world, exceeded only by the United States (USGS 2004). In 2002, Iran produced about 11.5 Mt of gypsum and exported about \$5.7 million worth (Hobbs 2002). Approximately 60% of the total annual production is estimated to be in the manufacture of construction plaster. Portland cement production in Iran during 2002 was about 30 Mt, and it is estimated that 1.5 Mt of gypsum was consumed in the manufacturing of portland cement, based on a usage of about 5% gypsum by weight.

Canada

The world's third largest producer of gypsum is Canada. There are 11 wallboard manufacturing plants in Canada, but a significant proportion of gypsum is exported to plants along the east coast of the United States. Canadian gypsum imported into the United States during 2003 was about 5.7 Mt, representing about 17% of the total consumption. Gypsum is produced in the provinces of Newfoundland, Nova Scotia, Ontario, Manitoba, and British Columbia.

The majority of Canada's production comes from Nova Scotia; National Gypsum Canada Ltd. operates the world's largest gypsum quarry at Milford Station, near Halifax. Fundy Gypsum Company and Little Narrows Gypsum, subsidiaries of U.S. Gypsum (USG), operate two large quarrying operations in Nova Scotia for export to the United States and external portland cement rock customers. There is only one active underground gypsum mining operation in Canada, located at Hagersville, Ontario, and operated by Canadian Gypsum Company Ltd., a subsidiary of USG.

Spain

Spain has abundant resources of gypsum located predominantly in the eastern half of the country and the Balearic Islands of Mallorca, Ibiza, and Menorca. Abundant gypsum resources occur along the Mediterranean coast between Gibraltar and eastward to the French border. Iberyeso is the largest producer in the country.

The Triassic-age gypsum deposits are significant in terms of reserves, quality, and minability (Regueiro and Barros 1995). In most cases, Triassic-age gypsum deposits have a gypsum purity of 93% to 96%. Tertiary-age gypsum deposits are significant in terms of the economic potential, continuity, thickness, and quality. Eocene deposits are relatively rare, but Oligocene-age deposits are extensive, have a high purity, favorable geographical locations, and ease of exploitation. Abundant Miocene–Pliocene-age gypsum deposits occur in the Alicante Area, between Almeria and Alicante. The gypsum has a high quality (about 94% purity) and is interbedded with marl. Studies by the Spanish government identified 77 large deposits with purities ranging from 70% to 96% and resources of more than 20 billion t.

China

The annual production of gypsum for all uses in China is about 11 to 12 Mt, primarily from the provinces of Shandong, Hubei, Jiangsu, Hunan, Shanxi, Sichuan, and Gansu. O'Driscoll (1994) reported 54 state-operated mines and approximately 100 privately

operated mines in 16 provinces. The major gypsum mining operations in China include Pingyi and Tai'an in Shandong Province and Yingcheng in Hubei Province. About 65% of China's gypsum resources occur in Shandong Province. Gypsum deposits in Hubei and Hunan provinces provide high-purity gypsum to the growing market for industrial gypsum products in the cities of Guangzhou and Shanghai. The gypsum resources in China are widely distributed and immense, with reserves estimated to be in the billions of metric tons. The reported reserves vary from 57 to 100 billion t. In the mid-1990s, gypsum reserves of 114 billion t were identified in Hubei Province alone.

The gypsum deposits in China are highly variable in the areal extent, in thickness, and in quality. The gypsum occurs as thin seams of fiber gypsum (satin spar), flake gypsum (selenite), and rock gypsum. Depth of the deposits varies from very shallow to about 600 m. Gypsum-bearing sequences from a few centimeters to more than 100 m in thickness occur throughout the country.

The mining and processing of gypsum in China are labor intensive. Underground mining is generally accomplished by manual methods such as sorting ore from waste, loading ore cars with gypsum, and tramping the cars to incline or shaft stations. Waste rock is hand-stacked to provide roof support. The gypsum is sorted at the surface into stockpiles of different grades depending on purity and end use. *Snow gypsum* is the term used often for white rock gypsum, and *fiber gypsum* is the term used for very pure satin spar gypsum.

Snow and fiber gypsums are used for the manufacture of ceramic plasters (sanitary and dinnerware), dental and orthopedic plasters, art plasters, chalk, glass-reinforced gypsum ceiling panels, and decorative architectural details such as cornices. Some plaster is produced for the brewery and tofu industries.

Mexico

Gypsum is mined in the following states in Mexico: Nuevo Leon, Coahuila, Colima, Chihuahua, Sonora, Puebla, Oaxaca, Jalisco, and Baja California del Sur. A significant amount of gypsum in Mexico is used internally in the manufacture of portland cement. Mexico is a significant exporter of gypsum to the Pacific coast of the United States and periodically to Pacific Rim countries such as Japan. Exports to the United States in 2003 were about 1.8 Mt.

The majority of gypsum exports are produced from two quarrying operations in Baja California del Sur. COMSA, on San Marcos Island in the Sea of Cortez, and CAOPAS, just north of the town of Santa Rosalia, provide the majority of gypsum to wallboard plants on the Pacific coast of the United States.

Numerous small gypsum plaster calcining facilities, known as *yerasas*, are distributed throughout Mexico. Yerasas manufacture construction plasters for local markets and vary in size from crude beehive kilns to relatively modern calcining operations.

Gypsum wallboard is currently manufactured at only three sites in Mexico. One plant is located in Puebla, about 120 km southeast of Mexico City, and two are near Monterrey, Nuevo Leon State, in northern Mexico.

GEOLOGY

The most common sulfate minerals are gypsum and anhydrite, which are formed from diverse origins. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is primarily formed as a chemically precipitated sedimentary rock in basin or sabkha environments, but it may also form as the result of solutional, karst, hydrothermal, and volcanogenic processes. Table 3 shows the chemical composition of gypsum and anhydrite. Anhydrite (CaSO_4) is the anhydrous form of the calcium sulfate family of minerals. Anhydrite may form as a primary mineral in a sabkha

Table 3. Chemical composition of gypsum and anhydrite, %

Mineral	Formula	Lime (CaO)	Sulfur Trioxide (SO ₃)	Water of Crystallization (H ₂ O)
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	32.6	46.5	20.9
Anhydrite	CaSO_4	41.2	58.8	0.0

depositional environment or deep-basin environments. The terms *gypsum* and *anhydrite* are commonly used interchangeably for the minerals and rocks that are composed primarily of these minerals.

Gypsum and anhydrite may be deposited simultaneously in a sedimentary environment and are easily converted from one to another under varying conditions of heat, pressure, and the presence of water. The occurrence and relationship of anhydrite and gypsum in a deposit is complex. Mineralogical, textural, cross-cutting relationships and microscopic examination may be necessary to determine the ultimate origin of anhydrite in a deposit. Some deposits exhibit multiple episodes of conversion from gypsum to anhydrite and vice versa.

Mineralogy

Gypsum forms monoclinic crystals with a perfect {010} cleavage and distinct cleavages along {100} and {101}. It is distinguishable from anhydrite by its lower Mohs hardness (2.0 versus 3.5) and specific gravity (2.24 versus 2.97 g/cm³). Pure gypsum is colorless, but may be tinted yellow, red, and brown because of the presence of impurities. Twinning is common along {100}, forming "swallowtail twins." Gypsum is relatively soluble in fresh water (about 0.2 g/100 g H₂O) and is easily dissolved or eroded in conditions of high humidity or rainfall.

Anhydrite forms orthorhombic crystals with perfect cleavages along {100} and {010} and a good cleavage along {001}. Anhydrite has a Mohs hardness of 3.5 and a specific gravity of 2.97 g/cm³. Pure anhydrite is colorless, but the color is variable from colorless to dark gray.

Lithology

Commercial deposits of gypsum may be almost pure or contain variable amounts of syndepositional impurities such as limestone, dolomite, clay, anhydrite, and soluble salts of potassium, sodium, and magnesium. Primary gypsum deposits consist of rock gypsum and alabaster. Selenite, satin spar, and gypsite are secondary varieties of gypsum. Anhydrite may occur as either primary or secondary minerals in a deposit, depending on its geological history.

Petrographically, most rock gypsum has a medium to coarse crystalline texture. Some deposits contain coarse crystalline gypsum poikiloblasts. Gypsum in the Upper Miocene Boleo Formation in Baja California del Sur, Mexico, contains euhedral selenite crystals up to about 25 cm in width. The Mississippian Windsor Group in Nova Scotia, Canada, contains abundant scattered poikiloblasts.

Petrographically, anhydrite has a massive or granular texture. Scattered gypsum crystals commonly occur in the anhydrite groundmass and increase near the gypsum-anhydrite contact. Complex hydrous salts of sodium, potassium, and magnesium sulfate commonly occur in conjunction with anhydrite and are concentrated in the gypsum near the contact.

Alabaster

Alabaster is a compact, fine-crystalline, translucent variety of primary gypsum that has been used by artists to produce statuary for thousands of years. Typically found in a variety of colors depending

on the type and amount of impurities present, alabaster generally occurs as zones within larger gypsum deposits.

Selenite

Large, clear, euhedral crystals of gypsum are known as selenite. Bladed selenite crystals commonly form in fluid-filled cavities. Selenite may also form along fault zones. Cleavage fragments may be mistaken for muscovite mica. Poikilitic masses of selenite crystals, commonly known as “gypsum roses,” are formed by the crystallization of gypsum from interstitial pore fluid in unconsolidated sand.

Possibly the largest selenite crystals in the world are located in Chihuahua State, Mexico. The Cave of Swords (La Cueva de las Espadas) has been well known since 1910 for the large-bladed selenite crystals. In 2000, however, a cavity containing enormous selenite crystals was discovered in the Naica underground silver and lead mine operated by Industriales Peñoles, SA de CV. The cavity was encountered at a depth of about 300 m and has dimensions of about 9 m by 18 m. The temperature in the cavity is up to 65°C with 100% humidity. Selenite crystals with a diameter of 1.2 m and up to 15 m in length occur in the cavity.

The Lechuguilla Cave complex, located near Carlsbad Caverns, New Mexico, contains large selenite speleothems. The caves are believed to have been formed at the groundwater table by the reaction of groundwater with sulfur dioxide rising from deeper natural gas deposits, producing sulfuric acid. The sulfuric acid dissolved the limestone forming very large openings and extensive speleothems.

Satin Spar

Satin spar is a fibrous variety of needle-shaped gypsum crystals filling fractures or along bedding planes. The needle-shaped gypsum crystals form with the C-axis oriented at a steep angle or perpendicular to the vein walls in fractured rocks undergoing deformation. The orientation and steepness of the crystals define the direction and amount of strain, such as dilation or shearing. It is important to recognize that satin spar is not an asbestiform mineral. The stresses may be caused by regional tectonism or induced in the rock by the hydration of anhydrite to gypsum. During hydration anhydrite undergoes a volumetric increase of 26% and may induce stresses of 2 to 69 MPa.

Satin spar is mined in China for use in the manufacture of gypsum plasters. Conco rdant, horizontally oriented veins of gypsum up to 0.5 m thick are interbedded with shale. The satin spar is mined and sorted by hand to produce an extremely pure product.

Gypsite

Gypsite is an earthy, pulverulent variety of gypsum that forms a surficial deposit in shallow saline lakes, playas, and salt pans in arid environments. The calcium and sulfur required to form gypsum are derived from the erosion and weathering of rocks and transported in surface and groundwater to closed basins. Gypsum precipitates at the surface by capillary movement and evaporation of groundwater. Since gypsum is less soluble than halite a crust of gypsite forms over the soft beds of halite. Gypsite is often contaminated by wind-blown sand or silt and clay from periodic flooding of the playas.

Rock Gypsum

The most common variety of the mineral is known as rock gypsum. Rock gypsum commonly consists of aggregates of gypsum crystals interbedded or mixed with mudstone, shale, siltstone, limestone, or dolomite. Gypsum rock and anhydrite may be nodular, massive, laminated, or bedded. The primary sedimentary structures in gypsum and anhydrite deposits are associated with the depositional

model and the proximity to terrigenous detritus. The Fish Creek Gypsum in California contains trace amounts of biotite mica. The Permian Castile formation, deposited in the Delaware Basin of Texas and New Mexico, contains well-laminated anhydrite with varves of organic matter and calcite that have correlated over a distance of more than 100 km (Blatt, Middleton, and Murray 1980). The evaporites were deposited in a standing, deep body of water. Alternatively, in a sabkha environment, gypsum and anhydrite form by the nucleation and growth of crystal masses from pore fluids within soft, unconsolidated tidal-flat sediments, consisting of terrigenous or carbonate mud. Nodular masses grow and displace the surrounding host sediments, forming a “chickenwire” texture. Gypsum may be precipitated within more rigid host sediments of clay or sand and form large poikilitic crystals that encase the host sediment. The Mississippian Maccrady Formation in southwestern Virginia contains gypsiferous mudstone with poikilitic gypsum crystal faces up to 50 cm exposed in underground mine workings.

Anhydrite

Anhydrite may form as a primary mineral in a sabkha depositional environment and deep basin, subaqueous deposits such as the Castile formation in the Delaware Basin. Gypsum may begin to dehydrate under the lithostatic loading below a depth of burial of about 600 m and transform into anhydrite. Subsequent uplift or erosion of overlying rocks decreases the lithostatic load, allows the percolation of groundwater through fractures and along bedding planes, and rehydrates the anhydrite to gypsum. Some deposits, such as the Devonian Wapsipinicon Formation in southeastern Iowa, exhibit evidence of several cycles of dehydration and rehydration. The gypsum-anhydrite contact is subhorizontal and the anhydrite cuts across enterolithic folds in gypsum as the result of an earlier phase of hydration.

Impurities

Most gypsum is white to grayish white, although type and amount of impurities in any given deposit determines the color of the rock. The impurities may be intimately mixed with the gypsum because of primary sedimentary processes previously described, or be present as the result of the secondary effects of solution, weathering, and erosion.

The most common impurities in gypsum are carbonates, clay, anhydrite, and soluble salts. With certain limitations, carbonate and clay impurities may not be detrimental in the manufacture of gypsum wallboard, plasters, and agricultural gypsum. Portland cement rock is less sensitive to the presence of anhydrite or soluble salts. The minimum gypsum purity (percentage content of gypsum) for wallboard and other quality-control parameters are established by organizations such as the American Society for Testing and Materials (ASTM) and Underwriters Laboratories (UL).

Impurities may have little or no effect on the quality of products manufactured from gypsum. Certain types of impurities, such as soluble evaporite minerals or montmorillonite clays, may expand on hydration in humid environments.

Carbonate

Limestone, composed primarily of calcium carbonate, has relatively little effect on the manufacturing of wallboard, the predominant gypsum product. The most significant effect is to increase the weight of the wallboard, which affects the level of installation effort and freight costs. Dolomite is a detrimental impurity in industrial gypsum plaster used for the manufacture of ceramics, such as dishes, and sanitary ware, such as sinks and toilets. Dolomite has a higher specific gravity

than gypsum. Particles of dolomite in ceramic grade plaster sink to the bottom as the slurry is poured into molds. The dolomite particles form projections at the mold–cast interface; these projections leave surface pits in the product being cast.

Clay

Clay is the second most abundant impurity in gypsum deposits. Clay impurities may be present as a result of both primary and secondary depositional processes. Primary impurities of clay occur as laminae, thin interbeds, internodular matrices, and intraclasts within the gypsum. Nucleation and growth of gypsum or anhydrite nodules from interstitial fluids in soft terrigenous or carbonate mud forms an internodular matrix, leading to the chickenwire description of its texture. Postdepositional solutional and erosional processes commonly result in the presence of clay, sand, and organic impurities in fractures.

The type of clay mineral, particularly members of the smectite group, may have deleterious effects on the quality of wallboard products. Smectite group clays have an affinity for absorbing multiple molecules of water or other liquids and, thus, increase in volume. This characteristic is useful in the manufacture of cat litter or oil absorbent, but may be deleterious in the manufacture of gypsum wallboard. Soluble salts, primarily sulfates, and chlorides of potassium, magnesium, and sodium adsorb onto clay crystals.

If wallboard containing a high percentage of smectite clays or soluble salts is installed in a humid environment, hydration of these mineral species results in an increase in volume and may cause a quality defect known as “humidified split.” Humidified split occurs when soluble salts migrate to the gypsum core–paper interface and absorb multiple molecules of water from the atmosphere, forming complex salts and blisters on the surface of the wallboard. Alternatively, the volumetric expansion of the smectite clays may also produce humidified split.

Improper control of the calcining temperature of gypsum during the manufacturing process may result in an inaccurate determination of gypsum purity. Calcining at a temperature that is too high may begin to thermally dehydrate the clay, giving a false purity determination.

Anhydrite

Anhydrite is a common impurity in deposits of gypsum and may occur as a primary depositional mineral or the product of dehydration of deeply buried gypsum. Anhydrite can be found as a massive rock or as a mixture of gypsum and anhydrite in partially hydrated deposits. Soluble salts, such as sodium, magnesium and potassium chlorides, and sulfates are commonly concentrated in a halo in gypsum adjacent to the anhydrite contact. The soluble salts are leached from the anhydrite during hydration and precipitated in tensional features, such as fractures, many of which form during the volumetric expansion during hydration.

Anhydrite may be viewed either as a contaminant in a gypsum deposit or as a marketable coproduct. As a contaminant, the anhydrite is harder and denser than gypsum and contains higher levels of soluble salts. Anhydrite increases the weight of the finished wallboard products and is abrasive to grinding and processing equipment. As a coproduct, quarry-run anhydrite or a blend of gypsum and anhydrite may be used as a portland cement rock. Portland cement manufacturers use a variety of products from gypsum, anhydrite, or an anhydrite–gypsum blend, depending on the manufacturing process. The primary function of gypsum or anhydrite in portland cement is to control the setting time of the finished product. The SO_3 content of the portland cement rock is the most important quality parameter.

Soluble Salts

Gypsum deposits commonly contain soluble evaporite minerals, such as halite (NaCl); sylvite, (KCl); mirabilite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$); and epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). Soluble evaporite minerals may form during (1) evaporation of seawater in restricted basins; (2) late-stage diagenetic processes in sabkha environments; (3) gypsumification of anhydrite; or (4) leaching from interbedded clay. During the evaporation of sea water in a restricted depositional basin, excess sulfate ions not consumed in the formation of gypsum or anhydrite may combine with either magnesium or sodium to form epsomite and mirabilite, respectively. Sodium and potassium may combine with chlorine ions to form halite and sylvite, respectively.

In a sabkha environment, gypsum and anhydrite are formed by diagenetic processes within tidal-flat sediments. The pore-water chemistry changes as dolomitization of carbonate sediments occurs. Soluble evaporite mineral components can be released from fluid inclusions within carbonate crystals, or be included in a disordered crystal lattice. Mud-rich sabkhas contain clay crystals into which soluble salts may be adsorbed. During the conversion of anhydrite to gypsum, soluble salts are released and form an enriched halo in the gypsum near the anhydrite–gypsum contact. The volumetric expansion during the conversion provides fractures for the transport of saline fluids.

Soluble evaporite minerals are rarely directly observable in outcrops in humid environments or drill core because they are highly soluble in fresh water. In arid environments, gypsum outcrops may have an efflorescent crust of magnesium sulfate formed by the wicking of water by capillary action at the rock's surface and rapid evaporation. Very fine, acicular crystals of epsomite form on the floor and roof in some underground gypsum mines by the evaporation of humid air.

Calcium sulfate hemihydrate reacts with water to form gypsum–water slurry in the manufacturing of wallboard. Soluble evaporite mineral components in the slurry migrate to the gypsum–paper interface by capillary action. The installation of wallboard containing a high soluble-salt content in a humid environment may result in the formation of complex salts of sodium, potassium, and magnesium sulfate with up to 15 molecules of water in their crystal structures. The volumetric increase associated with the absorption of more than two molecules of water may result in the failure of the gypsum core–paper bond and the formation of blisters, known as “humidified split.”

Other Impurities

Yellow to red discoloration results from mud staining and the presence of iron oxides. Dark purple to black discoloration may be caused by the presence of manganese oxide, carbonaceous limestone, mafic rock fragments, or detrital minerals. The presence of copper or certain types of algae may stain gypsum a greenish color. In some deposits trace amounts of celestite (SrSO_4) may be present, and siliceous nodules are found in some deposits.

Bassanite

Bassanite is an unusual type of an impurity in a few gypsum deposits, notably in the Miocene Fish Creek Gypsum in California. Bassanite is a naturally occurring form of calcium sulfate hemihydrate that forms from the interaction of hydrothermal fluids with gypsum. Although white, bassanite has a distinct earthy texture that differentiates it from gypsum. Bassanite will not rehydrate to form gypsum in the presence of water. Hill (1979) reported the unusual occurrence of bassanite in three small caves in southwest Texas. Although originally precipitated on the walls and ceiling as gypsum, high calcium

Table 4. Engineering properties of gypsum, anhydrite, and other evaporites

Property	Gypsum	Anhydrite	Halite (Rock Salt)	Potash
Specific gravity, g/cm ³	2.24	2.97	2.2	2.05
Dry density, mg/m ³	2.19	2.82	2.09	1.98
Porosity, millidarcy	4.6	2.9	4.8	5.1
Unconfined compressive strength, MPa	27.5	97.5	11.7	25.8
Point load strength, MPa	2.1	3.7	0.3	0.6
Young's modulus, GPa	24.8	63.9	3.8	7.9
Permeability, 10 ⁻⁹ m/sec	6.2	0.3	na*	na

* na = not available.

temperatures (up to 35°C) and low humidity (10% to 60%) resulted in the dehydration of gypsum.

Chemical Properties

Gypsum and anhydrite are able to undergo repeated dehydration and hydration, depending on the depth of burial and availability of water. Gypsum will begin to thermally decompose into the metastable species, calcium sulfate hemihydrate (CaSO₄•1/2H₂O), in heated air above 70°C and at 1 atm of pressure. Differential thermal analysis curves show two endothermic peaks between 100° and 200°C (Deer, Howie, and Zussman 1966). The first peak represents the loss of 1 1/2 molecules of water during the formation of calcium sulfate hemihydrate. Further heating totally dehydrates gypsum forming deadburned (anhydrous) anhydrite (CaSO₄), which is used as a filler in plastics and as a moisture absorbent. The second decomposition peak occurs when the remaining one-half molecule of water is removed. Calcining processes for the manufacture of gypsum wallboard and plasters involve heating gypsum to about 155°C for 1 to 3 hr, during which time calcium sulfate hemihydrate forms.

Heating gypsum liberates water vapor, which helps hinder the spread of fire. Specialized types of wallboard are formulated and manufactured for use as a firestop between multifamily housing, in the lining of elevator shafts, and in the walls and ceilings between living spaces and garages.

Gypsum's solubility in fresh water is approximately 150 times greater than that of limestone. This chemical characteristic provides a source of calcium and sulfur when gypsum is used in agricultural applications. The ionic exchange capability of calcium for sodium prevents the buildup of alkali in soils.

Although gypsum is a very soft mineral, specialized methods of calcining have been developed to manufacture denser, harder crystals. For most uses, the gypsum is ground to a powder and heated in a continuous kettle or batch kettle at 1 atm of pressure. This method of calcining produces anhydrite, rough, splintered crystals known as beta calcium sulfate hemihydrate. This product is used in the manufacture of wallboard and construction plasters. The calcination of pebble- to cobble-sized, high-purity gypsum in an autoclave at elevated pressure produces dense, euhedral crystals of alpha calcium sulfate hemihydrate. This product is used in specialized plasters and cements for art and statuary, architectural applications, industrial prototype modeling, and road and floor repair.

Physical Properties

The softness of gypsum is its most prominent physical feature. It is distinguished by its softness (Mohs hardness of 2) and three distinct cleavage planes. Anhydrite is distinguishable from gypsum

because of its higher specific gravity and greater hardness. When scratched with a piece of copper, gypsum will be gouged, but anhydrite will abrade the copper (a copper residue will be visible on the scratched surface).

Table 4 gives the basic engineering properties of gypsum and anhydrite, and the properties of the evaporates rock salt (halite) and potash for comparison.

ORIGIN AND MODES OF OCCURRENCE

Evaporites are deposits of minerals that formed from the evaporation of seawater or brine. The types and amounts of minerals formed depend on (1) the composition of the source water, (2) the relative solubilities of the dissolved mineral constituents, (3) the climatic conditions and extent of evaporation, and (4) the depth and extent of the depositional basin. Brine may have formed from evaporative concentration of seawater or might have been reconstituted by the dissolution of preexisting rocks (primarily evaporite rocks) by rainwater or groundwater and its subsequent recrystallization in closed basins in an arid climate. Seawater is concentrated by several mechanisms, described here.

The primary depositional environments for evaporites are considered to be either sabkha or subaqueous, with variations related to proximity of terrigenous material and the depth of the basin and seawater. Sabkha evaporites include continental deposits in playa lakes and the more extensive tidal flat deposits. Subaqueous evaporites are formed in either shallow- or deep-water basins. All modern evaporite depositional environments, however, including sabkha deposits, are believed to be of shallow-water origin (Pettijohn 1975). In either case, gypsum and anhydrite are formed from the concentration of dissolved mineral constituents in saline water. Kendall (1981a, 1981b) provides a good overview of each of the depositional facies. Other useful resources for determining depositional environments for gypsum are works by Dean and Schreiber (1978), Kendall (1978), and Raup (1991). There is considerable discussion in geological literature about whether the original mineral deposited is gypsum or anhydrite. Gypsum is metastable, converts to anhydrite at a depth of more than about 600 m, and is readily soluble in groundwater. Two additional environments are salt-dome cap rock and volcanogenic.

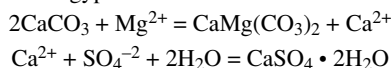
Brine Concentration and Evaporite Precipitation

Seawater contains about 3.5% by weight of dissolved solids (Pettijohn 1975). Approximately 78% of the dissolved solids consist of sodium chloride, and calcium sulfate accounts for about 3.6%. If a 1,000-m column of sea water of normal salinity were to evaporate, only 75 cm of gypsum and approximately 13.7 m of halite would be precipitated (Blatt, Middleton, and Murray 1980).

Gypsum will begin to precipitate in an evaporating basin of seawater when the volume has been reduced by evaporation by about 66% and if replenishment and dilution by fresher water do not occur. Halite does not precipitate until approximately 90% of the brine has been evaporated. A natural horizontal and vertical zonation of mineral deposition develops. Calcium carbonate will be precipitated first, followed by gypsum and anhydrite, halite, magnesium sulfate, and potassium salts. Normal seawater is undersaturated with respect to both gypsum and halite. The presence or absence of halite in a thick deposit of gypsum is an indicator of the degree of brine concentration, because considerably more evaporation and brine concentration are required to precipitate halite than gypsum.

Gypsum also forms from diagenetic processes during the dolomitization of carbonate sediments in tidal flat environments. As seawater evaporates to the point at which gypsum begins to

precipitate, the ratio of the activity constants for magnesium ($a_{\text{Mg}^{2+}} = 1.32 \times 10^{-2}$) and calcium ($a_{\text{Ca}^{2+}} = 2.34 \times 10^{-3}$) increases above the normal ratio in seawater of 5.6 (Blatt, Middleton, and Murray 1980). The molar ratio of $\text{Mg}^{2+}/\text{Ca}^{2+}$ also increases from about 5.2 to more than 20. Concentration of seawater by evaporation produces more dense brine that can sink downward through the pores of underlying calcareous sediments. An ion exchange reaction occurs with one magnesium ion replacing one calcium ion. Because the brine has already reached a concentration where gypsum precipitates, the additional calcium released during dolomitization is available to react with any excess sulfate in the brine to form additional gypsum. The chemical reactions that liberate calcium ions and form gypsum from saline brines are as follows:



Sabkha Evaporites

Sabkha is an Arabic term referring to a coastal tidal flat. Numerous geological studies in the 1960 and 1970s examined the formation of gypsum and anhydrite minerals along the Trucial Coast region of the Persian Gulf (e.g., Kinsman 1966, 1969; Butler 1970). These deposits are characterized by a distinctive suite of sediments, including lagoonal limestone, intertidal algal mat limestone and nodular gypsum, and anhydrite-bearing, fine-grained terrigenous or calcareous sediments.

Gypsum and anhydrite form by precipitation of supersaturated brine in the pore space of the tidal-flat sediments. Nodular gypsum and anhydrite are the most common forms, but large poikilitic selenite crystals may also form. Many of the commercially developed gypsum deposits in North America are probably of sabkha origin.

In the tidal-flat sediments a recalcareous, dolomitization occurs during the diagenetic reactions that form gypsum and anhydrite. If terrigenous clastic sediments are present, they are generally chemically unaffected but undergo soft-sediment deformation as the gypsum and anhydrite crystals and nodular masses form. The sabkha environment does not require the presence of a basin for deposition of evaporite minerals, and thick chloride mineral accumulation would not be expected (Schroeder 1970). Depending on the surface water chemistry, laminated gypsum and argillaceous limestone may be deposited in lagoons or ponds on the sabkha surface. The primary difference between carbonate-evaporite and mud-rich sabkhas is the amount of terrigenous sediment deposited on the sabkha surface.

Crystals of gypsum and anhydrite form in several modes in the sabkha environment. The most common mode is the nucleation and displacive growth of crystalline masses in the soft tidal-flat sediments. Soft carbonate or terrigenous clay or silt sediments are pushed aside as nodular masses of gypsum or anhydrite grow. Eventually, the nodules coalesce and the internodular matrix forms a fabric that looks like chickenwire. Laminated or bedded gypsum may be precipitated in shallow, hypersaline ponds, lagoons, or salt pans on the sabkha surface. If the ponds are periodically flooded by fresher water from surface runoff or precipitation, the sediments formed may be argillaceous, micritic limestone.

Carbonate-Evaporite Sabkha

The carbonate-evaporite sabkha environment consists almost entirely of dolomite and gypsum–anhydrite. The most seaward portion of a carbonate-evaporite sabkha environment consists of inner-shelf dolomitic mudstone and pellet wackestone. The dolomitic rock either is massive or has faint, wispy laminae of darker colored, organic-rich clay (subtidal algal mat). Proceeding landward are coarser-grained carbonates such as oolitic or pellet packstone and

grainstone that occur in the intertidal zone. The uppermost sediments (supratidal) include dolomitic mudstone and pellet packstone. Algal mat deposits are present as wispy, black, organic-rich clay. Gypsum intervals up to about 6 m thick are common.

Ancient examples of carbonate-evaporite sabkha gypsum deposits include the Wapsipinicon Formation (Devonian) in southeastern Iowa and the St. Louis Formation (Mississippian) in southwestern Indiana (Jorgensen and Carr 1972).

Mud-Rich Sabkha

In the mud-rich sabkha, most of the tidal-flat sediments consist of clay, silt, and some sand deposited by sheetflood flow from the mouths of wadi channels near the landward margin of the wadi plain (Handford and Fredericks 1980). Marine floodwaters such as storm surges rework the terrigenous sediments to form an extensive, low-slope, tidal-flat surface. Mud-rich sabkha sediments may occur along with carbonate-evaporite sabkha sediments, either interfingering with or prograding across the calcareous tidal-flat surface.

The Mississippian Maccrady Formation of southwestern Virginia and the Jurassic Arapahoe Shale in south-central Utah are ancient examples of mud-rich sabkha environments. Modern-day examples include the coastal mud flats at the mouth of the Colorado River delta at the northern end of the Gulf of California and along the Trucial Coast of the Persian Gulf.

Subaqueous Evaporites

Although most of the commercial gypsum deposits in North America are believed to be of sabkha origin, many thick, widespread, ancient evaporite deposits were deposited by subaqueous processes within enclosed or hypersaline basins. And even though there are several modern-day analogues of sabkha environments, there are no modern-day equivalent depositional environments of subaqueous evaporites.

Three general models of subaqueous evaporites have been developed based on conditions of the depth of the basin and the depth of water: (1) the deep water, deep basin model; (2) the shallow basin, shallow water model; and (3) the deep basin, shallow water model. Each model has one common factor: the presence of a seaward, subaqueous barrier (sill) that restricts the complete circulation of seawater in and out of the basin. High evaporation rates concentrate the trapped seawater and form brine, which is saturated or nearly saturated with respect to gypsum and halite. Crystal precipitation occurs at the air–water interface, and the crystals settle through the water column as a pelagic rain. Variations in the water chemistry from influx of seawater by storm surges, temperature, or evaporation rate form laminations in the rock column. Laminae of sulfate, carbonate, and organic matter 1 to 10 mm thick occur over large areas of the basin. Thin laminations have uniform thicknesses over short distances, and individual laminations have been stratigraphically correlated in wells over distances up to about 100 km.

Ancient subaqueous evaporite deposits include the Castile Formation (Permian) in the United States and the Zechstein Group (Permian) in Europe. The Castile Formation underlies almost 81,000 km² of western Texas, parts of New Mexico, and northern Mexico. The Zechstein Group underlies at least 250,000 km² of northern Europe, including Germany, Poland, and much of the North Sea.

Continental Evaporites

Continental evaporites are similar in origin to mud-rich sabkhas. Mineralization occurs at the surface of playa lakes or within the interstitial pore spaces of soft, terrigenous sediments. Gypsum,

halite, and complex salts of magnesium, potassium, and bromine are deposited in closed basins (no external drainage) in arid environments. Weathering and erosion of rocks in the surrounding higher terrain provide the mineral constituents for the formation of minerals in the playa. Coarser detritus is deposited in alluvial fans at the margins of the playa and surface runoff and groundwater transport the dissolved mineral constituents toward the center of the playa. Mineralization occurs at the surface and within the playa sediments by evaporative pumping and vertical movement by capillary action at the playa surface. Gypsum, with a lower solubility than halite, is deposited within the sediments and also as an efflorescent gypsite crust around the distal margin of the playa. Post-depositional inundation of the playa surface by storm-water runoff and wind erodes and reworks the exposed crusts and underlying soft sediments.

Economic deposits of continental evaporites occur in many parts of the world. The only deposit in the United States commercially used for manufacturing wallboard, however, is the Muddy Creek Formation (Miocene) near Las Vegas, Nevada. The deposit covers about 13 km² and is up to about 30 m thick (Papke 1987). Enormous deposits of playagypsum (gypsite) occur in Australia. Lake Macleod, located near the northwestern coast, covers 2,072 km² and has a gypsite crust about 2 m thick. Lake McDonnell in South Australia covers about 90 km² and has a gypsite crust about 5 m thick; the deposit occupies a former lagoon that was cut off from the sea in post-Pleistocene times. Periodic landward surges of storm water and high tides overflow the barrier and replenish the lagoon with seawater.

Salt-Dome Cap Rock

Gypsum commonly occurs in the near-surface portions of salt domes in the Gulf Coast basin of the United States. Thick layers of the Jurassic-age Louann Salt occur at a depth of about 9 km. Most salt domes are roughly circular in plan view and vary in diameter from 1 km to more than 10 km. Some near-surface domes have a surface expression of elevated topographic relief of about 20 m above the surrounding terrain. Salt domes are diapiric masses of rock salt (halite) that rose upward along fractures or faults by differential lithostatic loading and plastic flow. Salt domes occur in about 100 sedimentary basins worldwide. The Zechstein Salt in northern Europe contains numerous salt domes.

Salt domes contain 5% to 10% water-insoluble material. About 99% of the insoluble impurities in the Louann Salt are anhydrite and a trace amount of calcite (Walker 1974). As a salt dome rises through near-surface, water-bearing sediments, the halite dissolves and a residue, primarily anhydrite, accumulates in the upper portion of the dome. Increased upward vertical pressure occurs during the salt dome's rise and compacts the insoluble residue to form a massive anhydrite rock. As the salt dome rises near the ground surface, groundwater percolation rehydrates the anhydrite to form gypsum.

Salt-dome cap rock forms only minor economic deposits of gypsum in the United States. The gypsum generally contains high levels of soluble salt impurities that are detrimental to the manufacture of wallboard products. Some cap-rock deposits, however, have been developed for portland cement gypsum resources.

Volcanogenic Gypsum

Gypsum sometimes occurs in volcanogenic massive sulfide deposits (VMSDs). Only relatively small economic VMSD gypsum deposits, however, have been developed. The Falkland deposit in southern British Columbia, Canada, is an example. Although relatively small and rarer than any other type of deposits previously dis-

cussed, VMSDs warrant a brief description. They are associated with extensional tectonic settings and submarine depressions such as backarc, mid-ocean spreading centers, and intracontinental rift zones (Ohmoto 1996).

Seawater percolates into the thin crustal rocks and is heated by deep convective circulation in the vicinity of a heat source such as plutonic or upper-mantle rocks. Sulfate mineralization generally occurs during the later stages of hydrothermal activity. In the Kuroko (black ore) metallogenic model, sulfide minerals are deposited by the interaction of hydrothermal fluid (at approximately 350°C) emanating from sea-floor vents with cold seawater. The vents are known as "black smokers" because of the smoke-like appearance of the plume of instantaneously precipitated sulfide minerals. The precipitated minerals accumulate in mound-shaped deposits around the black-smoker vents.

Sulfate mineralization can also occur as a chemical precipitate around the sea-floor vents and as an alteration product of the country rocks. Precipitation of anhydrite is associated with the "black ore" mineral suite (sphalerite + galena + pyrite + barite + anhydrite) that occurs from the interaction of the hot hydrothermal fluids and cold seawater.

Anhydrite and gypsum can also precipitate in the porosity of lower temperature (<150°C) country rocks. Downward percolation of seawater through fractures in lower-temperature country rocks may precipitate disseminated sulfate (SO₄)²⁻ minerals. In the later stages of hydrothermal activity, gypsum and anhydrite may be reduced by Fe²⁺-bearing minerals and organic matter forming hydrogen sulfide (H₂S) that, in turn, leaches additional metals from the country rock.

DISTRIBUTION OF DEPOSITS

Gypsum occurs throughout the world—found to date on every continent except Antarctica (Table 5). More than 90 countries produce gypsum worldwide, and global gypsum resources are enormous. Some known occurrences contain as much gypsum as the total world annual demand. For example, Libya contains more than 80,000 Mt of Jurassic-age gypsum with an estimated purity of 80% underlying an area 65 km long, up to 25 km wide, and locally up to 400 m thick. Latvia contains gypsum resources estimated at 1,000 Mt at a depth of less than 50 m and 14,000 Mt at a depth of greater than 50 m (USBM 1993).

The first gypsum mining in North America occurred in Nova Scotia in 1779. Gypsum was first mined in the United States from Silurian deposits near Syracuse, New York, in 1808. Several gypsum-producing districts have operated continuously since the 1800s. Gypsum was found in the early 1800s during exploration for salt brines in the Mississippian Maccrady Formation in southwestern Virginia. The Plastarco, Virginia, operations of the United States Gypsum Company were worked continuously from as early as 1835. Jurassic-age gypsum has been mined in northwestern Iowa since 1872. The Mississippian-age Michigan Formation has produced gypsum in northeastern Michigan since 1862.

Since the publication of the 6th edition of *Industrial Minerals and Rocks*, some of the oldest gypsum-producing regions of the United States have ceased operations. Notably, the Silurian deposits of western New York and northern Ohio and the Mississippian deposits in Virginia ceased operations after more than 170 years. In most cases, the deposits were not depleted; rather the older, high-cost wallboard manufacturing plants were closed and the manufacturing capacity was replaced by new plants on a viable basis using synthetic gypsum from coal-fired power plants.

Considerable gypsum resources occur in the western part of the United States, Canada, and Mexico. These areas are gener- ally

Table 5. Worldwide distribution of principal gypsum resources

Geologic Age	North America	Europe	Asia	South America	Africa
Holocene	California	NA*	NA	NA	NA
Pleistocene	NA	NA	NA	NA	NA
Pliocene	NA	Greece	NA	NA	NA
Miocene	Nevada, California (Plaster City)	Bulgaria, Poland, Romania, Italy, Czech Republic, Slovakia	Saudi Arabia	NA	Egypt, Sudan
Oligocene	NA	Spain	NA	NA	NA
Eocene	NA	Romania	NA	NA	NA
Paleocene	NA	NA	NA	NA	NA
Cretaceous	Texas, Arkansas	NA	Laos	Brazil, Venezuela	NA
Jurassic	Iowa (Ft. Dodge), New Mexico, Colorado, Utah, Wyoming, Montana	England	NA	NA	Morocco, Tanzania
Triassic	NA	France, Germany, England, Austria, Spain	NA	NA	Algeria
Permian	Texas, Oklahoma, Kansas, Colorado, Wyoming, Nevada, Arizona	England, Austria, Lithuania, Poland, Hungary	NA	NA	NA
Pennsylvanian	NA	NA	NA	NA	NA
Mississippian	Nova Scotia, Michigan, Indiana, Virginia	NA	NA	NA	NA
Devonian	Iowa	Latvia, Lithuania	NA	NA	NA
Silurian	New York, Ontario, Ohio	NA	NA	NA	NA

* NA = not applicable (In this case, meaning that there was no occurrence of gypsum during the associated age.)

remote, vary in size from small to very extensive, have complex property ownership issues, and may not be workable year-round because of severe weather conditions. Very often the main factor that would make these deposits valuable is an inexpensive method of transportation of the raw materials or the finished products. Other factors are proximity to market area, work force, utilities, and other parts of infrastructure. Several small operations in the western United States produce portland cement or agricultural gypsum.

United States

Gypsum is currently mined in Arkansas, California, Colorado, Indiana, Iowa, Kansas, Michigan, Nevada, New Mexico, Oklahoma, Texas, Utah, and Wyoming. Outcrops of gypsum in the Arapahoe Shale in Utah and the Chugwater Formation in Wyoming cover hundreds of square kilometers.

In 2003, the top producing states were, in descending order, Oklahoma, Texas, Nevada, Iowa, California, Indiana, and Michigan; they accounted for 73% of the domestic output (USGS 2004).

Calcium sulfate minerals are found within geological strata ranging from the Ordovician through the Holocene. The largest production comes from Mississippian rocks in Atlantic Canada (Nova Scotia, Newfoundland, and New Brunswick), Michigan, Indiana, and, until recently, Virginia. Permian-age rocks are the second largest producer in Texas, Oklahoma, Kansas, Colorado, Wyoming, Nevada, and Arizona. Gypsum is produced from Tertiary-age rocks in California, Jamaica, and Arizona. Gypsum is produced from Jurassic-age rocks in Iowa, Colorado, Utah, and Wyoming.

Texas, Oklahoma, New Mexico, and Kansas contain inexhaustible resources of gypsum, and other chemically precipitated minerals such as salt and potash. The evaporite minerals were deposited in the enormous Permian Basin, which underlies portions of the four states. Two subbasins in west Texas and southeast New Mexico—the western Delaware Basin and the eastern Midland Basin—are separated by the Central Basin Platform. Where extensive hydration of anhydrite has occurred, the resulting purity is high

(>92% purity). Most of the high-quality, value-added products derived from gypsum are manufactured from Permian-age gypsum. The highest purity and whitest gypsum occurs in the Blaine Formation at Medicine Lodge, Kansas, and Southard, Oklahoma, and in the Easley Creek Formation at Blue Rapids, Kansas.

Oklahoma

The primary area of production of high-value-added gypsum products in Oklahoma is in the northwestern part of the state at Southard, Blaine County. In the Anadarko Basin in northwestern Oklahoma, economic gypsum deposits occur within the Shimer, Nescatunga, and Medicine Lodge members of the Blaine Formation in the middle portion of the Beckham evaporite unit. The stratigraphic relationships of the gypsum beds in the Blaine Formation are well exposed in Salt Creek Canyon, just north of Roman Nose State Park, in Blaine County. The Blaine Formation is also a major source of gypsum in southwestern Oklahoma, whereas the Permian-age Cloud Chief Formation contains significant resources in west-central Oklahoma.

The evaporite beds in the Blaine Formation are generally 3 to 9 m thick, and gypsum in the Cloud Chief Formation is up to 30 m thick. Gypsum within the Blaine Formation has a purity of 95% to 99%. Interbeds of shale 0.7 to 9 m thick separate the gypsum intervals. The gypsum beds are typically underlain by thin dolomite beds. Anhydrite thickness increases in the down-dip direction, toward the west, under increasing overburden thickness.

Texas

Gypsum is produced in west-central Texas from the Eskota Member of the Peacock Formation (Permian). Outcrops of gypsum occur along a low topographic escarpment with numerous incised lateral drainages. Hydration and erosion or solution occurs in the down-dip direction, and in lateral drainage courses formed along structural lineaments such as fractures. Several beds of gypsum up to about 6 m thick are interbedded with shale. Overburden consists

of sandy shale. The thickness of the overburden is a significant control on the hydration pattern of the gypsum.

The Castile Formation is an extensive occurrence of gypsum in the Delaware Basin of west Texas and southeastern New Mexico. It is a 440-m section of varved anhydrite and carbonate laminations (laminae 1 to 10 mm thick). Some of the laminae have been traced horizontally for more than 110 km (Anderson et al. 1972). Halite (NaCl) and sylvite (KCl) deposits of the Salado and Rustler formations overlie the Castile Formation.

Nevada

Two companies produce gypsum and anhydrite from the Late Triassic to Jurassic-age Nightingale Sequence of the Auld Lang Syne Group in northern Nevada. The evaporites occur as complexly folded and faulted sequences encased in metasedimentary rocks. A quarryable portion of the deposit is a geologically recent hydration rim extending to a depth of about 40 m. Three wallboard companies operate in the Las Vegas area of southern Nevada. One operation produces gypsite from Miocene-age playa deposits of the Muddy Creek Formation near the plant. The other two companies shifted from using gypsum from nearby quarries to using gypsum imported from northwestern Arizona, almost 160 km away. Papke (1987) published a comprehensive review of Nevada's gypsum resources.

Iowa

The largest concentration of gypsum mining and wallboard manufacturing operations in the United States is in northwestern Iowa, at Fort Dodge in Webster County. Gypsum has been mined continuously in this area since the 1870s. Gypsum occurs in the Jurassic-age Fort Dodge Formation, underlying about 40 km² near the city of Fort Dodge. Although originally deposited in a single evaporite basin, gypsum here occurs as discontinuous masses with a maximum thickness of about 10 m. The gypsum was deposited on an erosional surface that truncated the underlying Pennsylvanian and Mississippian strata. Postdepositional solution and erosion thinned the deposit in many areas, and in some places only remnants of the gypsum exist. The surface of the gypsum has been significantly affected by postdepositional processes. In some areas, the gypsum has been completely eroded by glacial processes.

Pleistocene glacial till covers the gypsum everywhere except where it is exposed in ravines near the Des Moines River. These areas were the first to be mined by underground methods in the late 1800s. In some areas, the gypsum is immediately overlain by the "Soldier Creek beds," an informal stratigraphic unit that protected the gypsum from dissolution and erosion. The Soldier Creek beds consist of calcareous siltstone and sandstone and shale up to 15 m thick that overlie the gypsum (Cody, Anderson, and McKay 1996).

Gypsum also occurs in the Devonian-age Wapsipinicon Formation in southeastern Iowa. USG produces gypsum for portland-cement rock and wallboard at Sperry, in Des Moines County. Gypsum occurs at a depth of about 200 m and has an average thickness of about 3.3 m. The single-level, underground mine began production in 1961 and is currently the deepest gypsum mine in North America. Gypsum is extracted using room-and-pillar techniques and conventional drilling and blasting. The mine underlies an area greater than 3.3 km².

This deposit originally might have been anhydrite. Geological relationships observed in the mine and drilling cores, however, indicate that the deposit has undergone multiple phases of hydration and dehydration. Horizontal bands of anhydrite crosscut upward-thrusted enterolithic folds in the gypsum seam. Maximum hydration is found along the deposit's solution margin and beneath preglacial valleys.

California

The only domestic source of gypsum used for manufacturing wallboard in California is located in Imperial County, the southernmost county of the state. The gypsum occurs in the Miocene-age Fish Creek Gypsum Member of the Split Mountain Group. This deposit, located on the flank of the Fish Creek Mountains, has the largest gypsum production in the United States. The gypsum interval is up to 50 m thick and was deposited on an unconformable surface consisting of granite, fanglomerate deposits derived from the underlying and nearby granitic rocks, arkose, and sandstone. The characteristics and stratigraphic relationships of the gypsum are very similar to the enormous occurrence of gypsum in the Miocene Boleo Formation midway down the Baja Peninsula. The gypsum is unusual in that it has very few impurities; the deposit is devoid of calcium carbonate. The gypsum does, however, contain zones that have been discolored by manganese and iron oxides and zones of bassanite. The bassanite and discolored zones are believed to be related to hydrothermal alteration. The deposit is on the western edge of the Salton Trough, a rift zone with a thin crust and both extensional and right lateral ground movements.

Holocene-age deposits of gypsite at the southern end of the Central Valley have been used as a soil conditioner for many years. These deposits produce gypsite with a purity of 45% to 75% gypsum. Although the purity is too low for use in portland cement or plaster products, the gypsite is useful in treating the alkaline soils of the great agricultural districts of the San Joaquin and Central valleys. A comprehensive review of the gypsum deposits and resources of California was published by Ver Planck (1952).

Indiana

Two companies operate underground gypsum mines in southwestern Indiana. An interval of gypsum 4 to 5 m thick in the Mississippian-age St. Louis Formation occurs at a depth of 100 to 250 m. The variation in depth is caused by the deeply incised surface topography developed in the overlying Pennsylvanian clastic strata. These deposits are good examples of the carbonate-sabkha depositional environment described by Jorgensen and Carr (1972). The St. Louis Formation is about 45 m thick and contains at least 10 discrete carbonate-sabkha depositional cycles. Only the uppermost two cycles, however, contain economic quantities of gypsum. The depositional cycles represent the transgressions and regressions of a very shallow sea over a broad tidal flat in a coastal sabkha environment.

The beds dip westward into the Illinois Basin about 6.6 m/km. The updip edge of the gypsum is exposed to subsurface groundwater activity and is actively undergoing solution. Groundwater percolating through the overlying strata and down dip from the Mitchell Karst Plain has formed an extensive cavity system of hydrogen-sulfide-bearing, water-filled fractures and caves. One of the mines has been flooded twice during its almost 50 years of operation. The first flood occurred when a development entry encountered the cavity system during blasting. The second occurred when groundwater continued to dissolve gypsum and worked around the engineered bulkhead constructed after the first flood. Careful evaluation of diamond core drilling information, mine planning, and ongoing underground examination assist in keeping active mining areas away from potential solution zones.

Michigan

Gypsum is produced in the eastern part of the Michigan Basin near the western shore of Lake Huron. Since the publication of the 6th edition of *Industrial Minerals and Rocks*, the underground mining operations in the Grand Rapids area have ceased. The deposits here are in the Michigan Formation of Mississippian age, and consist

of multiple units of gypsum from 1.5 to 13 m thick, separated by beds of shale varying from a fraction of a meter to 15 m thick. Overburden is glacial till ranging in thickness from 13 to 25 m. Three companies operate in the Alabaster–National City area: USG, National Gypsum Company, and Michigan Gypsum. These companies supply gypsum to wallboard plants in Detroit, Michigan, and Waukegan, Illinois, and cement plants in situ ated on or near Lake Michigan, Lake Huron, and Lake Erie.

Colorado

Extensive resources of Permian-age gypsum up to about 27 m thick occur near the town of Gypsum in Eagle County, west-central Colorado. One quarrying and wallboard manufacturing operation is located in the area. Gypsum also occurs in the Great Plains near the town of La Junta in southeastern Colorado.

Kansas

Gypsum occurs in Lower Permian rocks in central Kansas. The Georgia–Pacific operation extracts gypsum from Easley Creek Shale Formation in the upper part of the Council Grove Group. The National Gypsum Company quarries gypsum from the Medicine Lodge Member of the Blaine Formation in south-central Kansas, which corresponds to the lowermost gypsum strata that occur in the USG operations in northwestern Oklahoma.

New Mexico

Although considerable Permian calcium sulfate occurs in the Permian Basin deposits in southeastern New Mexico, none is currently being mined. There are, however, three operating quarries in the north-central part of the state that are producing gypsum from the Todilto Formation of Jurassic age.

Utah

Gypsum has been produced for many years from the Jurassic-age Arapien Shale in south-central Utah. Several stratigraphic intervals of gypsum are interbedded with shale and mudstone and have been complexly folded into a series of anticlinal and synclinal folds. The Arapien Shale outcrops in the foothills along the western slope of the southern extent of the Wasatch Mountains. The gypsum is more resistant to erosion than the clastic rocks and occurs as ridges. The Arapien Shale is also exposed on the western flank of the San Rafael Swell in southern Utah. The San Rafael Swell is an asymmetric structural dome and several beds of gypsum are exposed over more than 100 km².

Wyoming

Two companies produce gypsum in northwestern Wyoming. Large resources of gypsum are located southeast of Greybull in north-central Wyoming. A gypsum interval up to 22 m thick occurs near the top of the Chugwater Formation (Triassic). The gypsum is interbedded with shale.

Canada

The majority of gypsum produced in Canada comes from Nova Scotia. Several companies produce gypsum and various blends of gypsum and anhydrite from the Mississippian-age Windsor Group. The majority of the material produced is exported to gypsum wallboard and Portland cement customers along the Atlantic and Gulf coast regions. Several companies operate large quarries in Nova Scotia. The National Gypsum Canada Ltd. quarry at Milford, near Halifax, is the largest gypsum quarry in the world. Adams (1991) published a comprehensive review of gypsum deposits and occurrences in Nova Scotia.

Gypsum is also produced in other provinces, including Newfoundland, New Brunswick, Ontario, Manitoba, Alberta, and British Columbia.

Atlantic Canada

The major deposits of gypsum in Nova Scotia occur in the Mississippian Windsor Group, consisting of up to 760 m of interbedded marine evaporites and nonmarine sediments that were deposited in a large, complex intracontinental basin. Traditionally, the Windsor Group has been subdivided into five subzones, named “A” through “E” in ascending order. Giles (1981) reinterpreted the depositional history of the Windsor Group and identified five major transgressive–regressive depositional cycles. The cycles correlate with the earlier subzone nomenclature. Each cycle is characterized by one or more transgressive–regressive cycles. Economic gypsum and anhydrite deposits occur in the two lowest cycles. The earliest cycle (the A Subzone) represents a single rapid marine invasion followed by a slow regression of the sea. The A Subzone consists of up to 305 m of anhydrite with a variable thickness of gypsum near the surface. The depth of hydration varies from 0 to 76 m. The B Subzone also represents extensive evaporite deposition but consists of numerous transgressive–regressive sequences, all similar but on a much smaller scale than found in the A Subzone. The B Subzone consists of about 400 m of gypsum interbedded with dolomite, limestone, and siltstone. Gypsum occurs at a depth of up to 100 m.

The gypsum and interbedded waste units have been complexly folded and faulted into a series of anticlines and synclines. The folding is complex and varies from upright to recumbent. The folds have been refolded and truncated by normal and reverse faults.

Ontario

Only one company mines natural gypsum in Ontario: Canadian Gypsum Company, Ltd. A subsidiary of USG, it operates an underground mine in the Upper Silurian–age Salina Group near Hagersville, about 100 km southwest of Toronto. The gypsum seam is about 1.1 m thick, and the room-and-pillar mine is situated at a shallow depth (30 to 40 m) beneath the surface. The gypsum is overlain by 3 to 13 m of thinly bedded shale and dolomite and up to 15 m of glacial till. The gypsum has an average purity of about 85% and is beneficiated by heavy-media separation. The G-P Gypsum Corporation also operates a wallboard plant at Caledonia, near the Canadian Gypsum Company operation. Although natural gypsum was used for many years, production from the Caledonia mine has ceased and synthetic gypsum is currently used. The gypsum seam is 2.5 to 3 m thick and is located stratigraphically about 70 m below the Hagersville seam. The inactive and flooded Drumbo mine, formerly operated by Westroc Industries Ltd. (now a part of BPB North America), is about 75 km northwest of the Hagersville area. The Drumbo mine was active from about 1978 until 1993. The gypsum mining seam averages 1.8 m thick and is located 120 m below the surface.

Western Canada

Gypsum is produced in the provinces of Alberta, British Columbia, and Manitoba for wallboard-manufacturing plants in Edmonton, Vancouver, and Winnipeg. The quarries are far from the wallboard plants. The deposits in British Columbia are on the western flanks of the Canadian Rocky Mountains in environmentally sensitive areas. The VMSD at Falkland, near Kamloops, is quarried for Portland cement rock.

Mexico

Mexico has tremendous resources of high-quality gypsum located in many parts of the country. Although Mexico is the second-largest

exporter of gypsum to the United States for the manufacture of wallboard, it has only three wallboard plants in the country. The gypsum industry continues to grow in Mexico as more development occurs in the commercial and institutional sectors. The primary use for gypsum in Mexico is in manufacturing portland cement rock and building plasters. Gypsum wallboard is rarely used in residential construction. A smaller but growing market is industrial plasters used in the manufacture of ceramics (cups and plates) and sanitary ware (sinks and toilets). Numerous *yaseras* throughout the country supply the construction plaster needs of local markets.

Baja California del Sur

In this area, the gypsum occurs in the Miocene Boleo Formation, a marine-clastic sequence that is also the host for copper, zinc, and cobalt mineralization. Gypsum in the Boleo Formation shares similarities with the Miocene Fish Creek Gypsum in California. Up to 110 m of gypsum was deposited on an irregular bedrock surface consisting of andesitic igneous rocks of the Comondu Formation. The gypsum is overlain by marine limestone.

Puebla State

Deposits of Miocene–Pliocene gypsum occur to the southeast of Mexico City in the southern part of Puebla State. Several thick gypsum beds outcrop near the village of Izucar de Matamoros extending eastward to the village of Axochiapan. The deposits supply portland cement rock to numerous plants in the Mexico City–Puebla metropolitan areas. Gypsum from this region has also supplied the first wallboard plant in Mexico, located in Puebla, for more than 30 years, and numerous small plaster-calcining plants.

Nuevo Leon and Coahuila States

The cities of Monterrey and Saltillo, located in Nuevo Leon and Coahuila states, respectively, are areas of tremendous growth in northern Mexico. These cities are only a few hours south of the United States. There are several portland cement plants located in this region, and Monterrey is the center for the sanitary ware and ceramic industry in Mexico. Of the three gypsum wallboard plants in Mexico, two are located just north of the city of Monterrey.

Gypsum deposits in northern Mexico occur in the Cupido Formation (Cretaceous) and Minas Viejas Formation (Upper Jurassic). Near Monterrey, gypsum in the Minas Viejas Formation commonly occurs in the breached cores of complex anticlinal structures of the Coahuila Marginal Fold Belt, such as Portrero Grande and Sierra del Fraile. These structures are diapiric structures of rock salt that have pushed upward through Upper Jurassic and Lower Cretaceous strata. An oil well drilled in the Sierra de Minas Viejas fold/diapir structure penetrated approximately 4,000 m of evaporites (Weidie and Martinez 1970). Gypsum occurs as a capping of the rock salt in some of the large fold structures. The gypsum is often contaminated by fragments of rock salt, however, and generally is not used for wallboard manufacturing.

Gypsum of the Cupido Formation is widespread in northern Mexico. The gypsum occurs along the flanks of limestone ridges in Nuevo Leon and Coahuila states. Two unusual occurrences of gypsum outcrop between Monterrey and Monclova. The diapiric masses of Minas Viejas gypsum, elliptical in shape with a major axis up to 1.5 km long, have pushed through the upper crust an estimated distance of about 5 km. The gypsum contains inclusions of igneous rock plucked from the walls of the conduits during its upward migration.

Other Resources in Mexico

There are significant occurrences in other parts of Mexico, including Chihuahua, Colima, Oaxaca, San Luis Potosi, Sonora, and other

states. The most recently developed gypsum deposits are located in Colima in southwestern Mexico. Gypsum outcrops in a mountainous area covering almost 60 km between the villages of Coquitmatlan and Ixtlahucan. The developed gypsum deposits are located near the main transportation artery (*autopista*) between Guadalajara and the Port of Manzanillo. Quarried gypsum is transported about 70 km to a state-of-the-art, multiple-use, rock-loading facility in the Port of Manzanillo for shipment to the Pacific Northwest.

TECHNOLOGY

Exploration Techniques

Several direct and indirect methods exist for determining the presence of gypsum. Because gypsum has been used as a building material and artist's medium for several thousand years, much is known about the worldwide distribution of deposits.

The initial step in exploring for gypsum is a thorough literature search. The U.S. Geological Survey (USGS) published thorough reviews of the gypsum deposits of the United States in 1904 and 1920 (Adams 1904; Stone et al. 1920) and a comprehensive bibliography on gypsum and anhydrite in 1960. Dean and Johnson (1989) compiled a survey of anhydrite and gypsum deposits. Sources of information in North America include numerous state and provincial geological surveys and federal agencies such as USGS, the Instituto Nacional de Estadística Geográfica e Informática (INEGI) in Mexico, and the Geological Survey of Canada. Information on foreign resources may be obtained from similar organizations or international organizations such as the United Nations. Other sources of information include unpublished university theses and dissertations and records of water or oil and gas wells. For example, the initial discovery of two large deposits of gypsum in Iowa and Indiana came from water-well records that are required to be submitted to the state geological survey.

The potential for the existence of evaporite minerals can be determined by studying the stratigraphy in regions where sedimentary rocks occur. In North America, most of the significant deposits of gypsum occur in rocks of Silurian, Devonian, Mississippian, Permian, Jurassic, and Miocene age. If shallow evaporite rocks are believed to be present, then further information may be derived by examining outcrops and topographic maps. Deeper deposits can be initially investigated by examining geophysical logs, oil and gas lithologic strip logs, or water-well information. Many state agencies require samples of cuttings or of diamond drill cores for retention in a permanent repository. As the stratigraphic and lithologic details of a target area are developed, the structural conditions should also be ascertained. Primary, regional structural features such as folds and faults expose gypsum-bearing strata or are pathways for the hydration of deeper anhydrite strata. Linear structural features such as joints and fractures also determine the minability of a gypsum deposit.

Gypsum has some unique features that are directly visible or interpreted from the topography or hydrology of an area. For example, outcrops of gypsum are rare in humid environments because of the relatively high solubility in the presence of surface water or groundwater. Although gypsum is important in agriculture as a soil amendment, outcrops of gypsum support only sparse vegetation.

Stratigraphy

Gypsum and anhydrite are usually associated with common sedimentary rocks such as shale and dolomite. It is more commonly associated with dolomite than limestone because the formation of gypsum is often associated with dolomitization of micritic tidal-flat sediments. Megascopic fossils are almost universally absent in gypsum and anhydrite deposits because of the high salinity of the water in which the evaporites were deposited (Pettijohn 1975). The

physiochemical characteristics of gypsum generally rule out its preservation in igneous or metamorphic rocks, except for minor occurrences associated with hydrothermal fluids. A significant exception is the gypsum that occurs interbedded with marble and tremolite schist in Riverside County, California. The country rocks encasing several thick beds of gypsum and anhydrite were subjected to regional metamorphism. The uppermost portion of the evaporite seams was hydrated to form gypsum, but anhydrite occurs at depth. Underground mining to a depth of about 35 m was carried out from the 1920s to 1946.

Topography

The high solubility of gypsum results in areas of low topographic relief or highly dissected terrain in humid regions. For example, the gypsum-bearing portion of the Mississippian Maccrady Formation crops out for about 30 km along the footwall of the Saltville Thrust Fault in southwestern Virginia. Tectonically thickened portions of the Maccrady Formation occur as a prominent valley between more competent ridges of sandstone (Pice Formation) and dolomite (Honaker Dolomite) in the thrust fault hanging wall. The Mississippian Windsor Group in Nova Scotia consists of about 800 m of gypsum and anhydrite interbedded with limestone, siltstone, and sandstone. Pinnacles of gypsum and anhydrite occur with deep pockets and sinkholes filled with clay and organic material.

Quarryable gypsum occurs as a product of the near-surface hydration of anhydrite by groundwater. The deposits of Kansas, New Mexico, Oklahoma, and Texas occur in semiarid regions. The pattern and degree of hydration of anhydrite to gypsum are a function of: (1) stream drainage patterns; (2) type and thickness of overburden; and (3) structural features such as fractures, joints, and faults. Gypsum typically caps low escarpments in the semiarid environments. In the outcrop area, some of the gypsum has been dissolved and eroded, resulting in locally poor quarrying recovery. Headward erosion of gypsum along structural discontinuities aids in the transmission of groundwater to hydrate anhydrite in the downdip direction, but may also result in poor quality or recovery near the streams. In the downdip direction, the gypsum is overlain by an increasing thickness of overburden, generally consisting of sand, shale, siltstone, or limestone. The type of overburden and its permeability affect the degree of hydration of the underlying seam.

In arid regions, gypsum outcrops are often more resistant than commonly associated beds of mudstone or shale. The Jurassic Arapahoe Shale in south-central Utah consists of several gypsum intervals that have been complexly folded. The gypsum outcrops as hogback ridges with slopes of mudstone or shale. The Miocene Fish Creek Gypsum Member of the Split Mountain Group in Southern California is well exposed as barren hills along the limb of a syncline and is underlain by conglomerate and igneous rocks.

Vegetation

Although gypsum provides many benefits in agricultural applications, outcrops of gypsum are relatively hostile to the growth of vegetation. The development of karst topography on gypsum outcrops in humid regions such as in Nova Scotia supports vegetation primarily because of the accumulation of organic material in pockets of clay.

In arid regions of the western United States, outcroppings of gypsum are largely barren or only sparsely covered by vegetation. The uppermost part of the outcropping consists of soft, friable, secondary gypsum (gypsite) derived by the evaporation of capillary water from the underlying rocks. The surface often has the appearance of a wrinkled orange and is called "cryptogamic crust." The crust, consisting of gypsite, cyanobacteria, lichens, fungi, or mosses, forms when moisture is available.

A distinctive change in the density or type of vegetation often distinguishes gypsum from limestone in interbedded and folded sequences. Juniper shrubs (a conifer) commonly grow sparsely on gypsum outcrops, but grow more abundantly on limestone. Saguaro cactus thrives on some gypsum deposits in southwestern Mexico. In Colima, for example, the upslope contact of gypsum with limestone on steep, colluvium-covered slopes is generally defined at the highest occurrence of saguaro cacti. Beds of clay impurities within a gypsum deposit may support more vegetation, such as creosote bush.

Hydrology

Examining maps may provide a hint about the presence of gypsum. Sulfate-laden groundwater discharging from springs or in streams is often noted as "sweetwater" or *agua dulce*. For example, gypsum has been mined at Sweetwater, Texas, for almost 100 years. Sweetwater Creek flows across the outcrop area of the Permian-age Blaine Group. The high solubility of gypsum also forms karst terrain, with little to no surface drainage in some regions.

Deposit Evaluation

Drilling and Sampling

The primary method of evaluating a gypsum deposit is by diamond core drilling. Drilling is rarely done, however, on a regular sized or shaped grid. Rather, drill holes are best placed to answer basic or specific questions about the deposit regarding (1) its thickness and lateral extent; (2) the presence, type, and distribution of impurities; and (3) other factors that may affect minability or quality, such as solution zones, erosional cutouts, or an irregular bedrock surface.

The drilling campaigns to initially outline a gypsum deposit are not sufficient for the long-term planning and operation of a mine or quarry. Subsequent programs provide infill drilling information and answer localized questions.

The diamond drill core is generally sampled by splitting the core longitudinally, preserving one half and preparing the other half for quality analyses. The sampling interval is typically 1.5 to 2 m. The core is crushed in a laboratory crusher and ground in a pulverizing mill to about 100 mesh. The testing methods for the chemical analysis of gypsum are defined in ASTM C471M-01.

Testing Procedures

In general, testing gypsum rock for wallboard manufacture involves determining the amount of chemically combined water and soluble salts. The purity of the sample is determined by measuring the loss of weight after heating for a specific period of time and temperature range. Absorbed moisture (free moisture), however, must be removed first by drying the sample to prevent overestimating purity. Overheating the sample can also cause thermal decomposition of impurities such as carbonates and some clays, and can result in an overestimate of purity.

Free-moisture and combined-moisture losses may be measured by weighing samples with laboratory balances before and after heating in ovens. Computerized systems are also available that perform the drying, calcining, and weighing functions using only one analytical instrument.

Soluble salts are leached from the pulverized samples for determining the content of total dissolved solids (TDS) with an electrical conductivity meter and chloride ions with an ion-specific probe.

Whiteness and brightness are important in manufacturing and marketing industrial and ceramic plasters. Although the color of the calcined plaster may not affect the quality of the finished product, it may have an effect on competitive advantage in the marketplace.

Food- and pharmaceutical-grade gypsum is analyzed for the presence of heavy metals, such as lead, arsenic, and selenium, as well as for the presence, type, and amount of bacteria.

Mining

Most of the world's gypsum is produced by surface-mining operations. In North America, only five active underground gypsum mines were in operation in 2004. Two are located in Indiana, and one each in Iowa, Michigan, and Ontario, Canada. Four additional North American underground gypsum mines ceased operations early in the 21st century after extensive periods of operation. Gypsum was mined in southwestern Virginia from about 1830 until 2000—a period of about 170 years. Several long-term, underground mining operations in New York, Kansas, and Ontario ceased operations in the early part of the 21st century.

Quarrying

Gypsum is extracted from near-surface deposits by quarrying methods. Overburden consisting of glacial materials (till, sand, clay), shale, mudstone, siltstone, sandstone, sand and gravel, or limestone, is removed from the gypsum by various stripping methods. Stripping is performed by scraper, truck and excavator, front-end loader or hydraulic excavator and truck, dragline, and bulldozer. The maximum economic stripping limit (thickness) is about 30 m and depends on the method of stripping and the thickness of the underlying recoverable gypsum.

Final cleanup of the stripped gypsum surface is important, and is determined by the final products to be manufactured. If the quarried rock is to be used as agricultural products, Portland cement rock, or wallboard, then much of the impurities can be removed in the finer fractions during crushing and screening. Conversely, gypsum used for high-quality, high-value-added products requires more stringent cleaning. For example, articulated hydraulic excavators with multiple, interchangeable bucket widths scrape clay from the gypsum surface and fractures that extend deep into the gypsum.

Drilling and blasting is the primary method of quarrying gypsum. Quarry benches are generally about 8 m in height. Hydraulic rotary drilling and auger drilling are commonly used. Gypsum is soft and penetration rates up to 7 m/min are possible. Blast holes are generally 50 to 100 mm in diameter and spaced relatively close together to distribute the explosive forces throughout the rock mass. The blasting components used include ammonium nitrate and fuel oil (ANFO) blasting agent, cast boosters, nonelectric blast initiation systems. Bagged emulsion is used in wet holes. About 1 kg of blasting agents per ton of broken gypsum is an average tonnage factor. The elastic nature of gypsum, the presence of solution-enlarged fractures, and the possible presence of water contribute to poor and inefficient rock fragmentation. An incorrectly designed blasting pattern may result in irregular fragmentation, including excessive oversized rock requiring secondary breakage, excessive fines, or irregular floor conditions that are detrimental to the efficiency and maintenance of mobile equipment. Quarry haulage trucks or over-the-road dump trucks transport the quarry-run broken gypsum from the quarry site to the primary crusher.

Another method of extracting gypsum from quarries that is gaining acceptance is the use of a surface miner. This is an adaptation of highway-resurfacing technology in which a horizontally rotating mandrel with cutting teeth chips a way at the asphalt and either discharges the broken material in a windrow or directly into a haulage truck. Specialized machinery using this technology is being developed to quarry coal, gypsum, and limestone. The size, spacing, and arrangement of the cutting teeth on the mandrel are

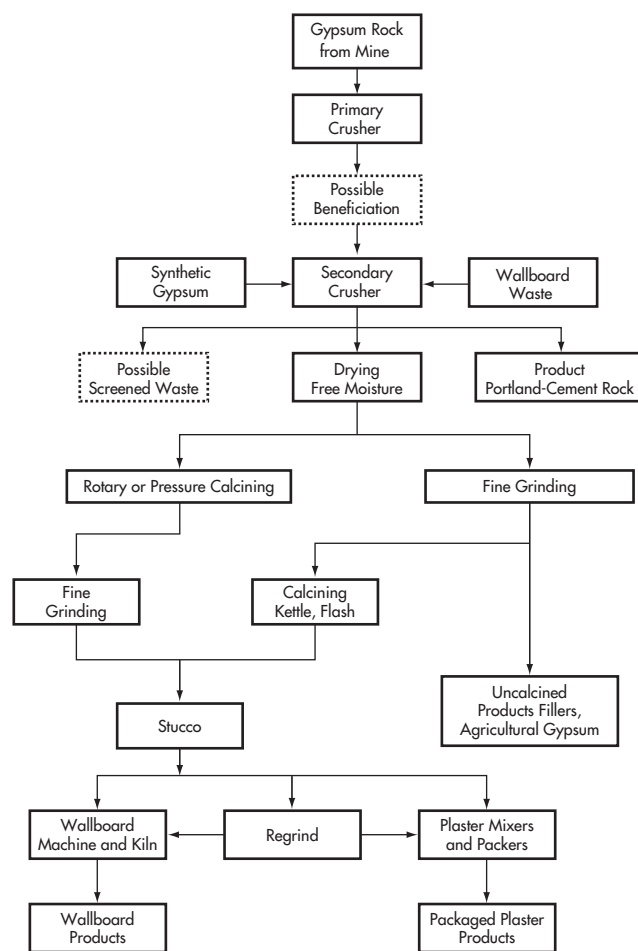


Figure 1. A general flow diagram of the manufacture of gypsum wallboard

important factors in the efficient production of gypsum rock. Advantages over standard quarrying techniques are the following:

- Elimination of drilling and blasting
- Elimination of primary crushing
- Direct removal of interbedded thin waste beds or low-purity zones
- Increase in recovered gypsum purity by removal of off-specification material from windrows
- Maximization of the overall recovery of the gypsum near structures or utilities

Underground Mining

Underground mining of gypsum is far less common than quarrying. There are currently only five active underground gypsum mines in North America. The mines are located at a depth of < 30 m (Hagersville, Ontario, Canada) to about 200 m (Iowa and Indiana). Access to the mine workings for workers, supplies, ventilation and escape, and production is by either vertical shafts or inclined adits (tunnels). The mined interval varies from 1.1 m (Hagersville) to 3.7 m (Iowa, Michigan, and Indiana).

Gypsum is extracted using the room-and-pillar method, in which pillars are left in place to support the roof strata and the

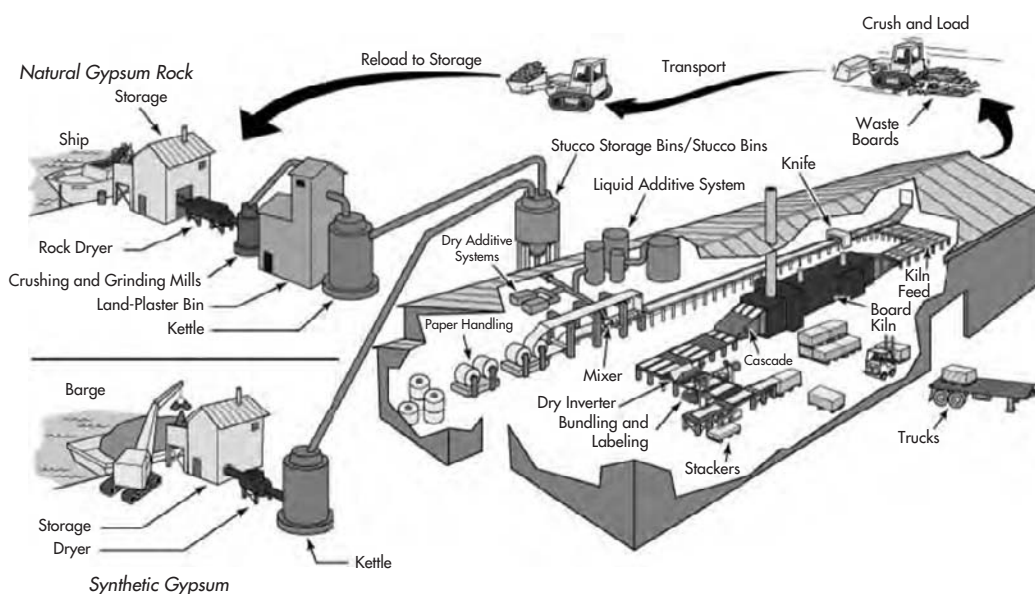


Figure 2. A conceptualized drawing of the manufacture of gypsum wallboard

gypsum is removed in a checkerboard pattern. The extraction ratio, which is the proportion of material mined to material left in the supporting pillars, varies from 65% to 80%.

Drilling and blasting of gypsum in underground mines is similar to methods used in gypsum quarries. The blast-hole pattern, however, is drilled horizontally into the advancing face of a mine heading. The number of drill holes, orientation, depth, and sequence of blasting are designed to maximize breakage of the gypsum and to maintain the integrity of the adjacent pillars and immediate mine-roof strata. The roof strata are reinforced by roof-control fixtures, generally epoxy resin-grouted bolts, up to 1.5 m long. The resin-grouted bolts bind the roof strata together to form an integral beam that is stronger than the individual strata.

Underground gypsum mines are generally very stable. Long-term measurements of roof and pillar convergence (vertical closure) at the USG mine at Sperry, Iowa, indicate that the structure should be stable for hundreds of years. An underground gypsum mine near Grand Rapids, Michigan, is currently being used as a computer network security center.

Processing

Wallboard Manufacture

Figure 1 is a general flow diagram for the manufacture of gypsum wallboard, and Figure 2 is a conceptualized drawing of that process. Three possible sources of raw material are shown: (1) natural gypsum rock delivered from an on-site quarry or underground mine, (2) synthetic gypsum delivered from a nearby power plant or by barge, and (3) off-specification wallboard recycled into the manufacturing stream.

Quality Assurance and Quality Control Issues

No single statement can be made about the effects of the presence of impurities in gypsum deposits. The manufacturing processes for wallboard can be adjusted for a wide range of gypsum purity. Wallboard can be made from relatively low-purity (low 80s) or very-high-purity (high 90s) gypsum. The key is that the purity of the gypsum supplied from the mine or quarry, as well as the calcined

gypsum stucco, should be consistent. Formulating calcined stucco with air-entraining agents can decrease the weight of the finished wallboard, enhancing its purity.

Most gypsum contains 10% to 15% impurities, although some deposits may be exceptionally pure (i.e., +95%) or somewhat impure (i.e., 80%). In general, the amount of impurity that can be tolerated depends on (1) the type of impurity, (2) the product being manufactured, and (3) the competitive situation.

Impurities are usually separated into three categories, based on their effect on the manufacturing process and finished products:

1. Insoluble or relatively insoluble minerals such as limestone, dolomite, anhydrite, anhydrous clay, silica minerals
2. Soluble evaporite minerals, including chlorides (halite, sylvite, etc.) and sulfates (mirabilite, epsomite, etc.)
3. Hydrated but insoluble minerals (e.g., the montmorillonite group of clays)

Insoluble Impurities

Insoluble impurities, especially carbonates, reduce the strength of the rehydrated stucco and increase the weight of the finished plaster or wallboard products. A greater amount of lower-purity stucco is required to obtain a specific strength plaster or wallboard. Wallboard products that are heavier increase both the transportation costs of the finished products and the difficulty of installation. These minerals can also occasionally act as hydration accelerators. Many commercial gypsum deposits contain as much as 10% to 15% insoluble impurities.

Chert is present only in trace amounts in some deposits and does not significantly affect the manufacturing of wallboard. Chert in the feedstock to the calcining mill can result in excessive abrasive wear of grinding equipment.

Dolomite is detrimental in industrial plaster used in the manufacture of sanitary ware such as sinks and toilets or ceramic products such as dishes. It has a higher specific gravity than gypsum and sinks in the stucco slurry, forming projections at the mold-cast interface and surface pits in the cast product.

Soluble Evaporite Impurities

Soluble evaporite impurities affect calcining temperature, fluidity of the stucco slurry, setting or rehydration time, and bonding of paper and core in wallboard. These minerals are usually limited to no more than 0.02 % to 0.03% by weight of the gypsum rock and strongly affect vapor pressure, which in turn affects the gypsum hydration–dehydration reactions.

Hydrous, Insoluble Impurities

The principal effect of hydrous, insoluble impurities is in the absorption of moisture in the finished product and on bonding characteristics of the rehydrated stucco core of wallboard to its paper covering. Hydrous clays up to 1.0% to 2.0% may be tolerated.

USES

Gypsum is a very versatile mineral that can be used in the manufacture of several hundred products. Processing methods vary from simply crushing and sizing of quarry-run gypsum to specialized methods of calcination in closed pressure vessels.

Uncalcined Gypsum

Gypsum that has been processed only by grinding and sizing is known as land plaster, portland cement retarder, and Terra Alba. Land plaster is used for agricultural gypsum and a raw feedstock for manufacturing wallboard and plasters. Portland cement retarder is used in the manufacture of portland cement. Terra Alba is used in food and pharmaceutical applications.

Uncalcined gypsum is principally used as a retarder for portland cement, soil conditioner, mineral filler, and in other minor industrial applications. About 25% of the gypsum mined in the United States is used in these markets. In countries where building practices differ from those in the United States and Canada (poured concrete, block, or brick), however, the relative usage of gypsum varies widely.

Although calcium sulfate deposits are the world's largest sulfur resources, only minor quantities of gypsum and anhydrite have been used to produce sulfur or sulfur compounds. This use is accompanied by a unique, site-specific set of economics, because sulfur is generally available from nongypsum sources at lower cost.

Agricultural Gypsum

Gypsum provides several benefits in agriculture. The specifications of agricultural gypsum are primarily related to the degree of fineness (particle size and surface area). As gypsum dissolves, it is a source of elemental calcium (25% by weight) and sulfur (20% by weight). Gypsum has a neutral pH (7.0) and is 150 times more soluble than ground limestone. Finely ground agricultural gypsum permits rapid dissolution and absorption by plants. Long-term availability of these elements during a growing season can be accomplished by applying agricultural gypsum of multiple particle sizes. Finely ground gypsum (100% passing through a 425-mesh screen) can also be dissolved in irrigation water for easy application.

Gypsum loosens and aerates heavy clay and wet soils. The acidity of aluminum-rich lateritic soils is buffered by gypsum. The gypsum particles act as nuclei for the flocculation of clay particles, producing more granular and well-drained soils. Cation replacement of calcium for sodium reduces the alkalinity of soil. Gypsum also combines with potassium-aluminum silicates in soil, releasing potassium as a nutrient. Applying gypsum prevents the formation of a crust in the soil where low electrolyte irrigation water is used or where the soil has a high sodium content. The soil crust contributes to excessive runoff and erosion in sloping terrain or pooling of water on more level ground.

In dairy-farm applications, gypsum can be applied to manure piles to prevent the loss of nitrogen by reacting with nitrogen to produce ammonium sulfate. An additional benefit is reduced ammonia odors.

Gypsum can be applied to bodies of water with high total suspended solids, such as muddy ponds, where it acts as a flocculating agent to settle the suspended clay particles.

Portland Cement Rock

Gypsum, anhydrite, or a mixture of gypsum and anhydrite is used in the manufacture of portland cement. Gypsum and anhydrite are used as a source of SO₃. Adding calcium sulfate also controls the early-strength characteristics of cement and product shrinkage during drying and curing. About 3 to 5 wt % of calcium sulfate compounds are ground with clinker to form portland cement.

Gypsum also aids in the grinding of clinker by reducing the tendency of fine particles to agglomerate and adhere to the walls of the mill and grinding media (Hansen et al. 1988). Gypsum is much softer than clinker, is easier to grind, and has a much greater fineness (surface area) than clinker. Portland cement rock is typically ground to a particle size of 6 to 65 mm. Calcium silicates and aluminates that constitute clinker have negatively charged oxygen ions on the crystal surfaces. The hydrogen ions in the water molecules of the gypsum particles bind to the negatively charged clinker particles. The neutralization of the electrical charges by the attraction of the gypsum to clinker particles reduces the tendency for agglomeration.

Terra Alba

Terra Alba is white, high-purity, uncalcined gypsum that has numerous uses in the food and pharmaceutical industries. It is made by fine grinding and air separation of gypsum with a purity of greater than 97%. Terra Alba has a minimum calcium content of 23% (by weight).

Beer Brewing

This type of gypsum supplies calcium ions to buffer the pH and reduce the hardness of water used in the beer-brewing industry. The yield of the main mash is increased by promoting the proper gelatinization of the starch in the cooker mash, as well as protein degradation and starch conversion. Flocculation and precipitation of undesirable protein complexes is achieved by adding Terra Alba. These effects produce beer with improved stability and shelf life.

Baking

In the baking industry, Terra Alba is used as a source of supplemental calcium. It is used in enriched flour and breads, pasta products, baking powder, yeast foods, and bread conditioners. Calcium enrichment of bakery products, in addition to providing supplemental calcium, also counteracts the effects of excess phosphorous in a person's diet. Many foods are high in phosphorous, but few foods are good sources of calcium. A deficiency of calcium makes the dough soft and sticky.

Pharmaceuticals

Terra Alba is used as a diluent and inert extender in pharmaceutical products such as aspirin tablets. It also provides a source of dietary calcium.

Other Food Applications

Terra Alba is also used in canned vegetables, cheeses, and artificially sweetened jellies and preserves.

Glass Batch

Relatively pure uncalcined gypsum, depending on glass-batch chemistry, can also substitute for salt cake (sodium sulfate) in glass manufacturing.

Oxidizing Agent

Thermal decomposition of gypsum in the glass melt produces sulfur dioxide as well as oxygen. The oxygen reacts with any free or reduced sulfur to form additional SO_2 . Increasing the amount of gypsum in the glass batch decreases the sulfur content in the melt and results in a lighter-colored glass. Iron pyrites and carbon or blast-furnace slag are commonly added to the melt to manufacture amber-colored glass. Green-colored glass has a natural amber hue.

Fining Agent

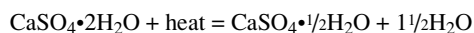
Adding gypsum provides a source of sulfate in soda-lime glass. Decomposition of gypsum produces sulfur dioxide, which, in low concentrations, removes seeds and forms a clear glass.

Removal of Surface Scum

Surface scum can form on molten glass because of improper flow conditions in the furnace, especially near the bridgewall. The presence of coarse sand and stratification of the raw materials in the batch may result in selective melting and the formation of a surface scum. Gypsum added to the glass melt reacts with sodium carbonate to form sodium sulfate. The sodium sulfate melts and reacts with free silica to form sodium silicate, which in turn separates from the molten glass and floats on the surface.

Calcined Gypsum

Gypsum chemically transformed by heat or pressure to remove three fourths of the water of crystallization is known as calcium sulfate hemihydrate, stucco, and plaster of paris. Different methods of calcination produce two products, beta hemihydrate and alpha hemihydrate, depending on the processing method used. The chemical reaction, however, is the same for both products and is reversible at atmospheric temperatures and pressures:



Many different products may be manufactured from alpha or beta hemihydrate or a mixture of both. The products are further mixed with portland cement, fiberglass, plastic resins, and other materials to produce products with high strength and density, fire and water resistance, and other specialized characteristics.

Beta Hemihydrate

Beta hemihydrate is produced by calcining finely ground gypsum (95%–100 mesh) in vertically oriented, cylindrical steel kettles at atmospheric pressure. The calcination can be a continuous process or a batch process. Continuous calcining of land plaster is used predominantly for producing stucco for wallboard. Batch calcining is used predominantly for manufacturing construction and industrial plasters. The beta hemihydrate calcining process produces rough, fractured, fragmented particles.

In the continuous calcining process, land plaster is introduced into the top of the kettle. As the molecular water is removed during calcination, the beta hemihydrate becomes less dense and rises to the top of the kettle. The beta hemihydrate overflows the top of the kettle into a hot pit where calcination is completed and entrapped steam is released. The beta hemihydrate is discharged from the continuous kettle at 140° to 154°C .

In the batch kettle process, the calcining is done on a measured amount of land plaster, and then the entire batch is dumped into a hot pit to complete the calcination and release entrapped

steam. Batch calcining produces beta hemihydrate with high plasticity, high strength, and high density. The product from batch calcination is used for construction and some industrial plasters. Batch calcining is performed at 150° to 165°C .

Gypsum Wallboard

Several different types of wall board are manufactured, including the common variety and specialized varieties, such as fire resistant, water resistant, and plaster lath. Gypsum wall board is manufactured by mixing beta hemihydrate stucco, water, and other additives to form a slurry. Additives such as a spalt emulsion, vermiculite, chopped fiberglass, and paper fiber impart to the wallboard characteristics such as water resistance, fire resistance, and strength. The slurry is discharged onto a continuous roll of paper, the edges of the paper are folded upward, and another sheet of paper is applied to the top to form a soft gypsum "sandwich." This sandwich travels along a conveyor until the stucco slurry has recrystallized to gypsum. The continuous stream of wallboard is cut into lengths varying from 2.4 to 4.25 m. It then enters a multideck drying kiln to remove excess water. Upon exiting the kiln, the wallboard is packaged into two-sheet bundles, stacked, warehoused, and shipped to customers.

Pottery and Ceramic Plasters

Plasters used in the manufacturing of pottery and ceramic products may be alpha hemihydrate, beta hemihydrate, or a mixture of both crystal phases. White art plasters used in schools or arts and crafts classes are made from beta hemihydrate.

The process of manufacturing pottery and ceramic products involves several steps from preparation of an initial model to the final product. An original block mold is manufactured from the finished model of the product to be manufactured. Then a case mold is made from the block mold. The case mold becomes a die for fabricating multiple working or production molds. The block and case molds are typically manufactured from alpha hemihydrate. The use of alpha hemihydrate allows for the production of dense, hard, strong, and durable molds which can be intricately detailed. Working molds, which are used for mass production, are manufactured from a blend of alpha and beta hemihydrate or from alpha hemihydrate. Industrial manufacturing processes for pottery and sanitary ware involve three major types of working molds: slip-cast molds, jigger molds, and press molds.

In slip casting, a relatively fluid mixture of clay and other ceramic raw materials, called "slip," is poured into a mold, which may consist of several individual pieces. The excess water in the slip is absorbed by the plaster mold. Slip-cast molds are generally manufactured from a mixture of 15% to 20% alpha hemihydrate and 80% to 85% beta hemihydrate. Examples of slip casting include the manufacture of sinks and toilets.

In jigger casting, a relatively soft, plastic clay mixture is placed on a rotating bottom mold. As the mold rotates, an upper molding template moves downward and forces the clay to fill the bottom mold. The upper molding template also impresses or cuts the desired design elements into the clay. This method is not very labor intensive and is used to manufacture lower-priced dinnerware items. Jigger cast molds are generally manufactured from a mixture of 70% alpha hemihydrate and 30% beta hemihydrate. The alpha hemihydrate gives the mold durability and hardness for use in longer production runs.

In press casting, the clay mixture is formed into the final product by hydraulically pressing a lump of clay between the halves of a mold. This method is used to produce products such as dishes, ashtrays, some cups, and bud vases. This method of casting

is also relatively fast and low cost. The molds are manufactured entirely from alpha hemihydrate.

Alpha Hemihydrate

Alpha hemihydrate is produced by calcining sized gypsum or lump rock in an autoclave at elevated steam pressure in a batch process. This method of calcination produces dense, orderly, well-formed crystals. Alpha hemihydrate can be used alone or mixed with additives such as beta hemihydrate, portland cement, resins, and fiberglass to produce very durable products.

Industrial Prototypes and Models. Gypsum-based plaster has been used for pattern, model, and mold making for more than 1,000 years. Alpha hemihydrate cements are used to meet the specialized needs of the aircraft, automotive, foundry, plastics, and other industries. The characteristics of the alpha hemihydrate cements allow for the manufacture of molds and patterns with high accuracy, high strength, high surface hardness, and low expansion during drying and curing. Patterns and molds can be made to close tolerances such as those required by the aircraft industry.

One of the latest innovations in preparing industrial prototypes and models is the development of machineable alpha gypsum cement. USG developed this product in the 1990s to meet the needs of the rapid-prototype tooling industry; it serves as a replacement for preformed polymer-based boards. The castable alpha gypsum cement can be poured into containment vessels or molds of any size and hardens in about 1 hr. Dimensional stability is achieved after 3 hr.

This material is typically used with computer-controlled, numerical-milling (CNC) machinery to produce prototypes and models. The material can also be used to produce forms for vacuum molding of sheet plastics. Milling of cast blocks of this material produces chips rather than dust and does not require lubricating fluids.

Art and Statuary. Alpha hemihydrate gypsum cement and plaster are used to manufacture dense, durable, three-dimensional art and statuary products. Art and statuary cement and plaster can be modified by adding polymers and glass fibers to produce resilient, chip-resistant castings. These products can be used to produce solid figurines, lamp bases, and hollow statuary.

Traffic Surface Repair. Traffic surfaces such as expressways, bridges, ramps, and commercial concrete floors that carry high volumes of traffic can be repaired with a mixture of alpha hemihydrate, portland cement, and a suitable aggregate. This is a quick and effective method to repair or replace traffic surfaces that cannot be out of service for long periods.

Traffic surface repair cement expands on setting to ensure a tight contact with the surrounding pavement. This characteristic protects reinforcing steel by restricting water and salt seepage. The product sets quickly and rapidly develops relatively high compressive strength. The total process of repairing or replacing sections of pavement can be completed in less than 5 hr. The cement will develop a compressive strength of about 25 MPa within about 1 hr; the compressive strength will reach about 69 MPa after 28 days.

Architectural Applications. Fiberglass-reinforced alpha hemihydrate cement (FGR) is used to fabricate highly detailed interior architectural features. Strong, resilient, high-strength architectural details can be produced with a thickness of as little as 0.10 in. Column capitals and covers, light coves, medallions, cornices, coffers, and wall and ceiling moldings are examples of details that can be fabricated from this material. Architectural detail elements can be precast off site from original pieces to exacting detail. Historical architectural elements can be easily replicated with stronger, lightweight, FGR gypsum cement.

Medical Applications. Gypsum plasters are used in dental and orthopedic applications. Dentists use the plasters for making impressions of teeth and gums to produce bridges, crowns, and dentures.

Orthopedic plasters are used in bandages and casts to immobilize broken limbs. Newer, more innovative applications include tissue engineering where gypsum is used to promote bone and tissue regrowth. It is used as bone-void filler, in which cast pellets of high-purity gypsum provide a temporary framework for tissue regrowth (Laurencin et al. 1999). Upon setting, the gypsum has a strength of about 24 MPa. The gypsum is biocompatible, stimulates bone regrowth, and is adsorbed by the body in 4 to 8 weeks.

Deadburned Gypsum

Gypsum which has been calcined at a temperature above 400°C loses both molecules of water of crystallization, forming a deadburned calcium sulfate (CaSO_4). Although it has the same formula as anhydrite, deadburned gypsum is relatively inert and insoluble. Deadburned gypsum is almost anhydrous, with more than 99.6% of water of crystallization removed during calcination. It has a high content of elemental calcium (29% by weight).

There are several high-value-added uses for deadburned gypsum. It is used as an inert filler in plastics. It is also used in agricultural products as a binder or carrier for herbicides and pesticides. Deadburned gypsum is used in pharmaceutical products such as aspirin tablets. It is also used in pizza dough and other bakery products, acting as a desiccant and a source of calcium. The deadburned gypsum absorbs moisture in products, which then can be manufactured and stored for a period of time before use without becoming soggy.

Deadburned gypsum is used as filler in thermoplastics such as polyvinyl chloride (PVC) products: vinyl siding, window frames, moldings, conduit, and pipe. The filler imparts acid resistance and low electrical conductivity. It is also used in food packaging.

PRODUCT GRADES AND SPECIFICATIONS

There is no single statement possible on the grades and specifications of gypsum because of the diversity of products produced from the mineral. Gypsum used in construction products and food and pharmaceutical products, however, must meet stringent regulations.

Construction Products

ASTM defines the specifications for testing uncalcined gypsum and construction products manufactured from gypsum. ASTM standard C471M-01 defines the testing methods for the chemical analysis of gypsum. ASTM standard C472-99 defines the standard testing methods for the physical properties of gypsum, gypsum plasters, and gypsum-based concrete. In 1999, ASTM began to phase in a new international standard for interior and exterior gypsum wallboard products and veneer plasters that combined nine separate earlier standards. This standard titled C1396, *Specification for Gypsum Board*, eliminated inadvertent inconsistencies in the separate standards.

Food and Pharmaceutical Grade

Gypsum is an approved additive on the Food and Drug Administration (FDA) "Generally Recognized As Safe" (GRAS) listing of food additives. The use of gypsum in specific food products is described in Title 21, Part 184 of the Code of Federal Regulations (21 CFR 184.1230). The permitted amount of gypsum allowable in different types of foods is defined in the Food Chemical Codex in the United States and the National Formulary in the United Kingdom.

ECONOMIC FACTORS

Pricing

Gypsum is a low unit-value, high place-value industrial mineral, and its ultimate value is based on value-added processing. The lowest prices are for ground gypsum used for portland cement and agricultural gypsum. Calcining gypsum for use in manufacturing

wallboard or construction and industrial plasters increases the price significantly. The most valuable products include specialty dental, orthopedic, and industrial plasters; food- and pharmaceutical-grade gypsum (Terra Alba); and industrial gypsum cement. The high price per ton for gypsum used in wallboard shown in Table 6 is deceptive because the wallboard industry is primarily vertically integrated. Almost all gypsum for wallboard is produced and used internally.

Gypsum prices are regularly published in periodicals such as *Industrial Minerals* and the *Engineering News Record*. The USGS publishes average annual information for the price of crude gypsum (f.o.b. mine) and calcined gypsum (f.o.b. plant) in the United States. Groups such as Roskill Information Services and the Fredonia Group Comprehensive produce market studies of the sources, prices, consumption, and other valuable information.

Competitive Substitutes

No competitive substitutes exist for gypsum used in the manufacture of wallboard and industrial plasters. Gypsum wallboard is not a universal manufacturing material. Masonry products such as brick, concrete block, poured concrete, and cement stucco are used throughout the world.

There is no practical substitute for gypsum, anhydrite, or a blend of gypsum and anhydrite used in the manufacturing of portland cement.

Synthetic gypsum, produced primarily as a by-product of the environmental controls on coal-fired electric-power plants, is a significant substitute for natural gypsum. Most of the new wallboard plants constructed in the late 1990s and early 2000s are designed to use 100% synthetic gypsum, primarily FGD gypsum. In 2003, synthetic gypsum accounted for 26% of the total domestic gypsum supply (USGS 2004).

Packaging

Gypsum is used in more than 400 products, and therefore many different forms of packaging are used for distribution to customers. Raw ground gypsum (land plaster) for agricultural uses and portland cement rock is distributed primarily by bulk truck. Wallboard panels are loaded onto trucks or railroad cars for distribution. Construction and industrial plasters are packaged in bags.

TRANSPORTATION

Truck

Trucking is the most common method of transportation of gypsum products. It is the most flexible mode of transport, but also the most expensive. In most cases, transport is between the quarry site and the manufacturing plant, using either quarry haul trucks or over-the-road dump trucks. Truck haulage is relatively low capacity (25 t) compared to other transportation modes. The cost of truck transport is in the range of \$0.10 to \$0.25/st-mile.

Rail

Transporting gypsum by rail is relatively rare, except for the delivery of portland cement rock. The BPB North America plant in Vancouver, British Columbia, Canada, however, receives gypsum by rail from sources along the western flank of the Rocky Mountains. It is more efficient to ship the intermediate calcium sulfate hemihydrate or finished products manufactured from gypsum. Calcium sulfate hemihydrate weighs only 84.3% as much as uncalcined gypsum.

Railroad transport of gypsum is limited by factors such as the proximity of manufacturing plants to railroad lines to avoid rehandling, limited routes, and the seasonable availability of hopper rail

Table 6. Prices for gypsum by end use

End Use	Cost per Ton
Portland cement retarder	\$12.37
Agricultural gypsum	\$23.65
Wallboard	\$87.02
Plasters	\$150.98

Source: Olson 2002.

cars during grain harvest season. Capacities of railroad cars are limited to about 100 t and the transportation cost is about \$0.04/st-mile.

Barge

Most of the new wallboard plants constructed in the United States during the last decade are totally dependent on the use of FGD synthetic gypsum and were constructed adjacent to coal-fired power plants or along navigable rivers or canals to facilitate the transportation of raw materials by barge. All of these plants are located east of the Mississippi River. There is, however, relatively little natural gypsum transported by barge. Gypsum and anhydrite are supplied to portland cement plants along the Mississippi River by a single source in southeastern Iowa.

Barge transportation is relatively slow and has limited distribution capabilities. The end user must be on a waterway or within about 160 km. Transloading from barge to truck dramatically increases overall transportation costs. Climatic conditions such as drought or flooding can interrupt delivery of products by barge. Barge capacities are limited to about 1,200 t in the United States and 1,500 t in Europe. The cost of transportation by barge is in the range of \$0.0075 to \$0.01/st-mile.

Ship

Wallboard plants along the U.S. coasts receive gypsum by ship. Gypsum producers in Nova Scotia, Canada, supply wallboard plants from New Hampshire to Florida. Gypsum is also supplied to a wallboard plant and to portland cement customers on the St. Lawrence Seaway. Fundy Gypsum Company's Hantsport, Nova Scotia, ship-loading facility is at the upper reach of the Bay of Fundy and has a tidal range of 15 m. Ships with a capacity of up to 36 kt are loaded within a 3-hr period during high tide.

Mexico supplies the western U.S. coast. Large deposits midway down the Baja Peninsula on the western coast of the Sea of Cortez provide gypsum for wallboard plants from Long Beach, California, to Vancouver, British Columbia. A new gypsum quarry and shipping facility near Manzanillo in Colima on the southwestern coast of Mexico began operations in 2001.

Transportation by ship is the least expensive mode of transport for industrial minerals, about \$0.001/st-mile. Transport by ship is highly restricted, however, to coastal areas and other large bodies of water such as the Great Lakes, and requires a significant infrastructure for loading, unloading, and storage.

Import Tariffs and Custom Duties

The U.S. International Trade Commission's Harmonized Tariff Schedule of the United States contains information on import tariffs and duties for raw and processed gypsum. There are currently no general or special import duties on raw gypsum, anhydrite, or calcined plaster products.

By-Products and Coproducts

Wallboard and plaster products account for 90% of the total consumption of gypsum in the United States. Agricultural gypsum

and portland cement rock account for most of the remainder of gypsum consumption. Although some operations specifically produce agricultural or portland cement rock, in most cases these are coproducts associated with the mining and crushing of gypsum for wallboard.

Depletion Allowance

The depletion allowance is an annual, taxable-income deduction to allow mining companies to locate and develop additional ore bodies (Peters 1976). The depletion allowance on domestic gypsum production and foreign gypsum imports is 14 %. Two methods of computing the depletion allowance are allowable in the United States. In the cost or unit depletion method, the total cost of acquiring a mineral property is prorated into the total tons or units extracted from the property during mining. In the percentage depletion method, the most common method used, a specific percentage of the mine's gross income is deducted annually. The deduction, however, may not exceed 50% of the before-depletion net income.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Health and Safety

Gypsum mines and quarries are regulated by numerous local, state, and federal agencies regarding health and safety. In the United States, the predominant agency is the Mine Safety and Health Administration (MSHA). Calcining and manufacturing operations are regulated by the Occupational Safety and Health Administration (OSHA) and, in some cases, state agencies such as CalOSHA in California. Explosives are regulated by the federal Bureau of Alcohol, Tobacco, and Firearms (BATF).

Land Use and Zoning

Underground gypsum mining does not generally affect the concurrent use of the overlying surface. In most cases, the overlying land use is agricultural or forest. Gypsum companies that operate underground mines generally own the mineral rights for gypsum and anhydrite, but not the surface rights on a majority of the mined land and reserves.

The gypsum companies usually own the quarried land. As quarrying progresses, the depleted areas can be concurrently reclaimed and converted to pasture. USG's Alabaster, Michigan, operation has created a significant amount of wetlands in depleted quarry areas.

Mined Land Reclamation

Gypsum mines and quarries tend to be very long-term operations, and some operations in the United States have been continuous for 100 to 150 years. Gypsum quarrying in Nova Scotia began in the 1700s and continues to the present. A large area of the mined lands was disturbed before the promulgation of local, state, or federal reclamation regulations. Modern mining, however, requires a comprehensive reclamation plan and activities to minimize the impact to vegetation, hydrology, slope stability, flora, and fauna, and so forth.

Financial surety is required for the future costs of reclamation. The cost for reclamation is estimated for the fulfillment of the obligations of the approved reclamation plan by a third party. The financial surety covers the government's cost of hiring a third-party contractor if the mining company goes out of business or is otherwise unable to perform the reclamation activities in the approved plan.

Concurrent reclamation may be possible in some areas. After quarrying, the overburden stripping spoil from another area can be placed in the previous cut, covered with topsoil, regraded, and

revegetated. Reclaimed acreage can be released from financial surety upon satisfactory completion of criteria set forth by the regulatory agency.

Pollution Control

Gypsum mining and processing are less environmentally sensitive than many other types of mining industries such as coal, gold, and copper. There is no acid-mine drainage as in a coal mine; chemicals such as sodium cyanide used in heap leaching of gold ore are not used in gypsum processing.

Storm-water management plans are required for the control, storage, and treatment of surface runoff containing fuel, lubricants, antifreeze, etc. Environmental controls are necessary for storing fuel and lubricants, including aboveground storage tanks with secondary containment structures such as berms or metal pans.

Fugitive-dust suppression and control is required for drilling equipment, haulage roads, crushing and screening plants, and load-out facilities in the mining and milling phase. Dust is collected throughout many of the calcining and manufacturing phases of wallboard and plaster production.

Local and state agencies such as a county air-pollution control district or a state department of environmental protection usually enforce air and water quality regulations.

Closure and Decommissioning

Several gypsum wallboard plants and mining operations have been permanently closed and reclaimed in recent years. Dismantling calcining and manufacturing plants is similar to most industrial facilities. The total deactivation of underground mines requires removing mobile equipment (if possible), draining fluids such as fuel and lubricants from mobile and stationary equipment, and removing transformers. These activities reduce the potential contamination of groundwater as pumping ceases and the mine fills with water. All mine entrances are permanently sealed. Subsidence monitoring may be necessary if there are long-term stability issues associated with the mine structure or flooding of the mine.

Surface mining deactivation includes similar activities for removing mobile and stationary equipment, fuel and lubricant storage facilities, and explosives. Access to quarry workings is limited by berms, boulders, fences, and other measures. The angle and height of quarry highwalls are reduced by blasting to form rubble slopes and to reduce the overall final slope.

OUTLOOK AND FUTURE TRENDS

There is no foreseeable shortage of either gypsum or anhydrite resources in the United States or the world. Paradoxically, there are instances where it may be difficult to find gypsum that can be considered economic at a given time and location, a problem that has its roots in place value. The best evidence of this situation is that the United States historically has imported 33 % to 36 % of its needs from Canada, Mexico, Jamaica, the Dominican Republic, and Spain.

Almost all the imported gypsum (with the exception of a few thousand kilotons of special-grade rock) is used by wallboard plants on the Atlantic, Pacific, and Gulf coasts of the United States. The basic reasons for this situation are as follows: (1) large markets for gypsum products are concentrated in and around the coastal cities, (2) there are no developed and producing gypsum deposits along any of the three U.S. coastlines, and (3) large gypsum deposits exist on or near deep water of the exporting countries. It costs less to ship rock from the exporting countries to these major markets than to ship it from inland desposits in the United States.

It is likely that these conditions will persist into the future. The industry has been built around these facts and has made large investments in offshore deposits, shipping facilities, and domestic port locations with appropriate marine rock-handling equipment. There is no import duty on crude gypsum rock, but duties are placed on processed gypsum, although continuing free-trade agreements and laws may change the duties.

Because of its wide spread occurrence and huge potential reserves, and also because its uses are such that it is not basic to survival in a national emergency, gypsum is not considered a strategic mineral. This has permitted natural economic factors to prevail in the development of the mineral worldwide, which overall is a healthy situation that should continue to prevail.

Competition between manufacturers of gypsum building products, and from manufacturers of substitute materials, has resulted in a continuing pressure to improve the quality of gypsum products. In turn, mine operators continually strive to reduce the quantity of impurities (increase the gypsum purity) and to maintain a consistent feedstock purity. Wallboard can be manufactured from gypsum with an average purity of about 70% to 100%. Manufacturing processes, however, are designed for consistent gypsum purity, whether low or high; frequent variations in the purity are intolerable. To date, the set objectives are accomplished by (1) selective mining techniques, (2) crushing and screening to the proper size-fractions to remove impurities and maximize the average feedstock purity, (3) blending during the mining cycle on quarry benches or mine faces, and (4) blending from crusher-feed stockpiles. In some cases, heavy-media beneficiation is used to remove anhydrite or dolomite impurities.

Processing of gypsum is energy intensive; energy requirements represent the largest single cost in the production of gypsum wallboard. Conserving energy meshes well with using synthetic gypsum from power-plant desulfurization processes, because waste heat from the power plant can be used in gypsum processing.

Gypsum mining does not result in some of the environmental issues that are commonly associated with mining, such as acid-mine drainage, contamination of surface water or groundwater heavy metals, or the use of cyanide in heap leaching. Gypsum mines and quarries are regulated by numerous local, state, and federal agencies for compliance with environmental and safety regulations.

Most states require the approval of an operating plan and/or reclamation plan by local, state, and/or federal agencies for mines and quarries. The approval of the reclamation plan requires the posting of financial surety to ensure that the plan will be implemented by the applicant or by a third party if the applicant abandons the mining site. Storm-water runoff management plans are generally required to control the introduction of potential pollutants, such as oil, grease, fuel, and antifreeze, into the surface water or groundwater aquifers. The transportation, storage, and use of explosives is permitted and controlled by the federal B ATF. Undisturbed areas may require baseline studies to determine the presence of threatened or endangered species of flora and fauna, and a plan to mitigate the disturbance of their habitat, if present, during reclamation. Alternatively, acquisition of additional property with suitable habitat conditions might be required. Revegetation of reclaimed areas may be required with periodic monitoring to determine the degree of success in the reestablishment of vegetation. State or federal agencies, such as the U.S. Fish and Wildlife Service, are involved in the evaluation of the biological impacts of mining. The U.S. Army Corps of Engineers and various state departments of natural resources are involved if mining activities potentially affect stream courses or wetlands. Cultural resources are evaluated by archaeologists and reported to state agencies for historical preservation.

Synthetic Gypsum

The usage of synthetic gypsum in the United States increased by 156% between 1998 and 2002: about 3 Mt was used in 1998, and the estimated usage in 2002 was 7.7 Mt. In 2003, synthetic gypsum accounted for 26% of the total domestic supply (USGS 2004). Synthetic gypsum is derived primarily from the FGD of high-sulfur-content coal at power plants. Minor amounts are made as a by-product of chemical processes, such as the production of citric acid, sugar from sugar beets, and titanium dioxide. Phosphogypsum, derived from manufacturing fertilizer, is not used in wallboard manufacturing because radionuclides and radon are present. The majority of the new gypsum wallboard capacity constructed in the United States since the late 1990s is dependent on FGD synthetic-gypsum sources, and new plants are close to the power plants or on navigable waterways.

Recycling

Waste wallboard is generated from (1) manufacturing, (2) new construction, (3) renovation, and (4) demolition. Manufacturing waste can be recycled into the raw-material stream. The wet wallboard waste can be disaggregated into the board core and paper fiber, both of which are used in manufacturing wallboard. New construction and renovation generate 10% to 12% of wallboard scrap. The disposal costs for new construction and renovation wallboard scrap in solid-waste disposal landfills are increasing. Scrap wallboard waste generated during new construction can also be pulverized for application as a soil amendment. Demolition waste, however, is often mixed with other materials such as lumber, nails, and fiberglass insulation, and therefore cannot be recycled effectively.

New Products

The most popular size and type of wallboard will continue to be the paper-clad sheet with dimensions 1.2 m × 2.4 m × 12.7 mm. New types of gypsum wallboard are expected to grow in popularity. For example, fiber gypsum board, a nonpaper face and back board, incorporates a homogeneous blend of gypsum and paper fiber for abuse-resistant wall and floor underlayment applications. Another example is a gypsum wallboard using fiberglass scrim to replace the facing and backing paper, which is gaining acceptance in water-resistant sheathing applications.

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Iodine

Stanley T. Krukowski and Kenneth S. Johnson

INTRODUCTION

Iodine is a heavy, grayish-black crystalline solid with a metallic luster. It has a density of 4.9 g/cm^3 , and is a solid at ordinary temperatures. It is a member of the halogen family, along with fluorine, chlorine, bromine, and astatine. Iodine melts at 114°C , and at 184°C it will volatilize to a blue-violet gas that has an irritating odor. It is only slightly soluble in water, and its solubility increases with temperature. At low temperatures, iodine is made up of diatomic molecules and readily dissociates, or sublimates, at moderately elevated temperatures.

Iodine is the heaviest of the halogens, and generally is less reactive than the others. Iodine, however, does not occur as an element in nature but occurs as iodates, iodides, or other combined forms. It is the 47th most abundant element in the earth's crust. It is a mild oxidizing agent in acidic solutions. Moist iodine vapor rapidly corrodes metals, with the exception of titanium and molybdenum stainless steels.

Bernard Courtois discovered iodine in 1811, after observing an unknown substance in the crude soda ash that resulted from the burning of seaweed. Samples of this unknown substance were identified to be a new element, and in 1813 Gay-Lussac named the substance *iode* in French, from the Greek word *ioeides*, meaning violet-colored.

Most people are aware of iodine as a dietary supplement in iodized table salt to prevent goiter. It is also remembered for its use as an antiseptic and disinfectant (tincture of iodine) found in first-aid kits and most medicine cabinets. The uses of iodine, however, are much more diverse. It is used, for example, in animal feed, photography, catalysts, and other applications.

GEOLOGY AND MINERALOGY

Compounds of iodine are minor constituents in seawater and brines, in certain marine organisms, and in minerals of the Chilean nitrate deposits. Sea water contains approximately 0.05 ppm iodine, and certain marine organisms, such as seaweed, sponges, fish, and some brown algae, are able to further concentrate iodine (Lyday 1999). Some seaweed can extract and accumulate iodine up to 0.45 % of their weight, on a dry basis.

The northern Chilean nitrate deposits in the Atacama Desert contain the following iodine minerals: lautarite, $\text{Ca}(\text{IO}_3)_2$ (calcium iodate); dietzeite, $\text{Ca}_2(\text{IO}_3)_2 \cdot (\text{CrO}_4)$ (calcium iodate-chromate); and bruggenite, $\text{Ca}(\text{IO}_3)_2 \cdot \text{H}_2\text{O}$ (Erickson 1981).

Various subsurface brines also contain iodine compounds. Some gas-field brines in the United States and Japan locally contain 30 to 1,300 ppm iodine. Several coals in Germany also contain iodine compounds.

Iodine has been recovered from brines mainly in Japan and the United States, but also in Java, Indonesia, Italy, England, and the former Soviet Union. Iodine has also been recovered from seaweed in China, Ireland, Scotland, France, Japan, Norway, and the former U.S.S.R. Seaweed was a major source of iodine for the world before 1959 (Lyday 1986), and it remains a large resource (Lyday 2004). For a more detailed discussion on iodine production from seaweed, see Lyday (1986). The reserves and future resources of iodine are large, even excluding the resources in seaweed and sea water (estimated by Lyday [2004] at 34 Mt), and are shown in Table 1.

Desert Evaporites

Originally, iodine was obtained mainly as a by-product during production of sodium nitrate fertilizer from caliche (*salitre*) deposits in the Atacama Desert of northern Chile. Today, however, it is produced as the primary product, or coproduct, of a process that extracts iodine from abandoned (unmined) nitrate ores and from nitrate tailings that remain from earlier nitrate mining (Velasco and

Table 1. Crude iodine: World mine production and reserves, thousand kg

Country	2002	2003*	Reserves
Azerbaijan	300	300	170,000
Chile	11,400	11,650	9,000,000
China	500	500	4,000
Indonesia	75	75	100,000
Japan	6,500	6,500	4,900,000
Russia	300	300	120,000
Turkmenistan	200	300	170,000
United States	1,420	1,750	250,000
Uzbekistan	2	2	na†
World Total‡ (rounded)	20,700	21,400	15,000,000

Source: Lyday 2004.

* Estimated.

† na = not available.

‡ Excludes other countries.

Gurmendi 1988). The nitrate fields are mainly in the Central Valley of Chile, called the Pampa del Tamarugal, which lies between the relatively low Coastal Range on the west and the high Andes Mountains on the east. The nitrate fields are mainly in Tarapaca and Antofagasta provinces.

The iodine-bearing nitrate ores—described by Erickson (1981, 1983), Erickson and others (1989), Garrett (1985), and Lyday (1985, 1999)—are extensive, and occur in a belt several hundred kilometers long and tens of kilometers wide. Caliche ore layers typically are 1 to 3 m thick, flat lying or gently dipping, and near the land surface. They contain evaporite minerals as cement in relatively unconsolidated surface materials, or as veins and impregnations in bedrock. The caliche is typically 5% to 30% sodium nitrate, and it contains iodine as calcium iodate (lauterite and dietzeite) in concentrations averaging 0.04% to 0.06% (Erickson 1983; Lyday 1999). Crushed caliche and tailings are leached to produce a solution containing sodium nitrate and calcium iodate (Lyday 1999). After precipitation of the sodium nitrate, the remaining liquid is then stripped of iodine.

The origin of the nitrate deposits is explained chiefly as a result of the uniquely favorable environment in which they were accumulated and preserved, rather than to any unusual source of saline materials. The essential conditions of this environment include an extremely arid climate (average annual rainfall less than 0.01 cm); slow accumulation of materials starting in late Tertiary (Miocene) through Quaternary times; and a paucity of nitrate-utilizing plants and soil microorganisms. The two chief sources of ordinary saline constituents (borate, sulfate, chloride, sodium, calcium, magnesium, and potassium) are water-soluble saline minerals in the volcanic rocks and volcanic emissions of the Andes Mountains, and particulate salts of evaporated spray from the Pacific Ocean (Erickson 1983; Harben and Kuzvart 1996). The former are leached by rainwater and carried into the desert by streams and groundwater; the latter are wind-transported into the desert.

The origin of the more exotic constituents (nitrate, iodate, perchlorate, and chromate) is less well understood. Nitrates originate from nitrogen compounds from ocean spray, and from photochemical and electrochemical reactions in the atmosphere; most, however, were probably formed by fixation of atmospheric nitrogen by microorganisms in desert playa lakes and associated moist soils (Erickson 1983). Initially, therefore, nitrates were associated with playa lakes, but subsequent to wind deposition, they were leached and redeposited by meteoric waters. The result was abundant, high-quality nitrate ore deposits that had undergone a secondary enrichment of sorts on the lower slopes of nearby hills. Perchlorate may have been formed by photochemical reactions between chlorine and ozone in the atmosphere; chromates may be the result of leaching large volumes of Tertiary and Quaternary volcanic rocks in the Andes (Erickson 1983).

The sources of iodine are most likely iodine-rich organic films on the sea surface, or gases and sublimates associated with Andean volcanism. From the former, iodine evaporates as a gas into the atmosphere or evaporates as a gas from ejected seawater spray. Iodine from the latter, in part, would be transported by surface waters and groundwater into the nitrate region. In both cases, the iodine would later be oxidized to iodate, probably by photochemical reactions in the atmosphere or at ground level on soil surfaces in the nitrate fields (Erickson 1983). Erickson (1983) also suggests the concentration of iodine by microorganisms in the playa lakes associated with the nitrate deposits.

Subsurface Brines

About 45% of the iodine currently consumed in the world comes from brines processed in Japan, the United States, the Common-

wealth of Independent States (CIS), and Indonesia (Lauterbach et al. 2001). In Japan, iodine is produced from brines associated with natural-gas wells. The iodine content of Japanese subterranean brines ranges up to 150–160 ppm. Iodine production in the United States comes from deep-well brines associated with petroleum and natural-gas fields. Iodine content in older iodine-producing rock formations in North America can range up to 1,500 ppm, but typically the iodine content of produced brines is about 300 ppm. Iodine production in the CIS is associated with oil recovery, principally in Turkmenistan, Azerbaijan, and Russia, which account for 97% of the total CIS production (Lauterbach et al. 2001; Lyday 2004). Uzbekistan also produces minor amounts of iodine.

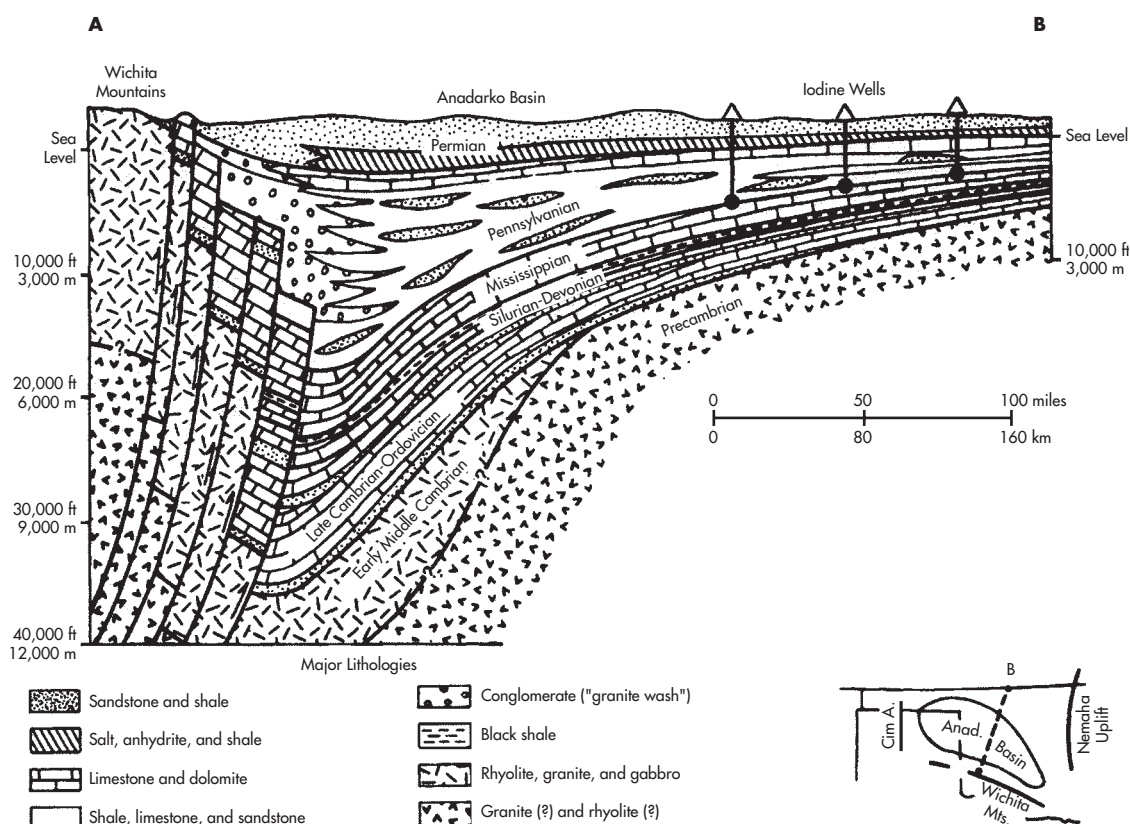
In Indonesia, iodine is present with trace amounts of bromine in oil-field brines in Pliocene sandstones and diatomaceous marls in the Gujangan anticline (Lyday 1985); however, Indonesian iodine typically comes from brines not associated with oil and gas deposits (Lauterbach et al. 2001). The relatively small amount of iodine produced is consumed domestically.

The major iodine-producing area in Japan is the southern Kanto gas field, which extends over Chiba, Tokyo, and Kanagawa prefectures, along the east-central coast of the main Japanese island of Honshu. This area accounts for more than 80% of Japanese iodine production. Almost all the reservoirs of natural gas are found within the sedimentary basin of the marine Kazusa Group (Late Pliocene to Middle Pleistocene). The Kazusa has a maximum thickness of 2,800 m (8,535 ft) and is characterized by “remarkable changes in sedimentary facies and thickness in lateral extent” (Fukuta and Fujii 1982). It is composed of predominant siltstone and sandstone facies, with some conglomeritic and muddy facies of bathyal and/or outer-neritic environments. The major iodine reservoirs occur in the middle Kazusa in the Kiwada, Otadai, and Ume-gase formations, but some iodine brines are also produced from the lower Kazusa. Based on the geochemistry of the iodine-rich brines, Fukuta and Fujii (1982) concluded that the origin of the iodine is closely related to the depositional environments.

About 13% of Japanese iodine production comes from natural-gas fields in Niigata Prefecture, located on the shore of the Sea of Japan toward the north end of Honshu Island, 250 km north of Tokyo. This area accounts for more than 75% of Japan’s production of natural gas. Natural gas is produced from reservoirs of uncompacted sands and gravels, and semiconsolidated sandstone beds, in a sedimentary sequence of terrigenous clastics that were continually deposited from the Late Pliocene to latest Pleistocene. The Pleistocene sediments may be up to 2,000 m thick. The major stratigraphic units in this sequence include (from oldest to youngest) the Pliocene Shiiya Formation, the Pleistocene Nishiyama and Haizume Formations and the Uonuma Group. Environments of deposition range from marine to estuarine or lagoonal. These sediments form a north-plunging trough flanked by structural uplifts. Major gas-producing reservoirs vary in thickness from 10 to 35 m and are composed mostly of fine to medium sands, some containing gravel. Iodine content of the brines has a range up to a maximum of 150 ppm (Fukuta, Nagata, and Fujii 1982).

The Sadowara gas field is located along the eastern coast of southern Kyushu Island. Iodine is contained in brines associated with the production of natural gas from the Sadowara and Tonogori members (Late Pliocene) of the Miyazaki Group. These are predominantly sands, with some silty bands in the Tonogori, and represent an outer-neritic environment of deposition (Fukuta and Fujii 1982).

The Okinawa gas field in southern Okinawa-jima has potential for future production of natural gas and iodine. The lowermost Tomigusuku Formation (Late Miocene to Early Pliocene) in the Shimajiri Group (Late Miocene to Early Pleistocene) is 1,000 m



Adapted from Johnson 1989.

Figure 1. Generalized north-south structural cross-section through the Anadarko Basin of western Oklahoma. Iodine-rich brines are produced from basal Pennsylvanian sandstones on the north flank of the basin.

thick, consists mainly of sandy and silty members, represents a shallow marine bathyal environment, and is known to contain substantial natural gas and iodine (Fukuta and Fujii 1982).

Iodine also has been identified in the Ishikari gas fields on Hokkaido. Total recoverable iodine reserves in Japan were estimated at about 10 billion kg (Harben and Kuzvart 1996); however, subsequent estimates by Lyday (2004) put the Japanese reserves at 4.9 billion t (Table 1).

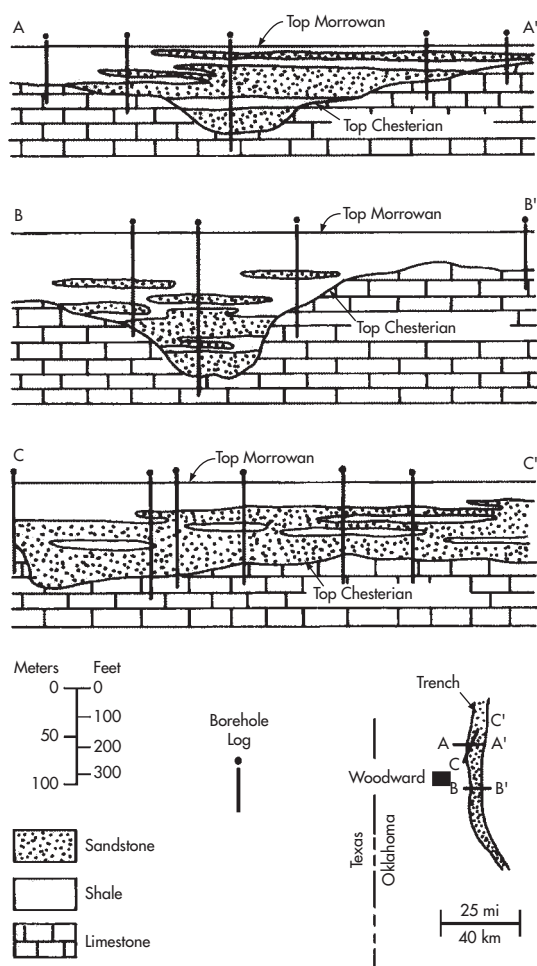
All iodine production in the United States now comes from iodine-rich (300 ppm iodine) natural brines in the deep subsurface of the Anadarko Basin of northwestern Oklahoma (Figure 1). Oklahoma's first iodine operation opened early in 1977. Discovery of iodine-rich brines at Woodward, Oklahoma, resulted from a 12-year program of analyzing brine samples collected by Amoco Production Company (Cotten 1978). Amoco noted unusually high concentrations of iodine in the Woodward area, with concentrations as high as 1,560 ppm in Chesterian (Mississippian) limestones and 700 ppm in Morrowan (basal Pennsylvanian) sandstones. Morrowan sandstones in the area are as much as 100 m thick and are preserved as channel sands in a south-trending paleo valley (the Woodward trench) cut into the Chesterian surface (Figure 2). Although iodine concentrations are higher in the Chesterian strata, the Chesterian limestones have low permeability and do not yield large volumes of water. On the other hand, Morrowan sandstones here have higher permeability and yield large volumes of brine, averaging about 300 ppm iodine.

The Woodward trench has an average width of 1.6 km and a known length of about 115 km (Cotten 1978). Brine-production

wells and injection wells are 2,130 to 2,290 m deep toward the northern end of the Woodward trench. Extraction of iodine-rich brines from Morrowan sandstones in a southern extension of the Woodward trench near Vici, Oklahoma, occurs at depths of 3,000 to 3,183 m. A miniplant near Dover, Oklahoma, serves as an oil-field brine-injection/disposal site, collecting waste oil-field brines from a number of producing oil and gas wells in nearby parts of northwestern Oklahoma. These oil-field brines are processed in the miniplant, where iodine is extracted before the brines are injected into wells at the site for disposal.

PRODUCTION AND TRADE

The major iodine-producing nations, in descending order, are Chile, Japan, the United States, with lesser amounts being produced in China, Azerbaijan, Russia, Turkmenistan, Indonesia, and Uzbekistan (see Figure 3 and Table 1). Annual world production in 2002 and 2003 was, respectively, 20.7 million kg and an estimated 21.4 million kg, of which about 32% is consumed in the United States. In Japan and Chile, the production of iodine depends on production of other materials, such as natural gas or nitrates, respectively, whereas in U.S. operations (in Oklahoma), iodine is the major product recovered from natural brines. Chile has established itself as the principal world producer of iodine from its nitrate-fertilizer operations with the installation of new iodine-processing plants, and Japan has maintained its level of iodine production. Reserve estimates for China have been significantly decreased based on new information from that country (Lyday 2003, 2004).



Adapted from Cotton 1978; Johnson 1989.

Figure 2. Cross-sections showing iodine-bearing Morrowan channel sandstones preserved in the Woodward trench, which has been cut into Chesterian limestones. Datum is top of Morrowan strata (length of A-A' and B-B' is about 10 km each; length of C-C' is about 15 km).

Chile

Chile is the leading producer of iodine in the world. For many years, Japan was the leading producer, but since 1997 it ranks second behind Chile (Lyday 2000). Chile produced 11.4 million kg of iodine in 2002, and in 2003 its production was estimated at about 11.6 million kg (Lyday 2004), or about 55% of the world's production. Originally, iodine was obtained mainly as a by-product during production of sodium nitrate fertilizer from caliche deposits in the Atacama Desert of northern Chile. It has since been produced as the primary product by a process that extracts iodine from abandoned nitrate tailings (Velasco and Guzmendi 1988) and crushed nitrate ore.

The Chilean Trade Commission reported nine iodine-producing companies in Chile in 2003 (ProChile 2003). The six major producers of iodine-operating installations in Chile were SQM Yoda, S.A., a subsidiary of Sociedad Química y Minera de Chile S.A. (SQM, the largest producer of crude iodine in the world); DSM Minera, a subsidiary of Dutch State Mines (DSM) of the Netherlands; Cosayach (Compania de Salitre y Yodo de Chile), a subsidiary of Inversiones Errazuriz S.A.; ACF Minera; a joint venture between DSM Minera

and the Urruticoechea family of Chile; Atacama Minerals Chile, a joint venture between Atacama Minerals Corp. of Canada and ACF Minera; and PCS Yumbes, owned by Potash Corporation of Saskatchewan, Inc. (PCS). The others include Ecolab S.A., Franmar Ltda., and Iodinex Chile Ltda. Chile exports its iodine primarily to Europe and the United States.

Japan

Iodine production in Japan, which began in 1934, comes from iodine-bearing natural brines that are recovered along with natural gas produced in three different regions of the country (Fukuta and Fujii 1982; Fukuta, Nagata, and Fujii 1982; Fukuta 1985; Wu 1985). Production of natural gas entails coproduction of associated brines, and the iodine is then removed from the brine before disposal of the brine. The three iodine-producing regions are the southern Kanto gas field (near Tokyo, in Chiba and Kanagawa prefectures), Niigata and Nakajog gas fields (about 250 km north of Tokyo, in Niigata Prefecture), and the Sadowara gas field (Miyazaki Prefecture in southern Kyushu). Chiba Prefecture accounted for about 90% of Japanese production in 2002 (Lyday 2002). In Japan, 11 plants, operated by eight companies, produced an estimated 6.5 million kg of iodine in 2002, and their combined capacity was 9.22 million kg.

Iodine production capacity in Japan, at the time this chapter was written, was about 7,000 Mtpy. This is based on 13 facilities operated by 8 companies: Ise Chemical Industries Co. Ltd.; Godo Shigen Sangyo Co. Ltd.; Kanto Natural Gas Development Co. Ltd.; Nihon Tennen Gas Co. Ltd.; Nippon Chemicals Co. Ltd.; Teikoku Sekiyu Oil Corp.; Toho Earthtech Inc.; and Japan Energy Development Co. Ltd. The largest producers are Ise, Godo, and Nihon Tennen.

The maximum iodine content of Japanese brines is about 160 ppm. In addition, iodine has been confirmed in the southern Okinawa gas field, on Okinawa, and in the Oshamanbe and Ishikari gas fields on Hokkaido (Fukuta 1985).

Iodine-rich brines in Japan are found in Miocene, Pliocene, and Pleistocene sands and silts. Most of these sediments are of marine origin, deposited in bathyal and/or outer-neritic environments, although those in the Niigata region are sands and gravels of shallow-marine to estuarine or lagoonal origin (Fukuta 1985). The iodine-rich brines of Japan are regarded as being primarily in origin, are derived from sea water, and are limited to the younger marine sediments. The iodine-rich brines are saturated or supersaturated with natural gas (mainly methane); however, some Japanese brines saturated with natural gas may not contain iodine, because methane can be derived from the remains of a variety of life forms (including land species) that contain little or no iodine (Fukuta 1985).

United States

Iodine was first produced in the United States between 1917 and 1921, from seaweed harvested in California; after distillation to produce acetic acid, the residue was processed for potash fertilizers and iodine (Lyday 1986). The first U.S. commercial production of iodine from brines was in Louisiana between 1928 and 1932; some of the Louisiana oil-field brines contained about 35 ppm iodine (Lyday 1986). Oil-field brines in parts of California contain 30 to 70 ppm iodine (Figure 4) in the Monterey Formation (Miocene) and Repetto Formation (Pliocene); these were processed at various times between 1928 and 1966. In Michigan, natural brines containing 15 to 30 ppm iodine are present in the Sylvan Formation (Devonian) at a depth of about 1,300 m. The Michigan brines were processed mainly for bromine, and by-product iodine, by Dow Chemical Company until the wells were plugged and abandoned in 1987.



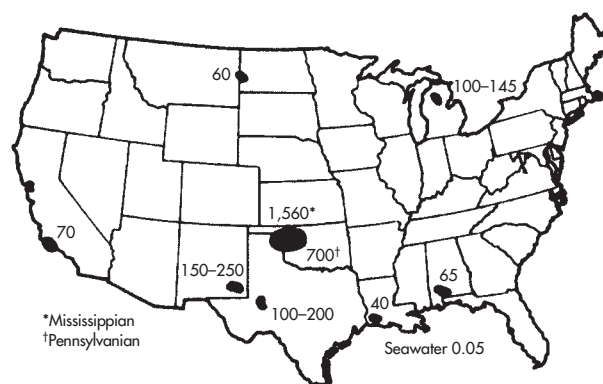
Figure 3. Countries producing iodine and estimated world production in 2003, kg

All iodine production in the United States today comes from iodine-rich (300 ppm iodine) natural brines on the north flank of the Anadarko Basin in northwestern Oklahoma (Figure 1). Oklahoma iodine production began in 1977. At present, three companies operate two major plants and one miniplant for the recovery of iodine. Total production from the three companies in 2002 was 1.42 million kg; production in 2003 was estimated to be 1.75 million kg, with an estimated value of \$19.7 million (Table 1).

Oklahoma's first iodine operation was the Woodward Iodine Corporation. It opened early in 1977 as a joint venture between Amoco Production Company and Houston Chemicals, a subsidiary of Pittsburgh Plate Glass Industries (Cotton 1978); in 1984 Asahi Glass Co. of Japan purchased the company (Lyday 1986), and then sold it to Ise in 1994 (USGS 1998; Johnson and Gerber 1999). Woodward Iodine Corporation operates 12 production wells in the Woodward trench, just north of Woodward, and injects the waste brine back into the trench through four injection wells; three additional wells are operated as disposal wells. Brine-production wells and injection wells are 2,130 to 2,290 m deep at Woodward.

Iochem Corporation of Japan started a second iodine plant near Vici in Oklahoma in late 1987. It also extracts iodine-rich brines in a southern extension of the Woodward trench, operating nine production wells and four injection wells at depths of 3,000 to 3,183 m.

North American Brine Resources (NABR) operates the remaining iodine installation in Oklahoma at a miniplant near Dover, where oil-field brines, collected from many producing oil and gas wells of northwestern Oklahoma, are processed. The company also had a major operation in the Woodward trench about 35 km north of Woodward, which included two production wells and three injection wells, at about 1,800 m deep; this facility began operations in 1989, but it is being dismantled. NABR began in 1989 as a joint venture of Beard Oil Co. (40% share) and two Japanese firms (Godoe USA, Inc., 50% share, and Inorgchem Development, Inc., 10% share) (Ohl and Arndt 1988). In 2003 NABR, as a joint venture between Mitsui & Co. of Japan and the Beard Oil Co., was



Adapted from Cotton 1978.

Figure 4. Areas of known iodine concentrations in the United States. Exceptionally high iodine concentrations, ppm, in northwest Oklahoma are in Mississippian and Pennsylvanian strata.

sold to a group of U.S. private investors and is now operated as a limited liability company (Krukowski 2004).

Other Countries

Other countries producing iodine are shown in Table 1, and they accounted for about 6%–7% of world production in 2002 and 2003 (Lyday 2004). The former U.S.S.R. had produced iodine since 1926 when borax springs at Baku (Azerbaijan) began yielding iodine as a by-product. Later, production came from oil-field brines that contained 67 ppm iodine at Lake Bejuk-Schor, near Baku. Brines in the Slavyansko-Troitsko Area of Russia are reported to contain 80 to 120 ppm iodine in the Neftechinski oil field near the Black Sea. Iodine was also produced from brines at the Nebit-Dag iodine/bromine plant in Turkmenistan (Lyday 1986), which continues to produce iodine.

Following the dissolution of the Soviet Union, the nations constituting the CIS began programs of finance reform and resource development that included privatization and private and foreign investment in their mineral industries. These programs sought investment to maintain and modernize facilities, develop new mines and processing plants, and improve worker safety and pollution controls (Levine 1995). A new iodine deposit was discovered in Astrakhan Oblast, at the Aksarai natural-gas field, and construction of a new iodine plant was planned; private and foreign investment was sought to expand and modernize the Troitsky iodine plant (Infomine Research Group Ltd. 1999). Azerbaijan proposed investment opportunities that would include construction of a plant to treat bromine-iodine waters to produce finished products (Levine 1997a). Similarly, the Ministry of Energetics and Industry in Turkmenistan sought investors for a number of new iodine and bromine production projects (Levine 1996, 1997b, 1999).

China produces iodine from seaweed resources in Shangdong, on the northern coast of Jiangsu, and in a part of Zhejiang; about 300 small companies located along the coast are dedicated to seaweed farming. Iodine is acquired as a by-product during the processing of sodium alginate from seaweed (Lauterbach et al. 2001). China has produced iodine from salt lakes at Chaerham, Yuncheng, and elsewhere, but data on this industry are not available (Lyday 1986). For a more complete discussion on iodine production from seaweed, see Lyday (1986).

The sole producer of crude iodine in Indonesia is P.T. Kimia Farma, a state-owned pharmaceutical firm with facilities near Mojokerto, East Java (Lyday 1988). In 2003, P.T. Kimia Farma added four new production wells to its iodine-production facilities, bringing the total number of iodine wells to 20. The annual production capacity thereby was raised from 150 to 200 t of crude iodine, sodium iodide, and potassium iodide (Laksamana.net 2002).

Italy produced iodine from treated mineral water at Salsomaggiore between 1925 and 1963, and during World War II iodine was extracted from coal dust in Germany and the former Czechoslovakia (Lyday 1986). Small amounts of iodine were produced from mineral waters at a depth of 1,800 m at Rabasomjen, Hungary, and as a by-product of the largest seaweed-drying plant in the world located in Iceland (Lyday 1988).

TECHNOLOGY

Exploration Techniques

Iodine production has historically been a consequence of either oil and natural-gas production or nitrate-fertilizer processing. Commercial extraction of iodine from seaweed was practiced from 1811 to 1959; however, seaweed is no longer an economical option. Cotten (1978) and Johnson and Gerber (1999) describe how Amoco Production Company approached the prospect of producing iodine from brines associated with oil and natural-gas exploration drill holes in the Woodward trench of northwest Oklahoma. Reports on the chemistry of subsurface water samples from these exploratory wells showed that a variety of potentially economic minerals were present. Feasibility studies indicated that iodine was the most favorable mineral for development, based on the fact that its concentrations were relatively high, and that the United States was almost entirely dependent on foreign imports for its supplies.

The scientists at the Amoco Research Center determined that 60,000 barrels per day of 300-ppm iodine-rich brine had to be produced over a 10-year period to be an economically viable project. Additional drill holes on 640-acre centers were drilled into the Morrow Formation (Pennsylvanian) in the trench, and their electric logs were examined to determine the thickness of water-bearing

sands with porosities greater than 10%. These criteria helped determine the concentration (grade) of iodine and the amount (reserves) of resources present. A joint venture by Pittsburgh Plate Glass Industries and Amoco Production Company brought the necessary expertise together to form the Woodward Iodine Corporation. In 1977 Woodward Iodine began producing iodine from the Morrow subterranean brines.

Harben and Kuzvart (1996) note a number of areas with similar geological characteristics to the gas fields of Japan; therefore, they are potential sources for the primary type of dissolved gas and iodine found there. Examples are in the Cagayan Valley, the southern Luzon central valley, and the Iloilo Basin in the Philippines; the Cholan Formation in the western foothills province of Taiwan; parts of East Java, Indonesia; and the southwestern part of New Zealand's North Island.

Iodine geochemical data obtained from surface soil samples are used as an exploration tool in the petroleum industry (Tedesco 1994; Tedesco and Goudge 1994; Tedesco and Andrews 1995; Leaver and Thomasson 2002). Positive anomalies of trace iodine geochemistry have been used as an indirect indicator of hydrocarbon accumulation in the subsurface. Perhaps future study of this phenomenon will lead to new exploration techniques in the search for subterranean iodine-rich brines.

Two sources of nitrate ores have been processed for their iodine in the Atacama Desert of Chile: primary nitrate ores found in caliche deposits, and *repasos*, or nitrate-mine tailings, from earlier mining operations. Exploration of these deposits consists of surface sampling of both types of ores and subsequent shallow drilling of the caliche and tailings deposits. These standard exploration practices determine the grade, the size, and the boundaries of the deposits in order to determine the mineral reserves.

Mining

Iodine produced from underground brines is pumped to the surface using electric submersible pumps and is transported to the processing facility through a system of pipelines. Natural gas is either flared off or extracted from the brines in a gas separator in which the natural gas is physically separated from the brine. The iodine-rich brine is collected in storage tanks before entering the processing plant for iodine extraction. Corrosion-resistant pipe and storage tanks are necessary to contain fluids and vapors during transport and storage; in addition, calcium-scale inhibitors are introduced to prevent calcium carbonate scale buildup from occurring on exposed metallic surfaces (W.W. Hamon, personal communication).

Mining methods in the *repasos* and nitrate ores of Chile consist of open-pit techniques. The *repasos* ore is extracted by front-end loaders or excavators and loaded into trucks for transport to heap leach piles or processing vats. Heap leaching is used where the nitrate concentration of the caliche ore is relatively low; vat leaching is used where nitrate concentrations are relatively high. Caliche-ore deposits may be ripped, or mined by conventional blasting and excavating. Heap leach piles, about 8 m high, are constructed on top of a prepared surface, which is lined with plastic to prevent contamination of the desert soils. An irrigation system pumps water onto the heap leach pads, and the resultant iodine-rich brines are pumped to a processing plant, where iodine is extracted (R.P. Clark, personal communication).

Production Process

Seaweed is no longer an economical method for the extraction of iodine. Iodine is a coproduct of sodium alginate and manitol from seaweed mainly in China. Dried seaweed is leached, obtaining an iodine solution containing concentrations of 0.5 to 0.55 g/L. This

solution is alkalinized to pH 12, then treated with sulfuric acid to produce free iodine (Lauterbach et al. 2001).

The blow-out process is the principal method for extracting iodine (I_2) from brines. Initially the brine undergoes a process consisting of skimming and settling that removes impurities such as oil, clay, and other undesirable materials. Chlorine (Cl_2) is then injected into the brine, where oxidation occurs:



The I_2 remains in solution and is extracted from the brine in a countercurrent air blow-out process in which free iodine is stripped from solution as it is exposed to large volumes of air (Johnson and Gerber 1999; Lauterbach et al. 2001).

The iodine-depleted brine is discarded or injected into wells, returning the brine to the original underground formation; this also serves to maintain fluid pressures in the reservoir and helps prevent subsidence. The iodine-rich air leaves the stripping column and enters an absorption column where the vapor is submitted to a co-current desorption process. A reducing environment is maintained by adding sulfur dioxide (SO_2) and water. The iodine is reduced to iodide:



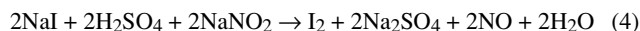
This hydriodic- and sulfuric-acid solution is kept in an interim-storage vessel. When chlorine gas is injected into hydriodic-acid solution, it undergoes oxidation and iodine crystallization:



The oxidized crystallizer liquor is actually a mixture of water, sulfuric acid, hydrochloric acid, and iodine crystals (Johnson and Gerber 1999).

The next step separates the iodine crystals from this liquor via batch filtration, followed by vacuum drying of the filter cake. Wet iodine filter cake is transferred to a fusion kettle. Sulfuric acid, coming into contact with the melted product, helps control humidity and removes impurities. The final step converts the fused iodine into a flaked or prilled product, and then it is packed for shipping (Johnson and Gerber 1999; Lauterbach et al. 2001).

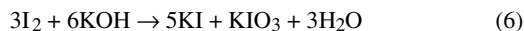
The carbon-absorption process, described in Lyday (1986) and Lauterbach et al. (2001), is used to recover iodine from brines of relatively low concentrations. Skimming and settling first separates impurities from the iodine-rich brines. This method consists of treating the clean brine with H_2SO_4 and sodium nitrite ($NaNO_2$) in large tanks:



The free iodine remains in solution and is recovered after it is adsorbed onto activated charcoal in the settling vats. The effluent acidified brine is neutralized with lime or ammonia. Hot caustic soda is used to extract the iodine from the activated charcoal, resulting in an iodate-iodide solution:



The adsorbed iodine could also be treated with potassium hydroxide (Lyday 1986):

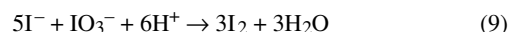
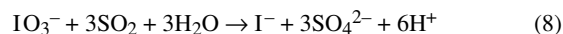
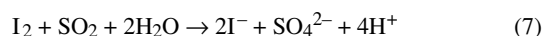


The iodide-iodate solution is acidified with H_2SO_4 and the iodine is then separated by filtration. The resultant iodine filter cake is subsequently sublimed or directly melted and flaked.

The ion-exchange process uses anion-exchange resins packed in columns to free dissolved iodine (I_2) from their oxidized brines.

Acidified brine is treated with chlorine, liberating the iodine, which is absorbed on an ion-exchange resin. Iodine is released from the resin by elution in two steps: the first, with a caustic solution of sodium hydroxide ($NaOH$); the second, followed by a sodium chloride solution ($NaCl$) solution. The resulting elutriant solution, containing sodium iodate ($NaIO_3$) and sodium iodide (NaI), is treated with sulfuric acid in a reactor. The iodine sludge is recovered by filtration or centrifugation, then purified by sublimation or melting under sulfuric acid. The equations for the chemical reactions in the ion-exchange process are illustrated in Lyday (1986).

In Chile, iodine is recovered from brines containing iodates that are leached from nitrate ores. The iodate is reduced to iodide in a reaction tower, where SO_2 serves as the reducing agent. SO_2 is relatively inexpensive and is produced through the combustion of elemental sulfur. Lauterbach and others (2001) listed the chemical reactions involved in the process:



The iodate solution is divided into two streams—most (five sixths) passes through the SO_2 absorption tower of the iodide plant (Equation 8); the remaining one sixth is combined with the iodide solution exiting the absorption tower (Equation 9). Depending on the concentration, the result is an iodine solution or suspension, which is sent to a kerosene-extraction process where iodine is reduced to iodide with SO_2 , then recovered as concentrated iodide solution (Equation 7) (Lauterbach et al. 2001).

The iodide solutions from the iodide plant and the kerosene-extraction process are combined with iodate solution to produce iodine (Equation 9). A resulting heavy pulp contains the iodine crystals, which are introduced into a heat exchanger in which the iodine is melted under pressure. The melt flows into a reactor for settling, and then enters a second reactor for sulfuric-acid drying and refining (Lauterbach et al. 2001).

MARKETING

Uses

Iodine products were first used commercially in the early part of the twentieth century as a remedy for goiter, as a disinfectant for cuts and abrasions, and for sanitation (Lyday 1999). Since then, iodine has been used in a variety of specialty chemicals for many commercial applications. Major uses include x-ray contrast media, iodophors and biocides, catalysts, stabilizers, animal feeds, disinfectants, pharmaceuticals, photography, and colorants. It is difficult to report the end use of iodine accurately since iodine-containing intermediates are marketed before being used in their ultimate form. Table 2 gives U.S. consumption by principal end-use during 2002. The following description of uses is summarized from Lyday (1999, 2002), Lauterbach and others (2001), and Harben (2002).

X-ray Contrast Media

Because iodine absorbs x-rays, it is included in the class of drugs known as radiopaques, which are drugs used to diagnose medical problems by media contrast. Radiopaques containing iodine are introduced into the body in anatomical areas that have insufficient natural contrast. The iodine absorbs the x-rays to a greater extent than do natural soft tissues or blood, thereby casting a light shadow on x-ray film and thus enhancing the contrast. The main x-ray procedures using iodine-contrast media diagnostically are angiography, CT scans, gastrointestinal series, and colicography.

Table 2. U.S. consumption (apparent*) of iodine in 2002

Use	Thousand kg	% of Total
Sanitation	2,934	45
Animal feeds	1,760	27
Pharmaceuticals	652	10
Catalysts	522	8
Stabilizers	326	5
Other†	326	5
Total	6,520	100

Source: Lyday 2002.

* Domestic production plus imports minus exports plus adjustments for government and domestic industry stock changes.

† Includes inks and colorants, photographic chemicals, laboratory reagents, production of batteries, high-purity metals, motor fuels, and lubricants.

As populations of the industrialized nations grow older—particularly in Japan, the United States, and Western Europe—there is a greater need for diagnostic testing to keep patients healthier longer and to reduce hospitalization costs (Lyday 2002). The increase in medical testing of older populations with x-ray contrast media will result in increased consumption of iodine in radiopaque drugs.

Iodophors and Biocides

An iodophor is an iodine complex weakly bound to a carrier molecule, or surfactant, which increases iodine solubility in water, permitting its gradual release and giving a residual effect to the compound (Lauterbach et al. 2001). The germicidal action of iodine results from its capacity to quickly penetrate the cell walls of microorganisms, rupturing their proteins and nucleic acid. For these reasons, iodophors and iodine-based biocides are used for their disinfectant and antiseptic properties in a variety of sanitation and cleansing applications in hospitals, dairies, laboratories, food-processing plants, and restaurants, and in dishwashing detergents, herbicides, swimming pools, and water supplies. In some instances, toxic biocides (for example, pentachlorophenol and tributyltin oxide) have been replaced with iodine-based alternatives in certain preservative applications, including cosmetics, paints, wood preservation, metalworking fluids, leather processing, inks, and starches (Lauterbach et al. 2001).

Catalysts

A major use of iodine is in catalysts. With development of the Monsanto process for producing acetic acid (using an iodide-promoted rhodium complex as catalyst) in the 1960s, about 90% of new acetic-acid capacities use this process. Acetic acid is used as a solvent in the production of terephthalic acid, a major component of polyethylene terephthalate, a plastic used for carbonated and other soft-drink containers. Iodide catalysts also are used in the dehydrogenation of butane and butene to butadiene, and in the preparation of stereoregular polymers.

Stabilizers

Iodine is used as a stabilizer in the manufacture of nylon for tire cord and carpets, and for converting rosins, tall oil, and other wood products to more stable forms.

Animal Feeds

Another major use of iodine is in the form of additives for animal feeds; about 27% of U.S. domestic consumption goes to that end use (Lyday 2002). Cattle and sheep are fed iodized salt and other

iodine compounds to regulate metabolism and to reduce certain livestock ailments such as soft-tissue lumpy jaw and goiter. Iodine supplements are especially important for breeding cows and calves. A deficiency in iodine during pregnancy and lactation increases the risk of weak births or stillbirths in cattle, pigs, and horses.

Photography

Photography is one of the oldest industrial uses of iodine. Almost all photography is based on the light-sensitive character of silver halides, particularly silver iodide and silver bromide. As much as 7% of the silver salt in the emulsions of negatives is iodide, and ammonium iodide is used as a photographic developer. The product supplied to the photographic industry is potassium iodide, which is then converted to silver iodide under proprietary processes. See Harben (2002) for more details on photographic emulsions.

Pharmaceuticals and Human Health

Pharmaceuticals are another major use of iodine (including radiopaque media, discussed previously). Potassium iodide is widely used in cough medicines as an expectorant, and iodine compounds are used in the synthesis of amphetamine, methamphetamine, ethyl amphetamine, antibiotics, corticosteroids, and other drugs.

Potassium iodide is used as a preventive of thyroid cancer. The U.S. Food and Drug Administration recommends it as a safe and effective means of blocking radioiodines from the thyroid in a radiation emergency, such as a nuclear accident. During nuclear accidents, a portion of the radioactivity is released as ¹³¹I, a major radioisotope of nuclear power plants. The Chernobyl nuclear accident released massive amounts of ¹³¹I, and several years later there was a sharp peak in thyroid cancer among children and adolescents in Belarus and Ukraine (Harben 2002).

Iodine is necessary for healthy human life. The thyroid gland requires iodine to produce the hormone thyroxine. Iodine deficiency disorder, or IDD, occurs when people lack iodine in their diets. It is especially serious for pregnant women and young children, where deficiencies may result in retarded fetal development and physical and mental retardation (cretinism being an extreme condition), respectively. The World Health Organization (WHO), United Nations Children's Fund (UNICEF), and the International Council for the Control of Iodine Deficiency Disorder (ICCIDD) have taken great strides in eliminating IDD. The major effort to ensure iodine intake is to add potassium iodide or potassium iodate to table salt and vitamin supplements. IDD may also lead to conditions such as goiter (enlargement of the thyroid gland, manifested in a swelling of the neck), abnormal physical development, and reproductive loss (Lauterbach et al. 2001).

Colorants

Iodine is a coloring agent in some dyes used in foods and materials. Red food coloring has been used in cherries, candies, carbonated soft drinks, powdered drinks, gelatin desserts, icings, and pet foods, whereas red dyes are used in dyeing or printing of cotton, half-silk, jute, and straw products. Other colorant applications include drugs, cosmetics, printer inks, and photographic sensitizers.

Other Uses

Iodine is used as an intermediate in the synthesis of fluorochemicals used in water- and oil-repellent emulsions in textiles and leather, and in fire-extinguishing foams. Iodine is also used in the modification of selenium to make semiconductors; in the manufacture of high-purity metals such as titanium, zirconium, boron, and hafnium; in the production of motor fuels; in additives in rechargeable dry cell batteries; as smog inhibitors; and as cloud seeders to induce rainfall.

Product Grades and Specifications

Iodine and its compounds are generally marketed in the form of crude iodine, resublimed iodine, calcium iodates, calcium iodide, potassium iodide, sodium iodide, and numerous organic compounds.

Commercial-grade crude iodine normally has a minimum purity of 99.5% I_2 ; the main impurities are water, sulfuric acid, iron, and insoluble materials (Lyday 1999). Specifications of the U.S. Pharmacopoeia XVII call for crude iodine to be not less than 99.8% I_2 .

Resublimed iodine is usually 99.9% pure, and American Chemical Society (ACS) specifications call for not more than 0.005% total bromine and 0.020% nonvolatile materials (Anon. 1971).

Prices

Actual prices for iodine are negotiated on long- and short-term contracts between buyers and sellers (Lyday 2002). U.S. prices for iodine (including cost, insurance, and freight charges for imported iodine) have fluctuated since peaking at \$17.46/kg in 1988 (Johnson 1994). Prices decreased because of factors such as economic recession (1989–1992; 2002–2004) and oversupply (for example, when Chile began increasing production in the early 1990s and at the turn of the century). Trends that caused prices to increase were additional demand for x-ray contrast media, potassium-iodide production for U.S. government contracts, and efforts to eliminate the effects of IDD. U.S. producers believed that large inventories of iodine, sold by the National Defense Stockpile since 1989, depress the price of iodine produced domestically; domestic production is competing with about 1 million lb of excess stockpile (Lyday 2002). Figure 5 shows the price trends for 1977 to 2001 (Lyday 2002).

Substitutes

Chlorine and bromine can be substituted for iodine in some chemical applications, but they are less desirable. Antibiotics, boron, chlorine, bromine, and mercurochrome can be used instead of iodine in sanitation and biocide uses. Salt crystals and finely divided carbon can be used for cloud seeding (Harben 2002; Lyday 2004). There are no substitutes for iodine, however, in some cattle feed, catalytic, nutritional, pharmaceutical, and photographic uses (Lyday 2004).

Recycling

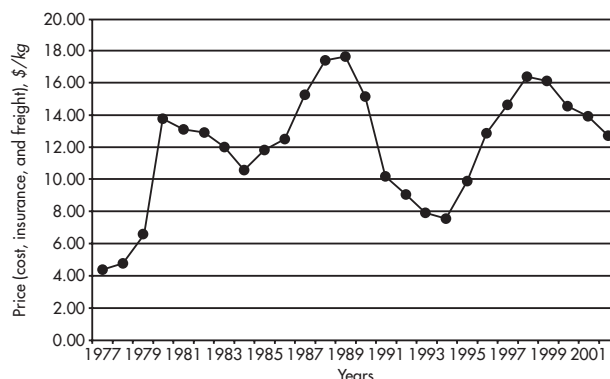
Harben (2002) reported that there is virtually no recycling of iodine; however, Lauterbach and others (2001) reported that several iodine-consuming companies recover iodine from side streams generated in their production processes. Iodine is recovered as a derivative from the incineration of process impurities that have been captured before being discharged into the environment.

U.S. Consumption, Imports, and Exports

Reported U.S. apparent consumption of iodine increased from 6,140,000 kg in 1999 to 6,650,000 kg (estimated) in 2003 (Lyday 2004); however, consumption was down in 2001 (3,650,000 kg) and 2002 (4,780,000 kg). A breakdown of consumption and uses during 2002 is presented in Table 2. In 2003, about 5,800,000 kg (estimated) was imported to the United States and about 1,150,000 kg (estimated) was exported. U.S. imports from 1999 to 2002 were from Chile (66%), Japan (30%), Russia (2%), and other countries (2%).

Packaging and Transportation

Crude iodine is shipped in double polyethylene plastic-lined fiber drums holding 45 to 90 kg each. Resublimed iodine is also shipped



Source: Lyday 2002.

Figure 5. Iodine price trends from 1977 to 2001

Table 3. Tariffs on iodine (2004)

Item	Number	Normal Trade Relations 12/31/03
Iodine, crude	2801.20.00	Free
Iodide, calcium and cuprous	2827.60.10	Free
Iodide, potassium	2827.60.20	2.8% ad valorem
Iodides and iodide oxides, others	2827.60.5000	4.2% ad valorem

Source: Lyday 2004.

in the same type of container, and in 11.3-kg glass jars and smaller bottles. Iodine is also shipped in 350-kg bulk bags and 1,800 -kg tote bags, depending on the mode of transportation.

The mode of transportation depends on the plant location, the infrastructure of the region, and the destination of the product. In Oklahoma, for example, iodine is shipped by rail and truck and can accommodate bulk shipments of fiber drums, bulk bags, and tote bags. For destinations along major waterways and overseas, barges and cargo ships, respectively, are the norms. Freight classification is "chemicals, not otherwise indexed by name" (NOIBN) and requires no special label.

ECONOMIC FACTORS

Depletion Allowances, Tariffs, and Stockpiles

The depletion allowance for iodine from both domestic and foreign production is 14%. Tariffs on iodine are reported in Table 3. Since 1989, the U.S. government Defense National Stockpile Center (DNSC) has sold surplus iodine stocks at about 454 tpy (1 million lb/year). These are released quarterly and sold at the prevailing market price.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Health and Safety

Unlike other halogens, iodine is relatively safe to handle because it is a crystalline solid at normal room temperature and pressure; it has a relatively low vapor pressure (1 kPa at 25°C) compared to other halogens (for example, 700 kPa for chlorine). Personal protective equipment (PPE) is not necessary when handling properly packaged containers; however, chemically approved gloves, clothing, eyewear, and masks or respirators should be worn when solid iodine is not packaged properly (Lauterbach et al. 2001).

An upper limit of 0.1 ppm iodine in air was set by the Occupational Safety and Health Administration because unprotected short-term exposure (up to 1 hr) can be hazardous to lungs and eyes. Severe irritation to the eyes and respiratory tract, which may lead to pulmonary edema, can occur from exposure to concentrations above 0.1 ppm over extended periods of time. Burns may also result if there is prolonged contact with the skin. Chronic absorption of iodine results in iodism, a condition whose symptoms include insomnia, inflammation of the eyes and nasal passages, bronchitis, tremors, diarrhea, and weight loss (Lauterbach et al. 2001).

Land Use and Zoning

Permits for brine wells are similar for oil and natural-gas wells, particularly if there is coproduction of these resources or if injection wells are part of the iodine-extraction operation. Most iodine operations are located in remote areas, so industrial zoning is not a major concern. When iodine-producing brine wells must be abandoned, the boreholes are plugged with concrete to seal producing formations to prevent contamination of water aquifers, other rock units, and the soils where the drill pad was located.

Pollution Control and Other Environmental Considerations

In the production of iodine, special considerations for chemical reagents such as chlorine, sulfur dioxide, ammonia, and sulfuric acid must be taken into account and documented in risk-management plans. This includes emissions from nonpoint sources (fugitive emissions) and single-point-source emissions. Fugitive emissions are those from leaking valves, corroded pipe, and others. Point-source emissions would be equipment (such as natural-gas compressors, boilers, and scrubbers) discharging noxious substances (usually as gases) into the environment.

In the United States, the Environmental Protection Agency requires that risk communication be filed with appropriate governmental entities. The Superfund Amendments and Reauthorization Act of 1986 (SARA Title 3; also known as the Right-to-Know Act of 1986) sets forth guidelines for essential emergency planning for local communities. Potential chemical hazards are identified by the producer, who files various risk communications annually with the local emergency committee, fire departments, departments of environmental quality (in Oklahoma, for example), and others. This notifies the respective agencies of potential problems associated with hazardous materials used at the site or plant.

In the United States, iodine is a federally regulated List II chemical under the Comprehensive Methamphetamine Control Act of 1996, so iodine producers are required to report to the Drug Enforcement Agency and other enforcement authorities all iodine buyers and customers. Iodine is an essential ingredient in the manufacture of methamphetamines, which are commonly produced illegally (sold as "meth" or "speed"). These customs requirements, therefore, call for iodine sellers to record all sales and to report detailed information about their customers. As a result, producers maintain tight control over their inventories and have increased security at warehouses and other storage facilities.

OUTLOOK AND FUTURE TRENDS

The 2000 Nobel Prize in chemistry was awarded for research that showed that oxidizing thin films of polyacetylene with iodine vapors increased their conductivity a billion times. This converted the polyacetylene from insulator to semiconductor. Applications related to electroluminescence will allow developments in ultrathin color screens for video and television. Other developments include advantages where the avoidance of static electricity is important (e.g., synthetic carpets and computer screens, corrosion inhibitors,

lightweight automobile batteries, electromagnetic shielding, and artificial nerves and sensors) (Lauterbach et al. 2001).

The popularity of digital imaging would seem to decrease the use of wet-processing film imagery; however, although digital video of live events, game shows, and other television broadcasts is recorded digitally, 75% to 85% of all televised programs in prime time are recorded on 35-mm motion-picture film. Most feature films also are photographed using 35-mm film. The use of iodine in films and processing may be limited to specialty imaging in the future as the cost of digital-imaging equipment decreases and recording, storing, and imagery reproduction increases in quality (Lyday 2002).

The use of fluoroiodocarbons has been identified as a replacement for halogen-based fire-suppression systems. The Montreal Protocol banned the production of some environmentally unfriendly chlorofluorocarbons, halons, and other ozone-depleting chemicals. This has opened a new area of research for the use of iodine compounds (Lauterbach et al. 2001; Lyday 2002).

The use of potassium iodate and potassium iodide in table salt has increased the use of iodine to alleviate the effects of IDD, especially in India and China. The largest inorganic-chemical complex in Asia is located at Mithapur, Gujarat, India. It produces iodized vacuum salt and is India's largest producer of iodized salt (Hamel 2003).

The use of iodine in individual water-purification systems in developing countries (Chile and Mexico, for example) represents a new application of a historical purification process. This should also consume large amounts of iodine in the future (Harben 2002; Lyday 2002).

Finally, the demand for diagnostic testing of an aging population in the industrial nations (Japan, North America, and Western Europe) is responsible for the increased use of iodine-based x-ray contrast media (Lyday 2002). Also, an additional market is developing in China for diagnostic equipment as the Chinese economy continues to grow. The giant market potential in China for all sorts of materials and goods, including industrial minerals, will have a noticeable effect on the demand for iodine in the future.

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Kyanite, Andalusite, Sillimanite, and Mullite

Palmer C. Sweet, Guy B. Dixon, and John R. Snoddy

Kyanite, andalusite, and sillimanite are naturally occurring anhydrous aluminum silicate minerals. Each has the same chemical formula, Al_2SiO_5 , but differing crystal structures. These variances in crystal structure give somewhat unique physical properties to each of the three minerals, and each is used in slightly different ways by modern industry. Mullite is a very rare mineral named for its discovery site on the Scottish Isle of Mull. Mullite, although seldom found in nature, can be artificially produced by heating any number of aluminum silicate minerals in certain proportions to the correct temperature. Synthetic mullite is classified as an aluminum silicate, and is addressed as such in this chapter.

The world's largest producer of kyanite is Kyanite Mining Corporation (Dillwyn, Virginia) in the United States. This company mines two massive deposits of kyanite quartzite in central Virginia. Internationally, small amounts of kyanite are produced in Australia, Brazil, China, Ukraine, and India—but mainly by divisions of refractory companies that produce only for their own parent corporations, or by small mining companies that sell low-grade material into their own domestic market (Figure 1).

The South African Mineral Resource Committee (SAMREC) and Denain-Anzin Minerais Refractaires Ceramiques (DAMREC), the South African and French divisions of the industrial minerals conglomerate, IMERYS, dominate worldwide andalusite production. Recently, however, a new South African company, Andalusite Resources, has begun major mining and beneficiation operations in the Northern Transvaal. Andalusite (mixed with prophyllite) is also produced by Piedmont Minerals Company, an American company based in Hillsborough, North Carolina, and in small amounts by various producers in India and China (Figure 1).

Sillimanite, which is much less widely used than either andalusite or kyanite, is produced in small amounts in Australia, Brazil, India, Spain, the Republic of South Africa, and the former U.S.S.R. (Figure 1).

Synthetic mullite production is dominated by C-E Minerals (also a division of IMERYS). C-E produces its famous “Mulcoa” products by mixing and calcining the various grades of bauxitic clays that it mines at its site in Andersonville, Georgia. A fused synthetic mullite is also produced by Washington Mills Electro Minerals Corporation in Niagara Falls, New York, and by a host of smaller—mostly Asian—suppliers throughout the world. Kyanite Mining Corporation also produces a synthetic mullite product by simply calcining the kyanite that it mines and beneficiates at its operations in central Virginia.

As of early 2004, annual world production of kyanite, andalusite, sillimanite, and synthetic mullite was approximately 690,000 t (115,000 t of kyanite; 315,000 t of andalusite; 25,000 t of sillimanite; and 235,000 t of synthetic mullite in its various forms). Almost all of this production is consumed by refractory/ceramic companies that use these minerals as raw materials in their heat-resistant products.

GEOLOGY

Mineralogy

Kyanite is a blue to light-green, triclinic mineral that occurs in long, thin-bladed crystals and crystalline aggregates in gneiss, schist, and pegmatites.

Andalusite is a yellow, brown, green, or red orthorhombic mineral that occurs in thick, almost green prisms in schist, gneiss, and hornfels. Gem-quality andalusite exhibits a strong pleochroism—brownish-green in one direction and brownish-red perpendicular to it. Andalusite also occurs in placer concentrations where it has weathered out of rock.

Sillimanite is a brown, pale-green, gray, or white orthorhombic mineral that occurs in long, slender, needlelike crystals in schist and gneiss.

Chemical and Physical Properties

Table 1 presents the chemical and physical properties of kyanite, andalusite, and sillimanite. Both andalusite and sillimanite are orthorhombic, whereas kyanite is triclinic. Andalusite has a hardness of 7.5, sillimanite 6.5, and kyanite between 5 and 7, depending on the direction from which the crystal is compressed. Andalusite has the lowest specific gravity of the three at approximately 3.18; sillimanite has a slightly higher specific gravity of about 3.23, and that of kyanite is significantly higher with an average of 3.6. Kyanite is the only one of the three minerals that irreversibly expands when heated (calcined to produce mullite).

Distribution of Major Deposits

Kyanite

Kyanite Quartzite. Kyanite quartzite occurs in the Piedmont region of the Appalachians and trends from Georgia through South and North Carolina into central Virginia. The kyanite quartzite, which is in the Ordovician Arvonian Formation in Virginia, is enclosed in a sequence of metamorphosed felsic and mafic flows



Figure 1. Kyanite, andalusite, sillimanite, and synthetic mullite production

Table 1. Chemical and physical properties of kyanite, andalusite, and sillimanite

	Kyanite	Andalusite	Sillimanite
Chemical formula	Al_2SiO_5	Al_2SiO_5	Al_2SiO_5
Composition	Al_2O_3 63.2% SiO_2 36.8%	Al_2O_3 63.2% SiO_2 36.8%	Al_2O_3 63.2% SiO_2 36.8%
Type	Aluminum silicate	Aluminum silicate	Aluminum silicate
Crystal system	Triclinic	Orthorhombic	Orthorhombic
Cleavage	(100) perfect (010) good	(110) good (100) poor	(010) good
Specific gravity	3.56–3.66	3.16–3.20	3.23
Hardness	5–7	7.5	6–7
Temperature at which mullite is formed	1,100°C–1,480°C	1,450°C–1,500°C	1,550°C–1,650°C
Volume change during calcination	Sizeable increase	Very slight increase	Slight increase
Density after calcining at 1,445°C	3.05	3.04	3.10

and volcanoclastic rocks on the southeast limb of the Blue Ridge Anticlinorium. The kyanite deposits, currently being mined at Wilis Mountain and East Ridge in Virginia, were originally deposited as basal quartz gravel or coarse sand overlain by silt and clay that was later metamorphosed to form kyanite. Hydrothermal fluids were later introduced (Marr 1992). Kyanite quartzites are rocks containing 15% to 40% kyanite and usually about 5% of other minerals such as pyrite, rutile, and mica. The remainder is quartz.

The kyanite-quartzite deposits in the Georgia–South Carolina–McCormick districts seem to be similarly formed because the mineralogy, and other factors, are virtually the same as in Virginia. The metavolcanics and sediments are known as the Little River Series in Georgia, but they are considered to be in rocks of the Slate Belt in Virginia.

There are at least 13 distinct deposits of kyanite quartzite within the Appalachians. Because of their resistance to weathering, which

results in their prominence above the surrounding countryside, all of them are known as mountains. The operation at Baker Mountain, Virginia, was closed in 1979 and the one at Graves Mountain, Georgia, was closed in 1986. From 1948 through 1969, Commercialores, a subsidiary of Combustion Engineering, worked the Henry Knob deposit in York County, South Carolina.

There is a zone of metavolcanics in southeastern California and extending into southwestern Arizona whose composition and lithology resembles that of the deposits in the Appalachians. This zone contains some deposits of kyanite quartzite. The kyanite in these deposits, however, although averaging 25% to 35% of the rock, has proven to be contaminated with extremely fine inclusions of quartz. As of 2005, it was not economically feasible to produce a competitive kyanite product from these western U. S. kyanite-quartzite deposits.

Kyanite quartzite has been described in several other places in the world, and usually occurs within a geologic framework similar to that of the deposits of the southeastern United States. Such deposits have been described and explored in Surinam, Norway, Kenya, and Austria. A kyanite deposit (Lac Croche property), located 35.4 km south-southeast of Fermont in Quebec, Canada, was reportedly being evaluated. Exploration indicated a zone with 20% to 40% kyanite in large bluish crystals, 1 to 2 cm in size, and gave an early estimate of 3,711,210 t to a depth of 32.8 m (Potter 1988). Other promising Canadian deposits include one located north of North Bay in Ontario, of which Kyanite Mining Corporation owns the mineral rights.

Kyanite Schists and Gneisses. Kyanite is very common in the highly metamorphosed schists and gneisses of the metamorphic regions of the world. Typically, the kyanite occurs in quantities ranging from a percent or two to as much as 25% in a gangue of biotite, feldspar, muscovite, garnet, and occasionally hornblende and other common rock-forming minerals. Rocks containing a few percent of kyanite are extremely abundant and widespread. They are exposed over hundreds of square kilometers in the eastern and western metamorphic areas of North America and in the metamorphic rocks of other continents. Repeated attempts to recover the kyanite from such rocks have been made and were described in earlier editions of *Industrial Minerals and Rocks*. The most recent attempt was in the Timiskaming District in western Quebec by North American Refractories of Cleveland, Ohio. An earlier effort was made in the late 1950s near Burnsville, North Carolina. As of 2005, no schists were being mined for kyanite.

If such kyanite is to be economically viable, it is necessary that the region be deeply weathered and of gentle relief so that a mantle or segregation of resistant kyanite nodules, cobbles, and boulders have accumulated at the surface. It is also necessary for labor to be abundant and inexpensive.

A great deal of literature has been published by the U.S. Bureau of Mines (USBM), the U.S. Geological Survey (USGS), and agencies of other governments describing investigations of kyanite-bearing schists. The USBM conducted an exhaustive study in Idaho on the huge deposits of kyanite, andalusite, and sillimanite at Goat Mountain and the kyanite deposit on Woodrat Mountain near Kamiah, Idaho (Van Noy 1970).

Massive Kyanite. Kyanite is found locally as nodules, knots, and huge boulder-sized segregations in very highly metamorphosed areas of aluminous sediments. This has been the principal source of kyanite from India for the past 40 years. Production was estimated to be 31,339 t in 1988 (Potter 1988), but the deposit has been exhausted over the years, and as of early 2005, the deposit was no longer producing. Similar segregations were the basis for the kyanite production in Kenya.

In several counties in Georgia, similar lumps of massive kyanite are found (Furcron and Teague 1945). Although the abundance and purity of the Georgia massive kyanite lumps meet the requirements for commercial exploitation, high labor costs make economic production by hand sorting and gathering unfeasible. Production was limited to a few carloads during World War II.

Kyanite mineral segregations are probably the result of local pneumatolytic migration of silica and alumina during the late stages of regional metamorphism. Introduction of alumina does not seem to have been a factor, because the overall composition of the segregations is similar to that of the country rock if the sample area considered is large enough to include the barren quartz segregations that in variably accompany the kyanite-corundum segregations. Aside from the size and abundance of the segregations in the Lapsa Bura deposits of India, they do not seem mineralogically dissimilar from kyanite segregations found occasionally in all kyanite schists.

Massive kyanite typically contains corundum and minor amounts of rutile. The kyanite is often felty and acicular and occurs in tightly interlocking aggregates. Kyanite from India is usually produced in lumps large enough to be hand sorted according to kyanite and corundum content, and three grades are offered. Massive Indian kyanite has properties quite unlike those of coarse kyanite crystals; it is essentially volume stable and calcines to a dense white aggregate that is much prized by European refractory manufacturers. On the other hand, the coarse kyanite produced from Georgia placer deposits in the 1940s, and more recently in Kenya, crumbles and loses much of its density and physical strength upon calcining. Apparently the interlocking acicular crystal mode of Indian kyanite prevents such expansion and consequent breakdown. Between 1968 and 1973, a kyanite-sillimanite concentrate was recovered as a by-product from the processing of Pleistocene beach sands in Florida.

Andalusite

Constituent of Metamorphic Rocks. Andalusite is a frequent constituent of metamorphic rocks, although it is not as abundant or common as kyanite or sillimanite. It is found in argillaceous and micaceous slates, in schists and gneisses, and as crystals resulting from the contact metamorphism of intrusive rocks. Andalusite will readily incorporate foreign matter in its crystals, and it frequently grows around preexisting materials, including carbon. One variety, chialolite, is so named for the crosslike inclusions of carbon oriented normal to the axis of the crystal.

In France, near Glomel in Brittany, an extensive, deeply weathered body of andalusite schist is currently being mined by D'AMREC. This company has been active at the site since 1969. The quarry is approximately 966 m² long by 40 m deep. About 618,535 t of material is moved annually, and of that amount, 53,606 t is commercial kerphalite (two grades of andalusite concentrates). Of the two grades of kerphalite, grade KA contains a minimum of 59% alumina, and grade KB contains a minimum of 52% alumina (Anon. 1989). Near Glomel, the andalusite occurs as matchstick-sized crystals embedded in a fine-grained black groundmass composed of biotite, hornblende, muscovite, and feldspar. The andalusite is evenly disseminated and constitutes about 20% of the rock. The rocks in the area are poorly exposed, and the geology of this occurrence is not well understood.

An extensive deposit of andalusite schist is near Canso, Nova Scotia. The andalusite makes up about 15% of the rock and is evenly disseminated as large porphyroblasts averaging about 1.3 to 2.5 cm in cross section. The groundmass is principally muscovite, garnet, and feldspar. The crystals of black andalusite incorporate about 10% finely disseminated magnetite and muscovite, however, and beneficiation is not practical.

Near Hillsborough, North Carolina, a monadnock of andalusite-pyrophyllite-sericite is being mined by the Piedmont Minerals Company, which is now a division of Resco Products. The ore consists principally of pyrophyllite and quartz and contains 15% to 20% of disseminated pink andalusite. The andalusite is mined along with the pyrophyllite, and, being calcined in part by nature, exhibits refractory characteristics usually found only with prepared calcined materials. The product is consumed by Resco Products in the manufacture of kiln car refractories, plastic and castable refractories, firebrick, and ramming and gunning mixes.

In the Goat Mountain deposit in Idaho, andalusite coexists with kyanite and sillimanite. No attempt has been made to separate it from the aluminum silicate minerals in the tests made so far. The andalusite in this deposit typically incorporates a great many deleterious impurities. The Goat Mountain deposit is extremely large, but to date, no commercial exploitation of the deposit seems feasible because of beneficiation difficulties (Abbott and Prater 1954).

In early 1991, exploration work by Ramsgate Resources Ltd. at Spargoville, in Western Australia's Eastern Goldfield, uncovered several occurrences of andalusite-bearing chorite-biotite schist. The andalusite occurs as discrete crystals, from 0.5 to 20 cm in length, in metamorphosed aluminous meta sedimentary rocks. Reportedly the andalusite is of very high quality, equal to if not better than South African material (Anon. 1991).

In the Vihorlat Mountains of East Slovakia, Slovak Republic, secondary quartz with corundum, mullite, and andalusite is found (Hruska 1991).

Residual Andalusite. Alluvial deposits of andalusite sand occur in the Republic of South Africa. The andalusite has been weathered from the parent rock and subsequently concentrated by the action of wind and water; apparently, concentration is still going on. Preliminary figures indicate that at production was 176,901 t in 2004. Concentrate grades averaging almost 60% alumina have been obtained. Total reserves are reported to be 41.65 Mt where the andalusite is found in metamorphosed shales of the Strubenskop Formation near Zeerust, in the weathered shales of the Timeball Hill Formation at Thabazimbi, and in the hornfels and schists of the Eastern Transvaal near Penge; all these units are of the Pretoria Group and have been intruded and metamorphosed by the Bushveld Complex. Until 2003, SAMREC controlled all operational mines, including the region's largest, the Rhino mine in Thabazimbi. Combined with their operations in France, this gave IMERYS a virtual monopoly on the supply of andalusite in the world. In 2003, however, a new competitor entered the market in South Africa. Andalusite Resources, as the new supplier is known, purchased the assets of an existing mine in the Thabazimbi area and restarted production in that region. Initial capacity figures place the Andalusite Resources mine at 27,216 tpy.

Crystals. In 1986, exceptionally large reddish to flesh-colored andalusite crystals were discovered in Campbell County, Virginia. Some of the single crystals measured 25.4 cm long and up to 11.7 cm wide. They were formed through contact metamorphism along both sides of a quartz vein that has intruded a staurolite-rich muscovite schist (Giannini and Penick 1986).

Sillimanite

Sillimanite Schist. Sillimanite is a very common rock-forming mineral in metamorphic rocks of relatively high rank. It is common in a series of metamorphosed rocks to find sillimanite, kyanite, and andalusite interchanging occurrences in given strata as the local conditions of temperature vary, as in proximity to intrusives. For this reason, the aluminum silicate minerals are

often used to identify parameters of metamorphic intensity. Sillimanite, although common, seldom occurs as potentially exploitable crystals. The typical mode is often called fibrolite, which is a felty aggregate of extremely fine whiskers of acicular sillimanite interlaced and interlocked with quartz, mica, and other minerals. Beneficiation is usually impossible. In some areas, the sillimanite occurs as nodules and buttons that have marginal potential, as in the Pelzer Area of South Carolina (Espenshade and Potter 1960).

In Hart County, Georgia, there is a northeasterly trending zone about 16 km long in which matchstick-like sillimanite occurs. Beneficiation tests showed that a limited production of sillimanite in the 35-mesh range could be accomplished. But the deposits are narrow and limited, and no existing market or incentive for production of sillimanite concentrates exists in the United States (Furcron and Teague 1945).

In 1991, the USGS reported that a 30-cm-wide vein of sillimanite in Namaqualand schist "might be economically mined on a small scale." The sillimanite vein is in the Bethanien District of Namibia, Africa (Murray 1991).

Massive Sillimanite. Massive sillimanite has been produced for many years from the state of Assam, India. The Assam deposits consist of huge segregations of sillimanite and corundum, commonly in intimate association and weighing several tons. Considerable hand effort is employed to recover the boulders in a form suitable for sawing to refractory shapes, particularly for the English glass industry. Production of sillimanite in 1988 was 15 kt (Potter 1988), and although exact production figures are vague, massive sillimanite production in this region was assumed to be the same in early 2005.

The most important deposits of massive sillimanite-corundum occur in the Republic of South Africa, in the Pella District near Pofadder, Namaqualand. Production reached a high of 46,184 t in 1963, but was down to 709 t in 1988 (Morgan 1990), and as of 2005, production had ended.

In the vicinity of Adelaide, South Australia, late-stage metasomatism resulted in a mixture of kaolin and included boulders and nodules of sillimanite. The sillimanite is recovered as a by-product in the process of manufacturing refractory clays. Other deposits of residual boulders of massive sillimanite have been exploited in this region. Beneficiation has been tried with some success on the sillimanite itself and on the by-products that are too low in grade to use directly. The Australian domestic market for such concentrates is limited, however, and as of 1988, no large-scale production had been described; reported production in Australia in 1988 was 66 t of sillimanite and 6,598 t of kaolinized sillimanite (Potter 1988). Although exact production estimates are unclear, it was assumed in early 2005 that production had ceased.

TECHNOLOGY

Exploration and Evaluation

Kyanite and its related aluminum silicate minerals have a relatively low value-to-weight ratio. Because they must be delivered to the consuming areas at competitive prices, an important preliminary consideration in any exploration project is the prospective cost of delivering the minerals to the market. Current freight charges range from \$20/t to \$80/t and vary greatly, depending on finite factors such as distance and fluctuating factors such as fuel costs. Kyanite is produced almost exclusively in Virginia and is therefore consumed mainly in the United States—or in the highly developed and industrialized countries of Europe and Japan that can be easily reached by ocean vessels sailing from the mid-Atlantic states. A similar pattern

exists with andalusite, where consumption is concentrated in South Africa and those parts of England, France, and Germany where the producers of refractories are concentrated.

A salable product must also be produced. Consumers become very accustomed to specific raw materials that have historically been used in the manufacture of their refractory products. Any deviation from the commonly accepted specifications imposes a considerable burden on products attempting to enter the market. When evaluating a prospect, one of the most important considerations in this regard is the liberation size of the crystals. This is especially true for kyanite, where the size of the kyanite particles has a direct impact on the expansionary characteristics of the material when fired. There are some attractive kyanite-quartzite deposits in the western United States, but the material cannot be beneficiated to the required specifications without grinding the ore to around 200 mesh, which is quite fine considering that most existing kyanite production is in concentrates in the size range of -28 to +35 mesh.

After initial investigation has indicated that both freight cost and the quality of the product can be competitive, normal techniques of surface sampling, geologic mapping, trenching, and diamond drilling are used to determine the quality of potential reserves. Because the kyanite deposits are produced by regional metamorphism, their composition is fairly consistent, although there may be variation of grade in zones. A pilot-plant production of the material would be the next step to determine if a salable product could be produced economically. It is important to produce, by reproducible pilot-plant techniques, a quantity of concentrates from a representative selection of ores sufficient to permit prospective consumers to test the new material extensively in their plants; there is no laboratory substitute for this kind of testing. Prospective producers of aluminum silicates have found, in many cases, that consumers may not be willing to use material from a new area. Competitive testing and specific approval is the only sure way that the marketability of a given kyanite product can be assumed.

Mining and Processing

Kyanite

In the United States, for most of the last 60 years, kyanite concentrates have been produced by flotation and magnetic separation. The two kyanite-quartzite deposits currently being mined (at Willis Mountain and East Ridge in Virginia) are monadnock features whose resistant ridges are exposed with little or no overburden. The deposits lie on the opposing limbs of the Whispering Creek anticline. Minerals other than quartz and kyanite associated with the deposit include muscovite, pyrite, rutile, topaz, magnetite, feldspar, and apatite. The rare mineral trolleite $[\text{Al}_4(\text{PO}_4)_3(\text{OH})_3]$, a hydrous aluminum phosphate, has also been noted in the kyanite quartzite (Giannini, Penick, and Fordham 1986).

The kyanite quartzite is drilled and blasted; secondary breaking is sometimes done with a hydraulic hammer. The ore is picked up with diesel-powered shovels, loaded in to trucks (up to 54.5-t loads), and hauled to the primary (jaw) crusher. At the primary crusher, the ore is reduced to -4 cm and passed by conveyor belt to the rod mill, which is in a closed circuit with a classifier, to grind the ore to -20 mesh. Water is added that creates a slurry from which the -200 mesh is removed (deslimed). The new slurry is conditioned with several ingredients and passed through a series of flotation cells that remove the pyrite and micaceous contaminants from the slurry. Tailings from the pyrite circuit are again deslimed and conditioned with other reagents and passed through a section of rougher flotation cells. The rougher concentrate goes to a two-stage recleaning circuit; tails of the rougher circuit go to waste.

The flotation concentrate consists of about 91% kyanite and 2% to 5% iron oxides, and the balance is quartz. The concentrates are dewatered by draining in open stockpiles or in drainage silos and are subsequently conveyed to a dryer where the moisture is reduced from almost 8% to near 0%. A reducing roasting technique in a rotary kiln elevates the temperature during the drying process to 482°C, followed by cooling in an oxygen-deficient atmosphere to render the iron oxide highly magnetic; ferric iron (Fe_2O_3) is converted to ferrous iron (Fe_3O_4). The dried concentrates are passed over a series of high-intensity and low-intensity magnetic separators, which reduce the iron content of the product to less than 1%. The result is a raw 35-mesh kyanite product, ready for shipment. Five mesh sizes (35, 48, 100, 200, and 325) are available. A typical analysis of the product is as follows:

Al_2O_3	57%
SiO_2	38%
Fe_2O_3	0.6%
TiO_2	0.8%

The magnetite is stockpiled, with no current market available, and pyrite tails are sold for use in the production of sulfur and as micronutrients in the fertilizer industry. The by-product quartz is marketed for golf courses, sand blasting media, masonry, and concrete sand, as well as for other applications.

Kyanite deposits of India have traditionally been exploited by labor-intensive techniques. In the beginning, it was sufficient to simply gather the cobbles and boulders of kyanite that had been exposed by weathering. Later, primitive mining methods were initiated and the large segregations were drilled, blasted, and hand cobbled in preparation for shipment. Dozens of these small operations employed numerous people. As time passed and the availability of readily hand-picked material decreased, the beneficiation methods became more sophisticated. The picking belt is still an important beneficiation technique, however. High-grade kyanite nodules, and those with segregation too low in grade to be shipped directly, are now crushed and subjected to more sophisticated beneficiation techniques, including flotation and magnetic separation. Currently, there are no large-scale integrated beneficiation plants in India of the kind employed in the United States.

Andalusite

In the Republic of South Africa, andalusite sands in the Marico District of the Transvaal are beneficiated with heavy media separators and high-intensity magnetic separators. A typical analysis of the product follows:

Al_2O_3	52% to 57%
SiO_2	35% to 44%
Fe_2O_3	1% to 4.5%
TiO_2	0.04% to 4%

In France, DAMREC produces andalusite concentrates near Glomel in Brittany. The black andalusite schist contains about 20% coarse euhedral andalusite porphyroblasts. The crystals are about the diameter of matchsticks and range from 1.9 to 2.5 cm in length. The schist is deeply weathered and friable to at least a depth of 9.1 m. The ore is drilled with a wagon drill, blasted, and transported with a rubber-tired front-end loader with a 2.29-m to 2.74-m bucket. It is fed into a surge hopper through a 20.3 × 20.3 cm grizzly and discharged onto a 61-cm conveyor belt by a reciprocating feeder. Oversized material is reduced by hand with a sledgehammer to pass the 20.3-cm grizzly.

The conveyor belt carries the broken ore about 45.7 m to an autogenous mill, which consists of a drum, 4.6 m in diameter, revolving on eight truck tires. This mill reduces the ore to 100% -0.3 cm before it travels to the furnace, which is air-swept with heated air in closed circuit with two air classifiers. The sized ore is fed into a hopper, from which it is passed over a four-roll high-intensity magnetic separator. The nonmagnetic fraction is conveyed to the heavy-media separator, and the magnetic particles are discarded.

The heavy-media separator circuit consists of a hopper in which the andalusite ore is blended with ferrosilicon slurry and then pumped through a hydrocyclone. The specific gravity of the slurry is controlled automatically by a water-metering device ahead of the blending hopper. The first stage of the two-stage heavy-media separator circuit is controlled at a specific gravity of about 2.3. The final effective specific gravity is adjusted by regulating the velocity of the slurry through the cyclone. The second stage is controlled in a similar fashion. The heavy (sink) product from the heavy-media separator is screened at about 35 mesh to recover the ferrosilicon media. The finished andalusite product consists of dark brown to black, roughly equidimensional grains ranging in size from -8 mesh to $+35$ mesh, and contains about 59.2% Al_2O_3 and 1.0% Fe_2O_3 .

In 1988, the Council for Mineral Technology (Mintek) published a review on the development of the andalusite industry in the Republic of South Africa. The publication discussed Mintek's role in early beneficiation methods and techniques developed since 1962; Mintek was also instrumental in introducing heavy medium separation as a standard beneficiation operation. The report also discusses treatment of both hard shales and andalusite fines (Potter 1988).

Sillimanite

Segregations of sillimanite-corundum rock occur in the Pellar District in the northwestern part of Cape Province, South Africa. They have been produced for many years using labor-intensive techniques similar to those employed in India.

Synthetic Mullite

Synthetic mullite results from four main heating processes: (1) melting of alumina and silica or bauxite and kaolin in an electric furnace at $1,914^\circ\text{C}$; (2) sintering alumina and kaolin, bauxite and kaolin, or alumina, kaolin, and kyanite above $1,763^\circ\text{C}$; (3) calcining kyanite at $1,300^\circ\text{C}$; or (4) sintering a siliceous bauxite or mixtures of bauxite and kaolin at about $1,561^\circ\text{C}$. U.S. production of synthetic mullite in 2003 was estimated to be 322,050 t.

C-E Minerals produces three grades of synthetic mullite of varying alumina content by sintering bauxite with kaolin in its two plants. The company mines bauxitic kaolin from pits in Sumter County, near Andersonville, and also from properties near Eufaula, Alabama. Washington Mills Electro Minerals Corporation produces standard and electric grades of synthetic mullite by fusing alumina and glass-grade silica. The company also produces a zirconium mullite that offers better resistance to the thermal shock for ceramic products.

The three grades of synthetic mullite produced by C-E Minerals are Mulcoa 47, which contains 47% alumina produced from the kaolin component of the ore; Mulcoa 60, which contains 60% alumina produced from the bauxitic kaolin; and Mulcoa 70, which contains 70% alumina produced from the bauxite lenses. (Mulcoa 47 is not, for the purposes of this chapter, considered a true mullite because its alumina content is well below the 60% threshold of theoretical mullite.) C-E Minerals' Georgia plants have a total capacity of 452,529 tpy. Five kilns were in operation in 2003.

Kyanite Mining Corporation's mullite plant has the capacity to produce 27,216 tpy of its calcined kyanite; a number that will soon be increased to 36,287 tpy as the company installs more efficient pollution controls. It is estimated that with the addition of a new product line of lightweight aggregates, production could easily reach 40,000 tpy by 2006.

USES

Although the three minerals that comprise the sillimanite group have different properties, they are all used primarily as raw materials in the manufacture of heat-resistant refractory ceramics. As such, the demand for each is driven largely by the health of the steel and foundry industries, and the changes in technology that affect the usage of refractories in those industries.

Today it is estimated that 70% of the kyanite output is used in refractories: 55% for smelting and processing of ferrous metals, 10% for nonferrous metals, and 5% for glassmaking and ceramics. The remaining 30% is used for other industrial ceramic applications such as investment casting, kiln furniture, and railroad friction products, among others.

The main uses of kyanite are in high-temperature (refractory) cements/mortars, ramming mixes, and castables. With clay or other ingredients, the kyanite is used in firebrick, insulating brick (brick for rotary kilns and furnaces), and in abrasive and other kiln furniture. The expansion characteristics of kyanite are valuable because they offset shrinkage of other ingredients and produce a stable refractory body. When calcined, kyanite increases in volume by 16% to 18%, compared to only about 4% and 6% for sillimanite and andalusite, respectively. Thus, when fired in a refractory mortar containing shrinkable components such as clays, kyanite will expand to form a tight lock in a furnace or kiln. Finely ground kyanite, in the 200-mesh range, is used in body mixes for sanitary porcelains, wall tile, casting molds, and special purpose ceramics where the expansion characteristics of kyanite are advantageous.

An even greater proportion of andalusite is consumed by the refractories industry—possibly up to 80%. Andalusite, which can be sold in much larger sized particles than kyanite because of the beneficiation processes involved and the mineral's lack of expansionary characteristics, is mainly used by refractory companies as the aggregate component in bricks and other precast shaped products. It has very good creep-resistant and load-bearing properties.

The largest market for sillimanite minerals is in the manufacture of refractory products, mainly for the iron and steel and nonferrous metal smelting industry.

All the sillimanite minerals convert to mullite (about 88%) and silica (about 12%) when heated to temperatures ranging from $1,250^\circ\text{C}$ to $1,500^\circ\text{C}$. Each of the minerals converts to mullite at a different temperature, with kyanite needing the least heat and sillimanite the most. Mullite is extremely refractory, has a small coefficient of thermal expansion, and is resistant to abrasion and slag. Because mullite is the mineral component that is sought after by refractory engineers, the sillimanite minerals could theoretically be regarded as mullite ore.

The addition of mullite to refractory and porcelain bodies will increase the fired strength as a result of the interlocking of mullite's long, needlelike crystals. Mullite's addition will also increase resistance to deformation under load, increase dielectric properties at both normal and high temperatures, and increase thermal resistivity. Mullite also decreases the coefficient of expansion, promotes a uniform rate of such thermal expansion, and reduces refractory and porcelain bodies' tendency to spall. The mullite produced in Virginia by Kyanite Mining Corporation and the synthetic mullites

produced from kaolin in Georgia are used for traditional refractory applications such as bricks, monolithics, and castables, as well as in the investment casting industry for stuccos and slurry coats. Ceramic uses of mullite include kiln furniture, hot-zone and car-top decks of tunnel kilns, and rollers for roller kilns. Mullite porcelains are used in spark plugs and laboratory-ware applications.

ECONOMIC FACTORS

Prices

Kyanite, free on board (f.o.b.) the plant in Virginia, is \$149 to \$196/t, and calcined kyanite (mullite) is \$248 to \$295/t on the same basis. The price of andalusite, f.o.b. Transvaal, South Africa, ranges up to \$286/t. Synthetic mullite is \$220 to \$1,320/t, depending on grade and type.

Reserves

Cooper (1965) noted that reserves of kyanite-bearing quartzose rock containing 10% to 30% kyanite in the United States were reported at about 82.5 Mt. Since that time, the only appreciable deductions from the 1965 estimate have been Kyanite Mining Corporation's extractions at the Willis Mountain and East Ridge mine sites in Virginia. In 1949, a USBM drilling program on Willis Mountain (Virginia) indicated that 53.6 Mt of 2.5% kyanite were exploitable by open-pit mining (Jones and Eiletsen 1954), and potential reserves were much larger. Over the course of the last half century, Kyanite Mining Corporation's activities at the Willis Mountain site have reduced reserves to roughly 47.6 Mt. Reserves of the East Ridge deposit, 8 km distant, are not included in this figure. Other deposits in Virginia include Woods Mountain in Buckingham County, as well as properties to the south in Prince Edward County. At an annual mining rate of 329,885 to 412,357 t of ore, the deposits of kyanite in Virginia are adequate for many years. At Graves Mountain, Georgia, where the deposit is no longer mined, previous geologic mapping and diamond drilling indicated a reserve of 24.7 Mt of 25% ore. In the Van Noy (1970) study of Goat Mountain and Woodrat Mountain, near Kamiah, Idaho, hundreds of millions of metric tons of 25% aluminum silicate ore were available for open-cut mining. Remoteness from major markets and the difficulty of beneficiation, however, have stalled development. If the schists and gneisses, which contain approximately 10% kyanite, are noted as resources in North America, the resource potential is probably very large and indeed may not even be recognized or discovered yet (Potter 1985).

According to the Minerals Bureau of South Africa, reserves of andalusite and sillimanite are 94.9 Mt. Kyanite reserves in Brazil are given at about 2.4 Mt. Andalusite occurs in France where reserves of andalusite content amount to about 2.4 Mt. Sillimanite deposits are located in Australia, India, and Russia (Potter 1985).

GOVERNMENT CONSIDERATION

Depletion allowance rates of 22% for domestic production of kyanite were unchanged through 2004.

From August 23, 1951, through March 4, 1970, the eligibility for stockpiling of lots of kyanite ore and concentrates, or of fused synthetic mullite, was determined according to criteria in the National Stockpile Purchase Specification P-27-R (February 29, 1960, superseding issue of August 23, 1951). The statement listed as chemically acceptable three types of kyanite if they contained not less than 59% alumina; not more than 39% silica; and not more than specified proportions of iron, titanium, lime, magnesia, alkalis, and total fluxes. Chemical requirements for fused synthetic mullite called for alumina within a range of 75% to 80%, silica 20% to 25%, and total impurities not exceeding 1%. Additionally,

both kyanite and mullite for stockpiling were required to conform to a catalog of specific physical properties and pyrometric cone equivalent ratings. Currently, sales of kyanite-group minerals are based on bargaining of the consumer and the seller. Chemical analyses, physical characteristics, and required service testing are usually not available. The stockpile of lump kyanite in September 1990 was 90.7 t; 783.4 t of nonstrategic-grade material were also retained in government stockpiles. As of early 2005, the government had sold its stockpile of lump kyanite.

FUTURE TRENDS

The overall use of sillimanite group minerals has increased slowly but steadily throughout the world over the last few decades—although there was a marked downturn in consumption of these minerals during the first few years of the new century. This downturn was primarily caused by overcapacity problems in the worldwide steel industry, especially in the United States and Europe. These problems seem to have dissipated as of late 2003 and early 2004, resulting from bankruptcies, plant closings, and mergers and acquisitions in the United States and Europe combined with a surge of economic growth in China and other Asian economies that stoked global demand for steel just when supply was being cut. This Asian-led economic growth has also driven up the price for almost all raw materials—many of which are partially or wholly competitive with one or more of the sillimanite minerals. For example, the quickly rising price of zircon and alumina has led to an increased use of mullite as a direct substitute in many refractory and investment casting applications.

There are, however, countervailing trends that could suppress demand—especially for andalusite. As steel companies continue to become more efficient and cost conscious, they are making strides to consume fewer pounds of refractory per ton of steel that they produce. In addition, more and more of the world's steel—especially in Europe and the United States—is being produced in electric arc furnaces from scrap metal. This kind of steelmaking process relies more heavily on refractory monolithic instead of refractory bricks. Because a large proportion of an alusite is used in making refractory bricks, the future growth prospects for that particular sillimanite mineral are difficult to discern.

Overall, however, demand for sillimanite minerals is likely to continue to grow slowly—but possibly not as steadily as it has in the past. A forecast for demand of kyanite, andalusite, sillimanite, and synthetic mullite in 2010 may be in the range of 700,000 to 770,000 t.

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Lime

Stanley T. Krukowski

INTRODUCTION

Lime, or calcium oxide (CaO), is known as one of the most versatile chemicals, and its manufacture and use is fundamental to society. Throughout history, civilization worldwide has relied on the use of lime. Because of the universal and fundamental nature of the global lime industry, this chapter focuses on lime production and use in the United States as representative.

A manufactured chemical product resulting from the calcination of limestone in its various forms, lime's major mineral component—calcium carbonate (CaCO₃)—is dissociated by the application of thermal energy, producing CaO and CO₂. When water is added, it is commonly known as *hydrated lime*, or *slaked lime* (Ca(OH)₂). Almost 40 different lime products are available, a fact that contributes to confusion and misunderstanding over the use of the term *lime*. Frequently, the word is used erroneously to denote almost any kind of calcareous material, including finely ground limestone and/or dolomite.

Lime is made from high calcium, or magnesium (or dolomitic) limestone and dolomite that has a minimum of 97% total carbonate composition. Normally, high calcium lime (quicklime) contains less than 5% MgO; the balance is CaO. When lime is produced from high-magnesium limestone (dolomite, CaMg(CO₃)₂), the product is referred to as dolomitic lime (dolomitic quicklime, or refractory dead-burned dolomite, CaO•MgO) and contains more than 35% MgO; the remaining balance is CaO. Magnesium lime, produced from magnesium limestone (also referred to as dolomitic limestone), contains between 5% and 35% MgO. Other typical lime products include high-calcium hydrated lime (calcium hydroxide, Ca(OH)₂), dolomitic hydrate Type N (Ca(OH)₂•MgO), and dolomitic hydrate Type S (Ca(OH)₂•Mg(OH)₂).

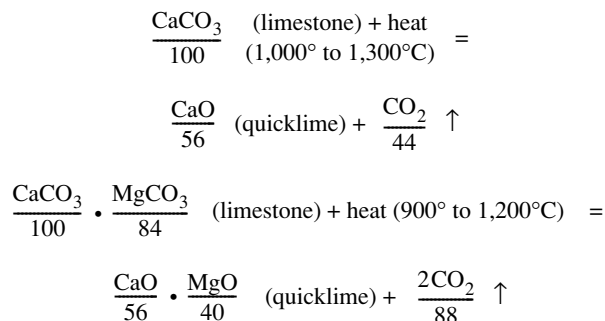
Calcination/Hydration

The major process in the production of lime, calcination refers to a broad class of reactions in which a substance is heated so that a chemical or physical change takes place. In the case of the limestone/lime reaction, limestone is heated to less than its melting point, resulting in the dissociation of calcium carbonate into calcium oxide and carbon dioxide.

The manufacture of lime probably was known in prehistoric times and certainly was well known in the ancient world. Any basic understanding of calcination most likely had its origins in the earliest days of alchemy; the general reaction class was identified in an

Arabic text printed in 1000 AD. It was not until the mid-1700s to the mid-1800s, however, that this basic reaction became understood from a scientific perspective. The production of lime is so basic and simple that its underlying scientific principles received only intermittent investigation over the years. Instead, most thinking on the subject was directed toward the development of kilns. Only in the last 40 years or so, as a consequence of kiln studies (particularly those focusing on energy consumption and fuel efficiency), has lime received any concentrated scientific investigation relative to thermodynamics and kinetics of calcination and hydration reactions.

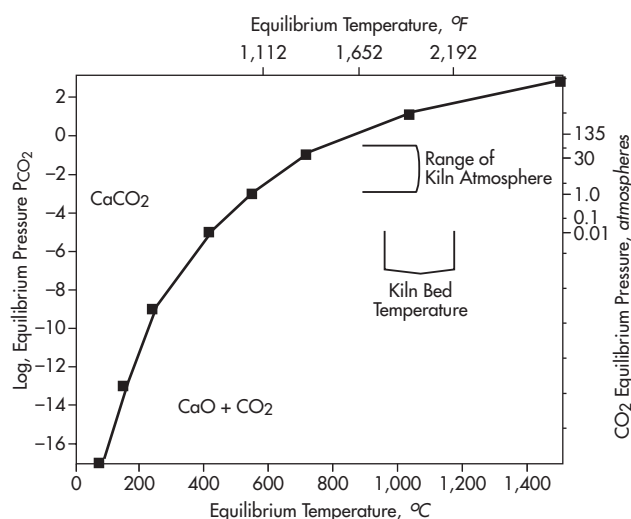
In the calcination of limestone, the basic chemical reaction is as follows:



There is nearly universal agreement about equilibrium conditions related to this limestone/lime reaction, and many different calcination models were developed for the reaction. The model in Figure 1 shows that calcination is a function of both temperature and CO₂ pressure. It provides no indication of the rate at which the reaction takes place.

Because calcination reaction starts on the exterior surface of limestone particles, then proceeds toward the center, calcination is strongly time variant with different limestones. As calcination progresses, CO₂ is released at the limestone/lime (CaCO₃/CaO) interface and must pass through the lime to exit at its exterior surface. Because calcination is limited by diffusion of CO₂ gas to the surface of partially calcined limestone, the following factors all play a significant role in rate of calcination:

- Natural impurities in the stone
- Differences in crystallinity
- Grain boundary chemistry



NOTE: Conditions below the curve cause the reaction to go toward lime (CaO), while above the curve the reaction proceeds toward calcite. Only on the curve is the equilibrium maintained and the reaction does not proceed in either direction. Most lime kilns have production bed temperatures of 1,000°C to 1,150°C.

Source: Thompson 1978.

Figure 1. Equilibrium graph for $\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$ as a function of temperature and CO_2 pressure in atmospheres.

Table 1. Typical analysis of commercial quicklimes

Component	High-Calcium Quicklimes Range, %	Dolomitic Quicklimes Range, %
CaO	93.25–98.00	55.5–57.50
MgO	0.30–2.50	37.60–40.80
SiO ₂	0.20–1.50	0.10–1.50
Fe ₂ O ₃	0.10–0.40	0.05–0.40
Al ₂ O ₃	0.10–0.40	0.05–0.40
H ₂ O	0.10–0.90	0.10–0.90
CO ₂	0.40–1.50	0.40–1.50

Source: National Lime Association 1992.

* The values given in this range do not necessarily represent minima and maxima percentages.

- Density variations
- Imperfections in the crystal lattice

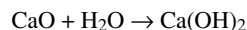
Therefore, only after completing adequate burn tests designed to evaluate a given limestone is it determined suitable. In coal-fired kilns, the process of calcination is even more complex when additional chemical substances are introduced into the calcination environment. The reader is referred to Boynton (1980), Oates (1998), and Beach et al. (2000) for more detailed descriptions of the complete calcination reaction and the inherent differences among kiln systems.

CO₂ is released during calcination of high calcium limestone, resulting in a 44% weight loss when the reaction is complete, or a 48% weight loss for a highly dolomitic limestone. The trade term for this weight percent reduction is *loss on ignition* (LOI) and is frequently used to measure the completeness of calcination.

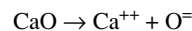
Because the calcination reaction is chemically reversible, *quicklime* or *burnt lime* is frequently referred to as being highly reactive, or unstable. The more stable form of lime, *hydrated lime*, is commonly preferred and specified by the consumer. Hydrated

lime is obtained by adding water to quicklime to produce a dry, fine powder. The affinity of quicklime for moisture is then satisfied, but it still retains a strong affinity for CO₂.

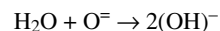
Hydration is the combining of calcium oxide with water in a reversible reaction to form calcium hydroxide:



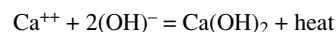
The reaction is exothermic; the accepted value for the heat of hydration is 15.456 kcal/g mol of CaO. This is actually a three-step reaction; the first is the dissociation of CaO into a Ca⁺⁺ ion and O⁼ ion:



Secondly, the water ionizes into two hydroxyl ions because of the strong attraction that the oxygen anion exerts on the water molecule:



Finally, calcium and hydroxyl ions combine to form calcium hydroxide:



Because this reaction is reversible, the hydrated lime may revert to the original oxide form when heated.

Chemical Properties

The success of calcination is measured by the available CaO content of the lime. In the case of dolomitic lime, this is expressed as total oxides. *Total lime* refers to the amount of calcium present in lime. *Available lime* is a measure of the amount of CaO in lime; that is, the amount available to combine with water to form calcium hydroxide. It is, in effect, a measure of the purity of the lime. Available lime is typically 3% to 5% less than total lime, because some calcium is uncalcined and remains as limestone core or has combined with other impurities in the kiln to form various oxides. Typical chemical analyses of commercial quicklimes are presented in Table 1. The purity of the limestone feed is the major factor influencing the purity of lime, followed by its manufacture. The major impurities are silica, iron, alumina, and sulfur. During calcination these impurities react with some of the calcium oxide, reducing the available lime by forming a variety of minerals such as silicates, aluminates, and ferrites. Consequently, even the purest high-calcium limes assay less than 95% in available lime, usually several percentage points less than total oxide content.

Reactivity of quicklime is the measure of the rate at which CaO will react with water, or the rate of release of the heat of hydration. The heat of hydration, or slaking, is the amount of heat liberated when quicklime reacts with water (1,140 kJ/kg of CaO). Impurities and uncalcined limestone core affect hydration by decreasing the amount of total lime. As an example, sulfur in the form of calcium sulfate inhibits hydration out of all proportion to its actual weight percent concentration, perhaps more than 100 times (Boynton 1980). If dolomite is present in the stone feed, it also can inhibit hydration, resulting in a slower reaction—nearly three orders of magnitude slower than that of calcium oxide. Early in the hydration reaction, dolomite appears practically inert but, given sufficient time, it will hydrate. The heat of reaction is nearly the same as for calcium oxide, but the time necessary for complete hydration to occur may be hours. Complete hydration of calcium oxide occurs in seconds. Only 2% to 5% magnesium oxide present in quicklime may render it unsuitable for many applications; however, when quicklime is used in steel-making, MgO is not considered an impurity.

Quicklime has a high affinity for water. After partial hydration, it also has a high affinity for carbon dioxide. The affinity for water causes quicklime to air slake, which may reduce its reactivity significantly. A reduction in reactivity also occurs when slightly

hydrated lime combines with low levels of carbon dioxide to form calcium carbonate.

Fuel such as coal also may contribute to the total amount of impurities in the lime product. Silica, alumina, iron, and sulfur are the main contaminants in this case also, but the finer fraction of run-of-kiln tends to have a higher content of these impurities. Trace elements such as lead, arsenic, molybdenum, and chromium, to name a few, may be considered toxic, making quicklime unsuitable for some applications (e.g., treatment of drinking water).

On slaking into a slurry, or milk-of-lime, the saturated solution ionizes immediately into Ca^{++} , Mg^{++} , and OH^- ions, creating one of the strongest bases. Even a trace of lime will yield a pH of 11.2 and up to nearly pH 13 at saturated solution and low temperature.

Unlike other strong bases such as NaOH and KOH, $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ are diacid bases. Therefore, one molecule of lime will neutralize two molecules of acid (sulfuric, hydrochloric, etc.). For example, at equal weights, CaO has 30% more neutralizing power than caustic soda (sodium hydroxide). Dolomitic quicklime has 16% greater neutralizing power than pure CaO because of its MgO content.

Major impurities in hydrated lime include calcium carbonate, calcium oxide, and magnesium oxide. Silica, alumina, iron oxide, and calcium sulfate (CaSO_4) are minor impurities that can influence the intended use of hydrated lime. High levels of toxic trace elements (such as lead, antimony, arsenic, cadmium, and chromium, to mention a few) can prevent the use of hydrated lime in specific applications (e.g., potable water treatment, foodstuffs, and pharmaceuticals).

The reader is referred to works by Boynton (1980) and Oates (1998) for excellent discussions on the chemical properties of quicklime and hydrated quicklime.

Physical Properties

Important physical properties of lime are listed in Table 2. Lime is typically white with varying intensities of brightness, although, depending on the presence of particular impurities, it may have a light cream, buff, or gray cast. Lime has either no odor or a slightly earthy odor. Although its texture is earthy, appearing amorphous, lime is actually microcrystalline. Both calcium oxide and magnesium oxide have cubic crystal structures.

Porosity of commercial quicklime is dependent, in part, on the original porosity of the limestone and on the decomposition process in the kiln. The severity of calcination (time and temperature) affects both the porosity and chemical reactivity of lime. When lime is *soft-burned* (lightly sintered and calcined at relatively low temperatures, 900° to 1,200°C), very little or no shrinkage occurs, and a porous, softer, very reactive lime is produced. Lightly burned lime can have porosities up to 55% by volume.

When lime is *hard-burned* (sintered at relatively high temperatures, 1,300° to 1,600°C and overburned), a denser (porosities typically below 25%), physically stronger, less reactive lime is the result. In either case, the lime will readily hydrate in water, although the rapidity of hydration is much greater with soft-burned lime than with hard-burned lime. Boynton (1980) and Oates (1998) present excellent discussions of the physical properties of both soft- and hard-burned lime.

In either case, the heat of hydration is appreciable: 1,134 kJ/kg and 886 kJ/kg of quicklime for high calcium and dolomitic types, respectively. This strong exothermic reaction will boil water easily and, under certain hydration conditions, temperatures of 290° to 315°C have been reached, causing dehydration of the freshly slaked lime. Quicklime can be so reactive that it will explode on contact with water. Associated with the reaction of quicklime with water is a corresponding increase of 2.5 times its original volume.

Table 2. Properties of typical commercial lime products

Quicklimes		
	High Calcium	Dolomitic
Primary constituents	CaO	CaO and MgO
Specific gravity	3.2–3.4	3.2–3.4
Bulk density (pebble lime), g/cm ³	0.88–0.95	0.88–0.96
Specific heat at 38°C, kJ/kg	0.4	0.94
Angle of repose*	55°	55°
Hydrates		
	High Calcium	Dolomitic
Primary constituents	$\text{Ca}(\text{OH})_2$	$\text{Ca}(\text{OH})_2$ + MgO
Specific gravity	2.3–2.4	2.7–2.9
Bulk density, g/cm ³	0.4–0.56†	0.4–0.56
Specific heat at 38°C, kJ/kg	0.62	0.62
Angle of repose*	70°	70°

Adapted from National Lime Association 1999.

* The angle of repose for both types of lime (hydrate in particular) varies considerably with mesh, moisture content, degree of aeration, and physical characteristics of the lime (e.g., for quicklime it generally varies from 10° to 13°C and for hydrated lime it may range as much as 2° to 26°C).

† In some instances, these values may be extended. The Scott method is used for determining the density values. In calculating bin volumes, the lower figure should be used.

Although limestone is almost totally insoluble, lime is slightly soluble in water in the range of 0.54 to 1.4 mg/L, depending on the temperature. As water temperature rises, the solubility of lime diminishes. The addition of sugar will increase these solubility values by many times.

The reader is referred to works by Boynton (1980) and Oates (1998) for excellent discussions on the physical properties of quicklime and hydrated quicklime.

HISTORY

Lime is one of the oldest chemicals known to humans. It was probably discovered in prehistoric times when limestone, which was used in the construction of fireplaces and hearths, broke down into its molecular constituents. Air slaking or hydration by rainwater produced a simple type of putty that prehistoric humans put to use principally as a binding agent.

Evidence from eastern Turkey revealed that lime mortar was used in terrazzo floors at an archaeological site dated from 7,000 to 14,000 years before the present (BP). Firm evidence exists for the early use of lime from 8,000 years BP in the Near East, as well as in the Balkans where lime mortar was used in the construction of a floor; the mortar was a combination of lime, sand, clay, and water. The ancient Egyptians used lime for plaster in the construction of the pyramids, while the Chinese added lime to mortar for the Great Wall; 5,000 years ago in Tibet, lime served to stabilize soil. Other ancient civilizations that used lime for various applications include the Greeks, Romans, Incans, Mexicans, and Mogul Indians. Several ancient texts mention the production and use of lime (e.g., the Bible, and the writings of Cato the Elder and Pliny the Elder).

A lime kiln was excavated in Mesopotamia and dated at about 2450 BC. Many ancient lime kilns are known from Roman archaeological sites, including army legion encampments throughout Europe. The Romans were probably the most innovative in the production and use of lime. They developed the technology of lime burning and experimented with an d further

developed the use of hydraulic lime, pozzolanic lime cements, lime mortars, and concrete. The formula for hydraulic lime cement was lost in time but rediscovered in 1756 when John Smeaton, a British engineer, patented it.

Lime was employed in the ancient world in a variety of processes including bleaching fabric, tanning hides, agricultural soil amending, glassmaking, painting (whitewashing), and in making putties and glues when combined with certain organic or inorganic substances. Aboriginal people as well as ancient Roman physicians used lime in different medical treatments. Well into the 20th century, lime was used most extensively in the building trades as the major constituent in mortars, plasters, and cements.

Little is known about lime chemical processes and technology during the Middle Ages, although alchemists began to wonder about and to study the phenomenon of calcination. An Arabic text printed in 1000 AD identified and addressed the general type of reaction responsible for calcination. Lime was widely produced and used during medieval times, however, and that knowledge is reflected in the writings of the day.

From 1750 to 1752, Joseph Black, M.D., studied and first described the calcination reaction of "magnesia alba," which consequently led to the discovery of carbon dioxide. In 1766, De Ramecourt published a treatise on the art of the lime burner, which detailed the design, operation, and economics of limestone quarrying and lime burning. Many treatises and books were written throughout the 19th century and into the early 20th century on the subject of lime production by, for example, Searle (1935), Vicat (1995), and Cowper (1998).

Up to the 20th century, lime kiln design was relatively simple. The easiest method of production was to dig a shallow pit, fill it with firewood and limestone, and set it ablaze. Lime produced in this manner most often was used locally for construction and agricultural purposes. Since ancient times, kilns were either a beehive oven design or a simple vertical shaft kiln. The former also was used for charcoal and coke production, while the latter produced lime in relative abundance, mostly for the building trades. Limestone was quarried from a local deposit, and softball-size stone was placed in the shaft with alternating layers of firewood. The fuel and limestone burned for several days. When the fire stopped and the kiln cooled to an appropriate temperature, the lime was removed out of the shaft from the draft tunnel at the bottom of the kiln. The product was then shipped in baskets or barrels to the work site. Some kiln designs allowed the continual addition of fuel and stone at the top of the shaft; the mixture burned in the shaft below, and the lime was drawn out at the bottom. Today, the manufacture of lime is more complicated and is explained in the next section.

PRODUCTION AND TRADE; RESOURCES AND RESERVES

U.S. Production

In 2003, the U.S. Geological Survey (USGS) reported that the United States produced 19.2 Mt of lime, an increase of 1.3 Mt (a 7.2% increase) compared with 2002 (Table 3). The value of lime sold or used was \$1.24 billion (Miller 2003). Production figures represent the total lime sold or used by domestic producers, including the commercial sale or captive consumption of quicklime, hydrated lime, and dead-burned refractory dolomite.

In 2003, 76 plants in the United States produced high-calcium quicklime, and 23 plants produced dolomitic quicklime. High-calcium hydrated lime was produced at 40 facilities, and dolomitic hydrated lime was produced at 7 facilities; most hydrators are located at lime plants and usually do not occur as stand-alone facilities. Ninety-six plants in 32 states and Puerto Rico made some type of lime product in 2003 (Table 4). Principal lime-producing states in 2003, in descending order of production, were Missouri, Ala-

bama, Kentucky, Ohio, Texas, and Pennsylvania. The top 10 companies, in descending order of production, were Carmeuse Lime, Chemical Lime Co., Graymont Ltd., Mississippi Lime, Global Stone Corp., Martin Marietta Magnesia Specialties LLC, U.S. Lime & Minerals, Western Lime Corp., Southern Lime Co., and Ispat Inland Inc. These companies operated 43 lime plants (less than half the total number) and eight separate hydrating plants, accounting for 87% of the combined commercial sales of quicklime and hydrated lime and nearly 83% of total lime production.

U.S. Imports and Exports

The United States exports and imports quicklime, hydrated lime, hydraulic lime, and dolomitic lime. In 2003, the USGS reported that the U.S. exported 97,800 t (107,806 st) of lime valued at \$13.7 million; about 94% went to the United States' nearest neighbors, Canada (about 88%) and Mexico (6%); about 4% was exported to Germany; and the remaining 2% went to various other countries. The United States imported 202,000 t of lime (223,000 st) valued at \$22.5 million in 2003, with 63% from Canada, 36% from Mexico, and the remaining 1% from various countries (Miller 2003).

Because of its high place value and low-to-moderate unit value, most lime consumed in the United States is manufactured within its boundaries. Because most exports and imports (more than 94%) are traded with Canada and Mexico, U.S. export/import statistics also reflect this.

World Production

In 2003, 120 Mt of lime were produced on a worldwide basis (Miller 2003). In 1990, the Soviet Union had been the largest producer of lime, a position it held for many years. Its collapse, however, in 1991 changed the production statistics since each of the new republics in the Commonwealth of Independent States (CIS) report their own respective production figures. Only in 1998 did the USGS begin to list the production figures of CIS countries separately, and not all were accounted for. Traditionally, lime usage in the Eastern Bloc nations, including the former Soviet Union, was focused on steel production.

European production also is largely dedicated to steel production and generally is consumed within the European trading community. Within the European steel industry, there has been a move toward greater use of dolomitic lime as well as an increased use of powdered lime rather than pebble lime. Powdered lime is used in synthetic slag and ladle furnaces during secondary steelmaking.

Table 5 lists the production figures from various countries. Variations in quality and types of lime, production technologies, and industries manufacturing lime, plus the frequent confusion with limestone data, make accurate reporting of world lime information extremely difficult and certainly incomplete (Miller 2003). Except from a few industrialized nations, accurate lime data are difficult to obtain.

The largest producer of lime products is China, followed by the United States. The steel industry is the largest user of lime in the industrialized nations. Consequently, the large lime producers in Table 5 also produce large quantities of steel and reduced iron. These countries are Brazil, China, Germany, Japan, Russia, and the United States. Mexico also is a relatively large producer of lime, the vast majority of its production consumed in steelmaking. In developing countries, substantial amounts of lime continue to be used in the building trades and agricultural applications, such as soil amendments.

World Limestone Resources

About 20% of the earth's sedimentary crust is formed by limestone, which is distributed widely throughout the world and exists

Table 3. Salient lime statistics,* in kt† unless otherwise specified

	1999	2000	2001	2002	2003
United States‡					
Number of plants§	107	106	103	99	96
Sold or used by producers					
Quicklime					
High-calcium	14,100	14,300	13,600	13,400	13,900
Dolomitic	3,000	3,000	2,580	2,420	2,460
Total	17,100	17,300	16,200	15,800	16,400
Hydrated lime					
High-calcium	2,010	1,550	2,030	1,500	2,140
Dolomitic	298	421	447	431	464
Total	2,310	1,970	2,470	1,930	2,610
Dead-burned dolomite**	300	200	200	200	200
Grand total	19,700	19,500	18,900	17,900	19,200
Total value, †† thousand \$	1,190,000	1,180,000	1,160,000	1,120,000	1,240,000
Average value, \$/t	60.40	60.60	61.30	62.60	64.90
Total lime sold	17,400	17,500	17,000	16,500	17,700
Total lime used	2,310	2,020	1,840	1,340	1,460
Exports††					
Quantity	59	73	96	106	98
Value, thousand \$	8,270	9,960	11,900	13,100	13,700
Imports for consumption††					
Quantity	140	113	115	157	202
Value, thousand \$	15,700	13,500	15,100	19,700	22,500
Consumption, apparent§§	19,700	19,600	18,900	17,900	19,300
World, production	116,000	118,000	119,000***	118,000***	120,000†††

Source: Miller 2003.

* Data are rounded to no more than three significant digits and may not add to totals shown.

† To convert metric tons to short tons, multiply metric tons by 1.102.

‡ Excludes regenerated lime; includes Puerto Rico.

§ Includes producer-owned hydrating plants not located at lime plants.

** Data are rounded to no more than one significant digit to protect company proprietary data.

†† Selling value, free on board (f.o.b.) plant, excluding cost of containers.

‡‡ Source: U.S. Census Bureau.

§§ Defined as sold or used plus imports minus exports.

*** Revised.

††† Estimated.

in relative abundance on every continent. In virtually every country in the world, limestone resources are produced on a large scale (Harben 2002). Many limestones are remarkably pure and contain less than 5% noncarbonate impurities, so that even when employing primitive methods of calcination, it is possible to manufacture relatively high-purity lime products. The USGS reports that worldwide resources of limestone and dolomite are adequate for the production of lime (Miller 2003).

GEOLOGY

Mineralogy

The principal mineral constituent of limestone is calcite (CaCO_3), but it may also contain the minerals dolomite ($\text{CaMg}(\text{CO}_3)_2$), aragonite (CaCO_3), siderite (FeCO_3), ankerite ($\text{Ca}_2\text{MgFe}(\text{CO}_3)_4$), and magnesite (MgCO_3). Calcite and dolomite are in the hexagonal crystal system and have perfect rhombohedral cleavage; aragonite is in the orthorhombic crystal system. Calcite and aragonite can be distinguished from dolomite by their immediate effervescence in cold, dilute hydrochloric acid. Calcite and aragonite have a hardness of 3 on the Mohs scale, while dolomite is slightly harder at 3.5 to 4.0. Unless the limestone under examination is nearly monomin-

erallic, the distinction between calcitic and dolomitic limestones may be difficult in hand samples. Most limestones are mixtures of the previously mentioned minerals. High-calcium lime is produced from limestone with >95% CaCO_3 , and high magnesium dolomitic lime is produced from dolomite with 40% to 46% MgCO_3 ; however, a wide range of dolomitic lime products are manufactured with varying amounts of MgCO_3 .

Geology of Limestone

Limestone is the raw material from which lime is manufactured. In its broadest definition, limestone is any rock rich in CaCO_3 . Other cations (e.g., magnesium and ferrous iron) occurring in limestone may change the carbonate mineralogy of limestone as well as its physical characteristics, such as color, brightness, specific gravity, hardness, and tenacity. Limestone also is classified further by texture, origin, fabric, structure, and geology. Almost all limestone was biogenic during one phase of its formation and was deposited in every geologic time period. Chemically precipitated limestone deposits usually are small, with the exception of some travertine deposits.

Limestones generally were deposited under marine conditions in relatively shallow near-shore environments; less common are

Table 4. Lime sold or used by producers in the United States, by state* †

State(s)	Plants‡	Hydrated, kt§	Quicklime,** kt§	Total, kt§	Value, thousand \$
2002					
Alabama	5	100	1,940	2,040	127,000
Arizona, Colorado, Idaho, Montana, Nevada, New Mexico, Utah, Wyoming	20	303	1,990	2,300	147,000
California, Oregon, Washington	8	55	233	288	29,100††
Illinois, Indiana, Missouri	9	312	3,420	3,730††	221,000
Iowa, Nebraska, South Dakota	3	W††	W	293††	17,800
Kentucky, Tennessee, West Virginia	5	100	2,170	2,270	131,000
Ohio	8	122	1,510	1,630	98,100
Pennsylvania	6	192	1,030	1,230	87,600
Texas	5	289	1,240	1,530	98,400††
Wisconsin	4	159	444	603	35,600
Other§§	26	302	1,980	1,990	126,000
Total	99	1,930	16,000	17,900	1,120,000
2003					
Alabama	5	151	2,140	2,290	151,000
Arizona, Colorado, Idaho, Montana, Nevada, New Mexico, Utah, Wyoming	19	304	2,300	2,600	167,000
California, Oregon, Washington	8	61	240	301	29,300
Illinois, Indiana, Missouri	8	462	3,250	3,710	236,000
Iowa, Nebraska, South Dakota	3	W	W	363	24,600
Kentucky, Tennessee, West Virginia	5	118	2,400	2,520	148,000
Ohio	8	127	1,760	1,880	114,000
Pennsylvania	6	184	1,000	1,190	90,100
Texas	5	638	989	1,630	110,000
Wisconsin	4	169	589	757	46,000
Other§§	25	394	1,910	1,940	128,000
Total	96	2,610	16,600	19,200	1,240,000

Source: Miller 2003.

* Excludes regenerated lime.

† Data are rounded to no more than three significant digits; may not add to totals shown.

‡ Includes producer-owned hydrating plants not located at lime plants.

§ To convert metric tons to short tons, multiply metric tons by 1.102.

** Includes dead-burned dolomite.

†† Revised.

‡‡ W = Withheld to avoid disclosing company proprietary data; included with "Other."

§§ Includes Arkansas, Georgia, Louisiana, Massachusetts, Michigan, Minnesota, North Dakota, Oklahoma, Puerto Rico, Virginia, and data indicated by the symbol "W."

deeper water marine deposits and freshwater lacustrine deposits. Deposits of limestone typically occur in layers or beds ranging from laminae (fractions of a millimeter in scale) to massive bedding (meters in scale). Although limestones usually occur as sedimentary rocks, marbles form when carbonate rocks are metamorphosed under intense heat and/or pressure, resulting in a coarsely crystalline, foliated, and monomineralic rock. For further reading, Oates (1998) presents a comprehensive discussion on the geology of limestone.

In the United States, high-purity limestone and dolomite are located mainly in the eastern and central parts of the country; however, their entire distribution is not well known. They represent only a small fraction of the total limestone and may occur in restricted areas. Much of the high-calcium limestone and high-purity dolomite occur in formations that are widespread and in minable thicknesses, and contain resources that are relatively large and are adequate for the manufacture of lime for the next several hundred years (Hubbard and Ericksen 1973).

Because limestone is so wide spread in time and space, large high-grade deposits are relatively ubiquitous. It is because of this that limestone reserves are considered adequate for the manufacture of lime on a worldwide basis.

TECHNOLOGY

Exploration Techniques

Reconnaissance Geology

Exploration for high-calcium limestone and dolomitic rock begins with a thorough review of geological survey publications, including geological maps. Most government geological surveys, whether at federal or state (or provincial) levels, have inventoried the limestone deposits within their jurisdictions. This information will help the geologist plan a field exploration program that begins with reconnaissance sampling and mapping. If the reconnaissance includes a preexisting quarry, channel sampling of the quarry wall is the most representative collecting technique. Chip intervals are samples the geologist collects along the ledges of limestone outcrop(s), vertically

Table 5. World production of quicklime and hydrated lime, including dead-burned dolomite, by country[†] and by year, kt

Country [†]	1999	2000	2001	2002	2003
Australia [§]	1,500	1,500	1,500	1,500	1,500
Austria [§]	2,000	2,000	2,000	2,000	2,000
Belgium [§]	1,750	1,750	1,750	1,750	1,750
Brazil	6,137	6,273	6,300	6,500**§	6,500
Bulgaria	1,068	1,388	2,025**	2,000**§	2,000
Canada	2,565	2,525	2,213**	2,237**	2,200
Chile [§]	1,000	1,000	1,000	1,000	1,000
China [§]	21,500	21,500	22,000	22,500	23,000
Colombia [§]	1,300	1,300	1,300	1,300	1,300
Czech Republic	1,142	1,202	1,300**§	1,120**§	1,200
France [§]	2,500	2,500	2,400	2,500	2,500
Germany [§]	6,440	6,850††	7,000	7,000	7,000
Iran [§]	2,138††	2,200	2,000	2,200**	2,200
Italy ^{§††}	3,500	3,500	3,500	3,000	3,000
Japan, quicklime only	7,594	8,106	7,586**	7,420**§	7,500
Mexico [§]	6,500	6,500	6,500	6,500	6,500
Poland	2,299	2,376	2,049**	1,960**	1,900
Romania	1,623	1,480	1,790**	1,829**	1,800
Russia [§]	7,000	8,000	8,000	8,000	8,000
South Africa, burnt lime sales	1,920**	1,391	1,615	1,598**	1,600
Spain [§]	1,500	1,500	1,500	1,500	1,500
Turkey ^{§§}	975	914	855**§	850**§	900
United Kingdom [§]	2,500	2,500	2,500	2,000	2,000
United States, including Puerto Rico	19,700	19,500	18,900	17,900	19,200††
Vietnam	1,026	1,156**	1,180**	1,200**§	1,200
Other [§]	9,020**	9,460**	10,600**	11,000**	11,000
Total	116,000	118,000	119,000**	118,000**	120,000

Source: Miller 2003.

* World totals, U.S. data, and estimated data are rounded to no more than three significant digits and may not add to totals shown.

† Table includes data available through April 6, 2004.

‡ In addition to the countries listed, Argentina, Iraq, Pakistan, Syria, and several other nations produce lime, but output data are not reported. Thus, available general information is inadequate to formulate reliable estimates of output levels.

§ Estimated.

** Revised.

†† Reported figure.

‡‡ Includes hydrated lime.

§§ Lime produced for steel production; figure does not include the widespread artisanal production of lime for whitewash and sanitation purposes.

or perpendicular to bedding. Care should be taken to flake or chop off any weathered rock surface, ensuring as fresh a sample as possible; all mud, or organic material (e.g., lichens), or soil also must be removed. It is important to construct a geologic map of the prospect, if only in a rudimentary manner, and to accurately plot the sample sites. These samples are sent to the laboratory for assay, and if they indicate high-grade limestone that is adequate for lime manufacture, a drilling program is planned next.

Drilling

Diamond core drilling gives the most representative picture of the limestone deposit. Many geologists plan a core-drilling program on a widely spaced grid to determine the size and boundaries of the limestone deposit. Attitude of bedding also influences the spacing and location of drill holes, as well as the direction or angle of the drill hole. This first phase of drilling will provide a skeletal framework to plan additional drilling with more tightly spaced drill holes, perhaps with rotary drilling, which is faster and less expensive. In either case, the geologist must accurately log the core or drill cut-

tings (along with the driller's logs) to interpret the down-hole geology. Accurate logging is necessary to correlate the geochemical assays with the subsurface geology.

Samples for geochemical testing are obtained by splitting the core, carefully maintaining sample integrity by washing off any foreign materials such as drill mud, and by including the entire length of core per sample interval. In North America, typical sample intervals for both core and drill cuttings from rotary drilling is 5 ft (1.52 m), but geologic considerations and drilling conditions may dictate the sample interval. In rotary drilling, it is important to maintain borehole integrity so that rock from above does not contaminate the sample cuttings downhole.

Geophysical Methods

Geophysical methods are varied and are used on a case-by-case basis; they usually are employed to locate and interpret geologic features. These methods range from simple aerial photography to gravity and radiometric surveys. The author, for example, has used aeromagnetic surveys to locate and define the boundaries of

high-calcium limestone deposits in heavily forested metavolcanic terranes. Most geophysical methods, however, are used to determine the nature and amount of overburden associated with a limestone deposit.

Evaluation of Limestone Deposits

Grade

The grade of the rock is the most critical part in evaluating a high-purity limestone deposit. Whatever the limits, this grade must be consistent throughout the deposit. For example, high-calcium limestone should have 95% or greater CaCO_3 , with less than 5% impurities (MgCO_3 , SiO_2 , Al_2O_3 , and Fe_2O_3). Variations in chemistry must be plotted and mapped to plan future exploration drilling and/or mine planning. Silica and alumina (as clays), along with iron pyrite and/or iron oxide finely disseminated throughout the stone and acting as fluxing agents, may increase sintering during calcination.

Decrepitation

Physical characteristics of limestone play an important role in evaluating a deposit. They determine how the limestone will behave during calcination and may determine the type of kiln in which to invest. A bulk sample (usually tens or hundreds of tons) test burned in a full-scale operation is the most desirable method; however, small pilot kilns for testing purposes also may give a close approximation. The latter is less expensive, involves smaller sample sizes, creates less environmental disturbance at the bulk sample site, and involves fewer personnel. Alternate testing methods consist of burning small quantities in a laboratory muffle furnace and evaluating the integrity of the lime product by some type of physical impact or buffeting. One laboratory refers to the “3-ft concrete” and “5-ft concrete” tests where a lime pebble of prescribed diameter is dropped from 3- and 5-ft heights, respectively, onto a concrete floor. The broken shards of lime are counted and recorded—the more desirable stone having fewer shards. Another test consists of rotating lime pebbles in a drum and measuring the size fractions of broken lime pebbles. These tests are rather qualitative and somewhat subjective because they depend on operator experience; however, over time and by testing large amounts of different limestones, an empirical and comparative database can be developed.

Certain physical characteristics in limestones may indicate a general disposition toward decrepitation during calcination; however, not all stones with these characteristics will decrepitate. Limestones that display the following attributes or conditions, alone or in combination, are prone to decrepitation: coarse crystallinity; friability; foliation (as in marble); excessive calcite veining; microfracturing; highly porous; and thinly bedded.

Infrastructure

Because of the cost of transportation, the value of most industrial minerals is dependent on their location. Lime has both high place value and relatively low unit price; therefore, proximity of limestone resources to railroads and highway systems is significant. The availability of electrical power, water, and natural gas pipeline (as a fuel source option) also is essential.

Of additional consequence is the disposition of the land where the deposit is located in terms of ownership, nearest neighbor(s), and zoning laws and/or regulations. In places where the government owns the resources or the land, there are usually incentives for mineral development with some restrictions and fees. For example, in the western United States, much of the land is administered by the U.S. Bureau of Land Management or the U.S. Forest Service. A prospector needs to stake a claim and pay administrative fees for

recording, usually on both federal and local levels. On land that is owned privately, the resources and/or land must be obtained through contractual agreement or outright purchase (e.g., in the eastern United States where most land is held in fee).

Because residents in rural areas tend to be scattered over large distances, a lime operation would not impose on them as much as in towns or suburban developments, where homes would be closer to the operation. In the case of the latter, provisions typically are made to mitigate the effects of quarry blasting, dust and emissions, and visual impacts. It is equally important to consult with the nearest neighbors about their attitudes toward mine development and plant operation. In cases concerning a boriginal people, the developer needs to address their cultural concerns. In areas where zoning ordinances mandate land use and mitigation of industrial impacts to the neighborhood, it is still a good practice to meet with neighbors and discuss the scope of the planned operation.

Mining

Details of stone preparation, which comprises surface quarrying or underground mining, crushing, and screening to produce kiln-size stone, are covered in the Limestone and Dolomite chapter of this book.

Open-pit methods with bench drilling and blasting are the preferred mining practices; however, if the resource is scarce and is of sufficiently high grade, underground mining may be economical.

The major concern in quarrying limestone for kiln feed, though, is the effort to maintain grade control. Standard quality-control practice in a high-calcium limestone quarry consists of chemical analyses of each blast hole to ensure product standards. In quarries where the beds are uniform in attitude (strike and dip and thickness) and grade, this is routine. In limestone deposits with a variable chemical profile, or whose sedimentary bedding is tilted or folded, the assay results from quarry blast holes must be carefully scrutinized. It may be necessary to stockpile stone of different grades for the purpose of blending so that the kiln feed is a uniform grade.

Faulting and/or fracturing (jointing) may concentrate deleterious materials such as silica, alumina, and iron compounds that blast-hole sampling may fail to detect. Therefore, it is necessary for the geologist or quarry manager to examine the quarry walls and conditions so that these potentially harmful materials can be avoided.

LIME MANUFACTURE

Production of lime typically involves three main processes: stone preparation, calcination, and hydration, although hydration is not necessary for several lime uses. The simplified flow diagram (Figure 2) outlines the various production steps. Details of stone preparation, which comprise surface quarrying or underground mining, crushing, and screening to produce kiln-size stone, are covered in the Limestone and Dolomite chapter. Because lime must meet certain chemical specifications, the various steps in stone production are controlled carefully to prevent contamination with impurities associated with the limestone deposit, particularly silica, alumina, and iron oxide. Sulfur and magnesium are other impurities with which some customers are concerned. Accordingly, many lime operations practice selective quarrying methods and also may wash limestone kiln feed.

Calcining

Although limestone calcining (or burning) is a relatively simple operation chemically, a wide variety of kiln systems are used today. These include vertical, rotary, rotary with preheaters, and multiple-shaft regenerative. This variety of production methods is in striking

contrast to the portland cement industry, which almost exclusively utilizes rotary kilns with preheaters.

The most important factors in selecting a lime kiln are the burning characteristics of the stone, fuel consumption, and capital equipment costs. Other factors are market requirements, fuel availability, and air quality regulations. The various calcining systems and their relative advantages and disadvantages are described in the next section.

Types of Lime Kilns

Vertical Kilns

Vertical kilns (also known as vertical shaft kilns or shaft kilns) traditionally have burned only larger stone, 75 to 300 mm, with a size range of approximately 1:2. Newer designs, however, can manage stone sizes as small as 20 mm and a wider size range up to 1:4. Relative lower fuel consumption is a major advantage of shaft kilns, which normally require less than 5.2 kJ/t of lime produced. This has been improved with newer designs, which operate as low as 3.3 to 3.9 kJ/t of lime produced. The use of oil, natural gas, or coke for fuel is one disadvantage of traditional vertical kilns in the energy environment of today; however, progress in burner technology has made it possible to utilize pulverized coal in modern shaft kilns.

Vertical kilns may be built of stone masonry, reinforced concrete, or boiler plate construction. The most widely used kiln has a refractory-lined steel shell and is usually circular in cross section. These may be 2.7 to 7.3 m in diameter and 15 to 48.5 m high. Capacities vary from as low as 8.2 tpd to in excess of 576 tpd, with the newer generation of kilns producing the higher range of tonnage.

Among the newer vertical kilns are the center burner, gas-fired (Azbe, Union Carbide), oil-fired annular (Catagas, Beckenback), and the Beckenback double-incline (Cascade). Also, several multiple-shaft parallel-flow regenerative kilns are now operated in the United States.

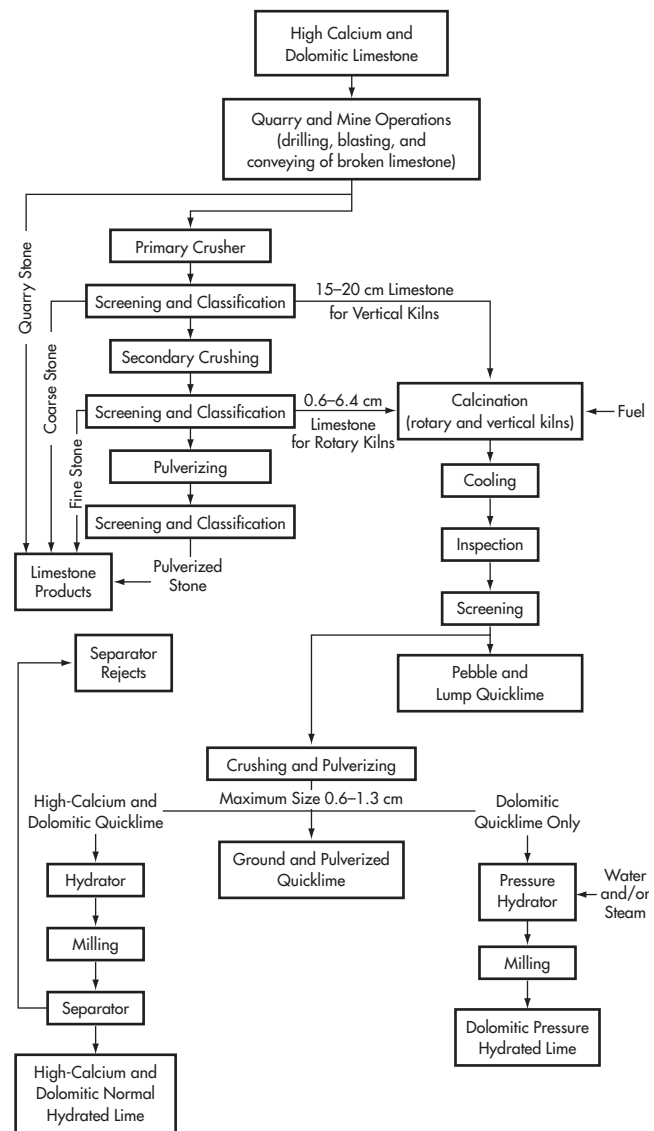
Older-style vertical shaft kilns are used by sugar companies processing sugar beets. These kilns tend to be lower in volume, less than 227 tpd, and are captive to their respective sugar plants.

Multiple Shaft Kilns

Although multiple shaft kilns (MSKs) were developed to burn small stone with sizes of 20 mm to 120 mm, the newer technologies allow burning with sizes smaller than 20 mm. They utilize the parallel-flow calcining principle in double and triple shaft units. Shafts are interconnected in the burning zone, and, while one shaft is being fired, the other is preheated (Figure 3). Fuel and combustion air are supplied to the burning shaft from above and ignited at the upper end of the burning zone; the lime is then calcined in uniflow. Next, exhaust gases pass into the second shaft, preheating the stone in counterflow. After a 10- to 15-min interval, the shaft firing is reversed, and cooling air is blown into both shafts simultaneously. Because of this novel heat regenerative system, fuel consumption in MSKs is 3.5 to 4.0 kJ/t of lime produced. MSKs vary in capacity from 81.6 tpd up to 907 tpd. Although MSKs normally are fired with natural gas or oil, recent advances in burner technology have made it possible to fire the kiln with pulverized coal. Kilns of this type have had a favorable response from the industry on a worldwide basis, and several are producing lime in the United States.

Annular Shaft Kilns

The burning process in annular shaft kilns is based on counterflow for preheating and calcining, and uniflow for residual calcination. Partitions provided by an inner cylinder and by staggered bridges in the burning zone permit even distribution of heat and uniform downward flow of material through the kiln. Stone as small as 25 × 75 mm



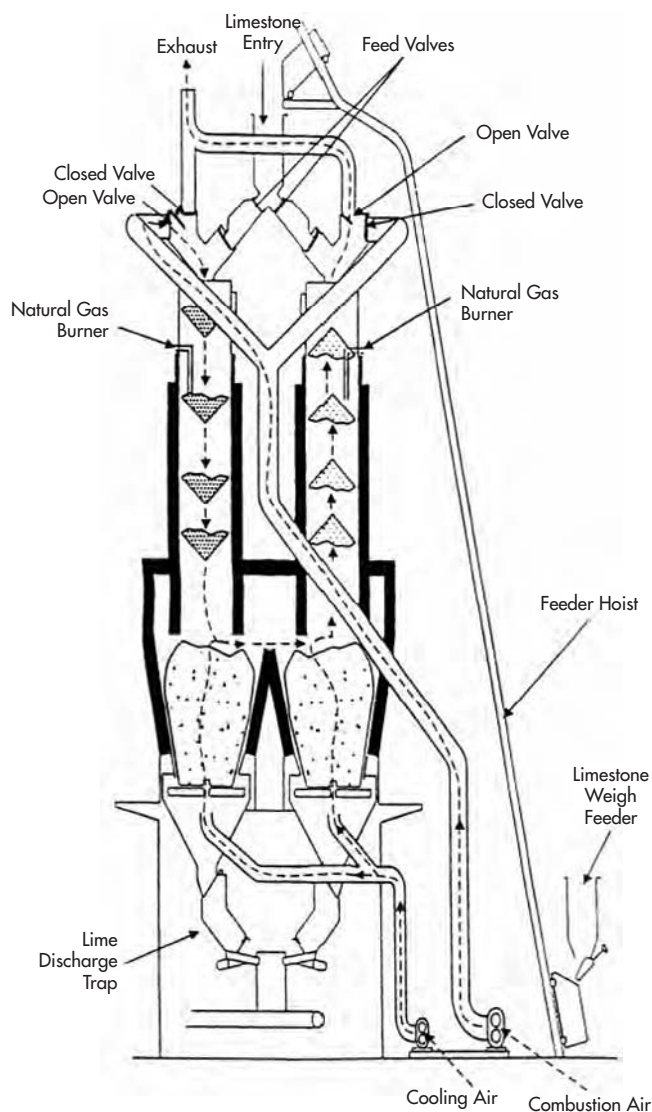
Source: Boynton 1980.

Figure 2. Simplified flow sheet for lime and limestone products

can be calcined to produce a soft burned lime (i.e., higher reactivity lime versus hard-burned lime) using either oil or natural gas for fuel. Capacities vary from 81.6 to 245 tpd with fuel consumption under 6.2 kJ/t.

Rotary Kiln

Unlike vertical kilns, which operate fully charged, the rotary kiln has about 90% of its volume filled with flame and hot gases. The kiln slowly rotates, exposing new surfaces of stone to the hot gases, but there is little flow of gases through the solids. Hence, radiation interchange among gas, solids, and the refractory wall is an important part of the overall heat-transfer mechanism. Rotary kilns are less efficient than shaft kilns because a relatively small area of the solids is exposed in a rotary kiln; they recover less heat from the exit gases of the kiln; and the radiant heat loss from the shell is much higher. Although the rotary kiln has the advantage of burning stone from 6.5 to 57 mm, the size ratio generally is 1:3 in order to



Source: Beach et al. 2000.

Figure 3. Multiple-shaft parallel-flow regenerative kiln

minimize segregation and to promote thorough calcination. While this sizing minimizes the amount of residual limestone core in the individual lime fractions, at the same time it allows a thorough soft burn of all the limestone feed. In addition, when using rotary kilns, it generally is not necessary to crush the final product, because it is in the form of an acceptable size of pebble lime.

Rotary kilns vary greatly in size, ranging from 2×25 m to 5.5×190 m, with capacities of 40.8 to 1,361 tpd. Because of the relatively high length-to-diameter ratio, these kilns have become known as long kilns. In North America, long kilns are typically 2.5 to 4.0 m \times 45 to 105 m long, producing 163.3 to 372 tpd of lime. The largest rotary kilns are 907 to 1,361 tpd capacity. Although rotary kilns can burn a wide range of fuels, a major drawback is their lack of fuel efficiency. Many of the earlier rotary kilns required in excess of 12.6 kJ/t of lime produced. This high fuel demand has been reduced to 7.4 kJ/t through the implementation of internal heat exchangers and dams, recuperative-type coolers, more sophisticated and complex instrumentation, and improved refractories.

Rotary Preheater Kilns

The most important improvement concerning the efficiency in rotary kilns is the move away from the long kiln to a medium-length kiln with an external preheater (Figure 4). The vertical, cylindrical, or shaft-type preheater kiln is available through Kennedy Van Saun (KVS; in 1989 KVS became part of Svedala Industries of Sweden and today it is part of Metso Minerals, Inc., of Finland), Fuller Company, and Allis-Chalmers. The preheater is a refractory-lined chamber located below the raw feed bin and in front of the kiln. Exhaust gases from the kiln are drawn countercurrent through the stone, preheating it to 540° to 900°C . Retention time within the preheater is 1.0 to 1.5 hr, depending on the design of the system, burning characteristics of the stone, and other factors previously listed. Even before the stone is discharged into the kiln, approximately 30% calcination is achieved during the preheating stage. Directly following preheating, the partially calcined stone is sent to the kiln at a predetermined rate by means of hydraulically actuated plungers. This type of preheater has been adapted to the new large-volume kilns, which typically may be 5.2 m in diameter by 62.5 m long, with a capacity of 816.5 to 907 tpd.

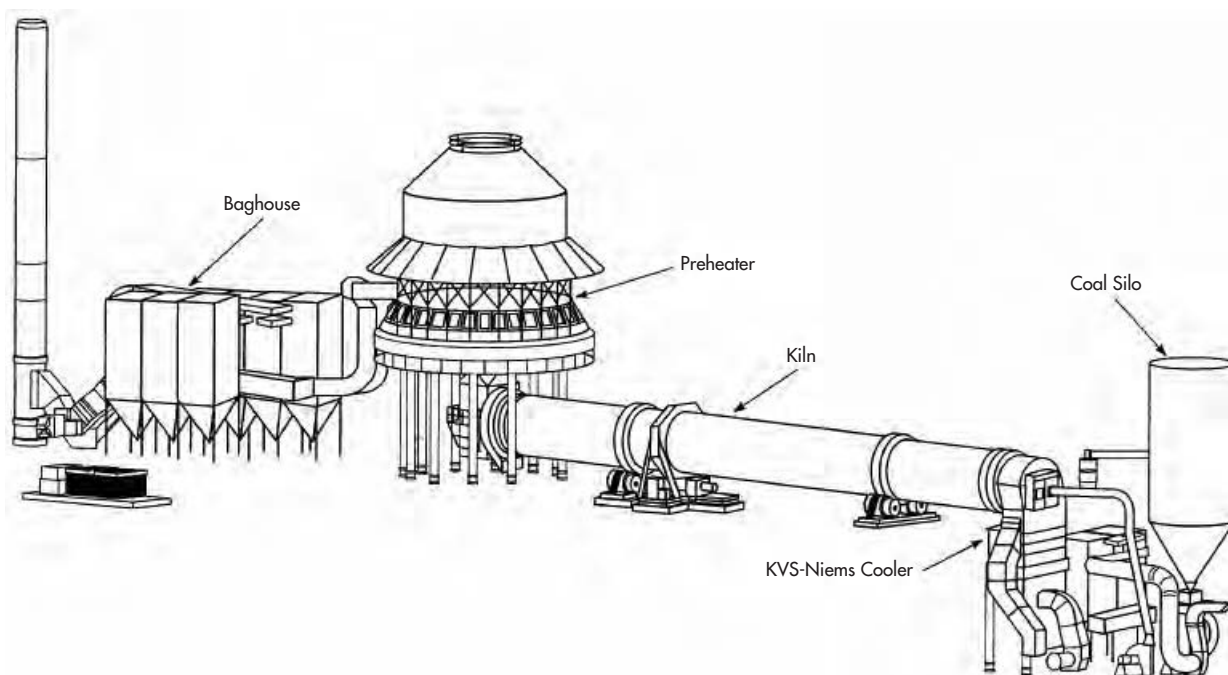
Allis-Chalmers also developed another type of preheater kiln, which is known as a grate kiln. This is a single-pass, downdraft, enclosed traveling grate on which finer-sized stone, placed on top of coarser-sized stone, is calcined while the coarser stone is preheated. In the rotary kiln, the coarser stone is calcined, and the finer stone is protected from overburning, having sunk into the kiln load through a sifting action. Grate-kiln systems of 245 to 490 tpd capacity are in operation in North America.

Heat exchangers and coolers that recuperate waste heat also are utilized to improve fuel efficiency. Heat exchangers, principally trefoil or quadrant sections, are mounted at the feed end. Their purpose is to turn the stone over more effectively and to increase the turbulence of the hot gases. Dams and lifters may be used to turn the stone over, create gas turbulence, or retard the passage of the stone. Coolers, on the other hand, located at the discharge end of the kiln, serve to return hot gases to the kiln as secondary air. Three types of coolers generally are used with the rotary kilns: the shaft or contact, the planetary, and the rotary. The most prevalent type is the Niem's contact (counterflow), which is refractory lined and mounted below the kiln hood. Cooling air is provided by a fan of sufficient size to reduce the lime temperature to 65°C or less. The planetary cooler consists of eight or more tubes, approximately 4.2×6.2 m in size, mounted at the discharge end of the kiln. Lime is moved in each tube by conveyor flights counterflow to the cooling air. The rotary cooler is generally not as effective as the other two cooler types and has the additional disadvantage of attrition loss during rotation.

The net effect using both shaft and grate preheaters, and improved heat exchange recovery within the kilns, is to reduce fuel ratios in rotary kilns from 4.7 to 6.3 kJ/t of lime produced. In addition, advances in instrumentation and monitoring have reduced worker requirements and increased product quality and uniformity. Together with these advances, the large-capacity rotary kiln with preheater has become the most commonly selected system today for new or expanded lime production facilities.

Calcimatic Kilns

The rotary hot calciner, or calcimatic kiln, consists of a preheater, circular hearth, and cooler, which are all refractory lined (Figure 5). Like the rotary kiln, this kiln can burn small stone, which is typically sized at a 1:3 ratio. The stone is carried on the hearth in a thin layer, and one revolution of the hearth constitutes the calcining cycle. Numerous burners inside and outside the hearth are used for firing,



Source: Gutschick, K.A. 1995. *Kirk-Othmer Encyclopedia of Chemical Technology*. 4th edition, Volume 15. Copyright © 1995 John Wiley & Sons, Inc., New York. This material is used by permission of John Wiley & Sons, Inc.

Figure 4. Preheater rotary kiln system used in lime production

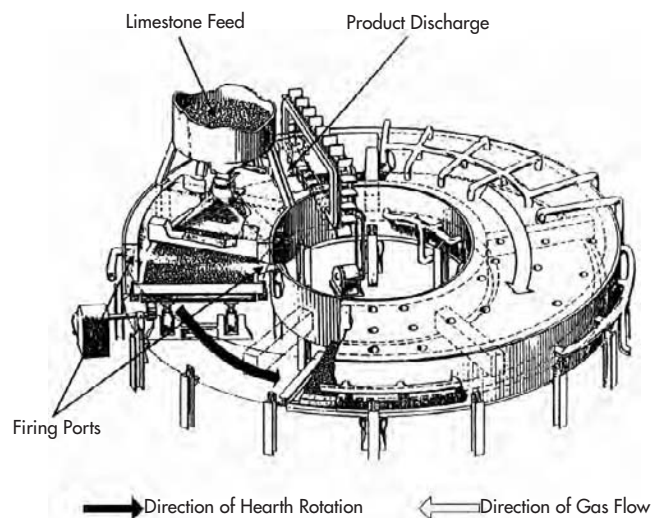
utilizing gas, fuel oil, coke oven gas, and, more recently, pulverized coal. Fuel requirements approximate 7.7 kJ/t and can be adjusted to accommodate a wide range of calcination. A significant advantage of the calcimatic kiln is that mechanical attrition loss is negligible. Stone is set virtually motionless on the hearth, permitting the utilization of soft limestones that otherwise would be subject to high mechanical degradation (decrepitation) during calcination. At present, only a few companies operate calcimatic kilns in North America, although there are several 81.7- to 245-tpd capacity kilns in use in Europe.

Fluo-Solids Kilns

For limestone that is friable or decrepitates during calcination, the Dorr–Oliver Fluo-Solids kiln, which is a fluidized-bed system, has been used to produce a highly reactive lime (Figure 6). In this fluid-bed process, the material is maintained in suspension in a rising current of hot gases until calcined. Kiln feed is normally 60 to 65 mesh in size. The system can be fired with natural gas or oil and incorporates a FluoDry unit (preheater) and a FluoSolids reactor (calciner) that resembles a rotary kiln. Fuel consumption is approximately 7.8 kJ/t of lime produced. Fluid-bed calciners are available in size ranges of 40.8 to 204 tpd; however, the only kilns of this design in North America are operated by Specialty Minerals Inc. at its North Adams, Massachusetts, plant.

Flash Calciners

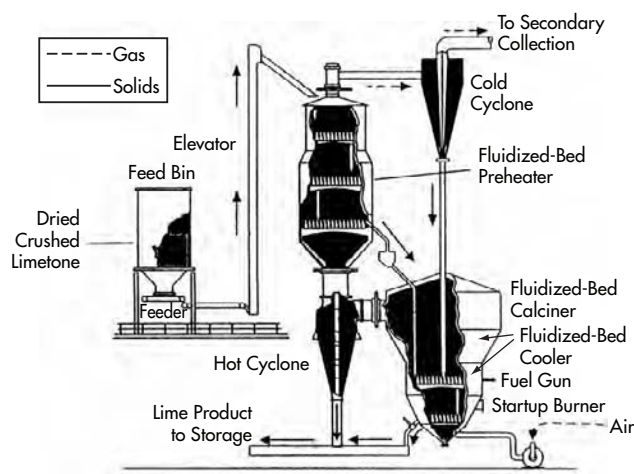
The flash calciner is one of the more recent developments in calcination, but it is not really a kiln. Developed by Fuller Company, this system is designed to calcine the undersized material, or fines, that remain after the primary kiln feed is sized. There are three elements to this system: a preheater, a flash calciner, and a cooler. Preheating is achieved in a series of cyclones where the heat from rising hot gases is absorbed in the counterflowing material, which is fed from



Source: Beach et al. 2000.

Figure 5. Calcimatic kiln with cross-sectional view of one firing zone

the top, and attains a temperature up to 980°C. As the preheated feed drops into the furnace or calciner, a forced air vortex flow pattern pulls the particles into the center of the furnace and then up the sides before discharge. In the furnace, the temperature is 1,200°C, but retention time is only a few seconds. A suspension-type cooler recovers heat from the calcined product before it is conveyed to the product bin. The system is designed in two modes depending on the size of the feed. Where limestone fines are to be calcined, 60% to



Source: Beach et al. 2000.

Figure 6. Fluidized bed kiln

80% of calcination occurs in the furnace. The final calcination takes place in a fluid bed located between the furnace and the cooler. In systems where material of -28 mesh is fed to the calciner, no fluid-bed reactor is necessary. This system can utilize natural gas, oil, or coal, and will normally require 6.2 to 8.5 kJ/t of product.

Milling and Hydrating

After cooling, quicklime is carefully inspected to avoid unburned limestone core, or pieces of uncalcined rock. This is particularly necessary for shaft kilns that burn large stone. The quicklime is then crushed and sized for shipment. Generally, fines are converted to hydrated lime.

Hydrated lime is shipped in 23-kg bags or in bulk and typically is available in two forms: standard or normal grade with 75% to 95% passing a No. 200 sieve (75 μm); and fine grade where 99.5% passes a No. 325 sieve (45 μm). These in turn are manufactured in two types: Type N (normal) and Type S (special, see ASTM C 207-04), each including high calcium or dolomitic hydrates, respectively.

Type S limes are hydrated to a high degree by processes involving steam pressure. They contain less than 8% nonhydrated oxides and develop high and quick (15 min) plasticity and high water retention. Demand for Type S lime grew rapidly after World War II, and currently it is the chief lime for structural uses. Lime manufacturers now add air-entrained catalysts into the lime to increase plasticity and durability (called Type SA and Type NA lime).

A variety of mechanical hydrators are designed for the production of Type N lime, including batch hydrators such as the Clyde and continuous hydrators such as the Kritzer, Schaffer, Knibbs, Harding, and KVS (see National Lime Association 1995 for an excellent discussion on types of slakers). In the hydration process, water is added slowly to quicklime (usually in crushed or ground form), and the lime is agitated to produce intimate contact of lime and water. Accurate proportions are ensured by using flowmeters for water and weighing feeders for lime. Water exceeding the theoretical requirement for hydration is necessary, because some water is lost as steam from the heat of hydration. Following hydration, the product typically is fed to a pulverizer or tube mill equipped with an air separator. The air separator rejects core and most of the siliceous and alumina impurities. Various grades of hydrated fines are made by adjusting the separator.

Type S hydrate dusts are manufactured by various processes, but the principal one is the Corson explosion method of continuous pressure hydration. In this process, ground dolomitic quicklime and water are fed automatically into a high-speed slurry mixer in constant and exact proportions. Hydration then takes place in an insulated autoclave that operates at about 5.3 kg/cm² at 150°C. After about 30 min of retention time, the product is discharged continuously (or exploded) through a small pipe at 3,050 m/sec into a special cyclone collector at atmospheric pressure. There the hydrate and water are separated by the spray-drying principle. To increase plasticity, the product is ground in a tube mill. Several U.S. plants use the Corson process, marketing their products under the registered trade name Miracle Lime.

MARKETING

Uses

Lime is one of the top five chemicals produced and used in the United States. Its level of consumption reflects both economic conditions as well as changing consumption patterns. For example, in 1990 the major end uses were the following:

- Chemical and industrial, 66% (includes 29% in steelmaking, 7% in paper and pulp, about 4% in sugar refining, and 1.5% in precipitated calcium carbonate)
- Environmental, 24% (includes 9.6% flue gas desulfurization)
- Construction, 8%
- Refractory dolomite, 2%

Captive lime included in the se figures was used mainly in sugar refining and the production of steel. These figures are based on data from Miller (1991).

The major end uses in 2003 were for the following (Miller 2003):

- Metallurgical, 35% (includes 29% in steelmaking)
- Environmental, 28% (includes approximately 18% in flue gas desulfurization)
- Chemical and industrial, 23% (includes 4% in paper and pulp and nearly 7% in precipitated calcium carbonate)
- Construction, 13%
- Refractory dolomite, 1%

Captive lime accounted for less than 8% of consumption and was used mainly in the production of steel in basic oxygen furnaces, sugar refining, magnesia production, and refractories.

Steelmaking

Over the past 40 years, the steelmaking industry has been the largest consumer of lime. Although this situation continues today, the industry has seen a decline in sales. In the United States, from 1980 to 1990, lime consumption in the steel market dropped from 6 Mt (38.1%) to 4.6 Mt (29.4%) of lime production. Since then, up until the year 2003, lime consumption for steelmaking has hovered at about 29% to 31% of annual lime production. The U.S. importation of both steel and automobiles has caused decreasing lime requirements for steelmaking. Also, the use of more polymer composites in car and truck design and manufacturing, along with greater steel production from mini-mills, reduced the demand for lime in steelmaking.

Nevertheless, the basic oxygen furnace (BOF) is still the dominant steelmaking process and continues to utilize approximately 80% of the lime sold for steel production. The lime required for a typical BOF process is 60 to 65 kg/t of steel produced, versus an average of 30 kg/t of steel produced in an electric furnace or mini-mill. Both these applications use lime as a scavenger or flux to

remove impurities such as phosphorus, silica, alumina, and sulfur. While quicklime is the product of choice for a BOF furnace, 10% to 30% of dolomitic quicklime is used with high-calcium lime to extend refractory life. Dead-burned dolomite, or refractory lime, is used in open hearth steel furnaces for the same reason.

Lime used in steel production is normally highly reactive at 90% to 93% available lime with less than 0.06% sulfur. Either pelletized lime or pebble lime (1.25 to 5 cm in diameter) normally is required. A recent development in steelmaking (known as the Q-BOP, or Quelle Basic Oxygen Process) is the use of ground or pulverized lime that initially was used in European mills. The steel industry also uses lime in wire drawing steel plants for the following:

- Removing SO₂ in flue gases in the sinter plant
- Neutralization of sulfuric pickle liquors
- Effluent water softening and treatment
- Coating molds for pig casting

Experiments making a self-fluxing ferrous sinter with hydrated lime have assessed the feasibility of using hydrated lime instead of pulverized limestone.

Nonferrous Metallurgy

In 2003, nonferrous metallurgy utilized approximately 1.07 Mt of lime per year, or about 5.5% of total U.S. lime consumption. Recovery of nonferrous metals from their ores normally involves processing them through some form of flotation method. Lime is used to control pH, neutralize sulfuric acid waste liquors, or curtail the loss of cyanide in processes employing cyanide. Lime is used to neutralize the acidic effects of pyrite and other iron sulfides associated with base metal ores. It also acts as a flux in the sintering of low-carbon chrome and in the recovery of nickel by precipitation.

Gold. Lime controls the pH of sodium cyanide solutions used to leach gold and silver from their ores. When large particles of ore are involved, the process is called *dump leaching*; when particles of ore are small, it is called *heap leaching*; and when the ore is leached in agitated tanks, it is called *carbon-in-pulp cyanidation*. These leaching operations require crushing the ore, mixing it with lime for pH control and agglomeration, and stacking the ore in large heaps or pads for treatment with cyanide solution. Lime is used to maintain the cyanide solution pH between 10 and 11, which maximizes the recovery of the precious metals and prevents the formation of hydrogen cyanide. Lime also is employed to extract uranium from gold slimes.

Lime is used to treat tailings from precious metals mining, which may contain elevated levels of cyanides. Lime also can recover cyanides in treatment processes such as alkaline chlorination, Caro's acid (H₂SO₅), Cyanisorb, and sulfur dioxide/air (Miller 2003).

Copper. Most domestic copper mining companies use lime as the principal reagent in beneficiating copper ores during flotation. Lime neutralizes the acidic effects of pyrites and maintains the proper pH. Pebble lime is used in smelters as a flux to react with silica, alumina, and other impurities forming a molten slag. Employed to scrub SO₂ from stack gases of copper smelters, lime is used similarly as a flux in the smelting of lead, zinc, and antimony.

Alumina. The manufacture of alumina by the Bayer process frequently requires large quantities of lime to causticize sodium carbonate solutions that are used to regenerate sodium hydroxide for recycling. Nearly all plants use some lime for secondary desilication in refining alumina. The U.S. Bureau of Mines (USBM) required lime for experimental processes in which alumina was made from clay or kaolin rather than from bauxite.

Magnesia. Most methods for the manufacture of magnesia, such as the Dow seawater and natural brine processes, ferrosilicon processes, and seawater magnesite processes, require lime. Although dolomitic lime generally is preferred because of its magnesium content, high-calcium lime also is used with success. Dolomitic lime, however, cannot be used in the manufacture of magnesium metal, because this process requires a very high-purity, high-calcium lime.

Pulp and Paper

In the basic kraft pulping process used in the paper industry, wood chips and a liquor of sodium hydroxide and sodium sulfide are heated in a digester. The cooked wood chips, or pulp, are discharged under pressure, along with the spent liquor; the pulp is then screened, washed, and sent directly to make paper or for bleaching. Sometimes lime is used to produce calcium hypochlorite bleach for bleaching paper pulp. The spent liquor enters a recovery furnace where dissolved organics are burned to recover waste heat, sodium sulfide, and sodium carbonate. The sodium sulfide and sodium carbonate are recovered and diluted with water before treatment with slaked lime recausticizes the sodium carbonate into sodium hydroxide (caustic soda) for reuse. Pulp mills recover 90% to 96% of lime employed in the process by reclaiming dewatered calcium carbonate sludge, which occurs as a by-product of caustic soda production. It is still necessary, however, to purchase significant quantities of lime to make up the difference. The paper industry also uses lime as a coagulant aid in the clarification of plant process water.

The global competition from low-cost Asian imports has forced the U.S. paper industry to reduce capacity in recent years. In 2003, lime consumption in the U.S. pulp and paper market decreased by more than 11% (Miller 2003).

Lime is used to make precipitated calcium carbonate (PCC) that serves as a specialty filler and coating for premium-quality papers. In the United States, the most commonly used method to produce PCC is the carbonation process, where CO₂ bubbles through milk-of-lime to form a precipitate of calcium carbonate and water. Reaction conditions determine the size (<5 µm) and shape (uniform spheres of multiple scalenohedral calcite, rhombohedral calcite, or acicular aragonite, or crystal twins) of the resulting PCC crystals. A shift in U.S. paper manufacturing from clay to alkaline sizing in the 1980s increased the use of PCC, which enhances the qualities of paper: whiteness, brightness, opacity, gloss, pH neutrality, and bulk.

Precipitated Calcium Carbonate

Specialty Minerals, Inc. (formerly Pfizer Specialty Minerals, Inc.) pioneered the concept of onsite PCC production in which PCC facilities are adjacent to the paper mill. It was this innovation that expedited the conversion from acid-based to alkaline-based paper-making technology. Some lime companies operate onsite PCC plants in order to make a value-added product available to their customers. Carbon dioxide captured from kiln stack gases is used in the adjacent PCC plant.

PCC also is used in the manufacture of polyvinyl chloride (PVC) plastics and in pharmaceuticals, such as antacid tablets and calcium and other mineral supplements. It is added to sealants and adhesives for rheological enhancement and is used as an industrial filler in paint and inks, rubber products, and thermoplastics. Special applications include use in problem powders as an anticaking agent and for flow improvement by reducing interparticle attractions and by absorbing moisture. Because of its relatively high surface area, PCC can also be used as an inert carrier for liquid catalysts.

Chemicals Manufacture

Lime is used in the manufacture of many chemicals.

Alkalies. In the manufacturing of soda ash and bicarbonate of soda, the Solvay process employs lime to recover ammonia for reuse, requiring 635 kg of quicklime per ton of soda ash produced. In the process, lime reacts with chloride ions to form calcium chloride, which is recovered and sold commercially. The process also yields by-product PCC that is recycled and reused. In addition, lime causticizes sodium carbonate solutions to produce sodium hydroxide (caustic soda). Lime usage for this application, however, has dropped tenfold over the last 10 years as the Solvay process has lost most of its market share to natural soda ash (trona) and electrolytic caustic soda.

Inorganic Chemicals. Inorganic chemicals made from lime include mono-, di-, and tricalcium phosphates, chrome chemicals, purifying salt brines used to produce U.S. Pharmacopeia (USP) food-grade salt, pesticides such as lime-sulfur sprays and powders, and calcium arsenate. Hydrated lime also can be found in proprietary water paints that are used in masonry applications, white portland cement, and some paint pigments. Lime has minor uses in varnish manufacture, celiac pain ts, and certain performance pigments.

Organic Chemicals. Lime is required in the manufacture of ethylene and propylene glycols in the chlorohydrin process in calcium-based organic salts, such as calcium stearate, acetate, lactate, and lignosulfonate. It also is used in the manufacture and refinement of citric acid and glucose. In the petroleum industry, lime has a limited role in neutralizing organic sulfur compounds and SO₂ emissions control in oil refineries. It also is used in the manufacture of certain lubricating greases and drilling muds.

Environmental

Lime use for environmental purposes ranges from smelting stack scrubbing to water treatment. Its primary features in this regard are its diacid nature and its reactivity.

Water and Wastewater Treatment. More than 1.38 Mt of lime was used in 2003 in the United States for the treatment of municipal potable water and industrial wastewater. Lime or lime in combination with soda ash is used to soften water in systems where ion-exchange processes are not employed. Its purpose is to eliminate temporary calcium and magnesium bicarbonates, or hardness, from the water. By raising the pH to 11.5 or higher and by temporarily raising water temperature, lime serves as a secondary sterilization agent to chlorine. With retention times of 3 to 10 hr at this high pH, 99% of waterborne bacteria and most viruses are killed. Afterward, CO₂ is introduced into the lime-treated water, returning pH to an acceptable level and reacting with most of the lime to precipitate and form calcium carbonate sludge.

When surface waters (rivers, lakes, and reservoirs) are used for potable water, lime together with the coagulants alum and iron salt helps to eliminate turbidity; that is, suspended and/or colloidal matter is removed. Here, lime controls pH, neutralizing the acidic effect of the coagulants and achieving optimum efficiency in coagulation.

As an added benefit, after lime returns the pH to lower levels, say between 5 and 8, aluminum, iron, manganese, and other heavy metals, as well as organic compounds (such as tannins), are removed from solution. The control of pH also minimizes corrosion of water pipes and equipment. The benefits of water softening in municipal water systems include the ability of soaps and detergents to lather; the reduction of scale formation in pipes and valves; and improvement in the taste of drinking water.

In the treatment of sewage effluents and wastewater, lime serves the following functions:

- Acid neutralization
- pH control during treatment or before discharge
- Precipitation of metals including heavy metals
- Precipitation of sulfates and fluorides (at pH >10)
- Reduction of nutrients (e.g., phosphates and nitrogen at pH >10), particularly to prevent eutrophication in surface waters
- As an efficient and cost-effective disinfectant

Lime modifies wastewater sludge in a positive manner (by improving settling and filtration in a dewatering coagulation) and through the flocculation of solids; by reducing its moisture content through the hydration of quicklime; and by adding strength for landfill disposal.

Over the last decade or so, federal and state environmental requirements for sewage treatment became more stringent. As a result, chemical treatment processes have become more important and preferred over biological sewage treatment processes.

In addition to potable water and sewage treatment, lime also is used in a variety of methods directed at treating industrial wastewater. For example, lime can neutralize acid mine drainage and precipitate iron in coal-washing plants. Wastewater from sulfuric acid pickling plants and plating waste are neutralized with lime, as are chemical and pharmaceutical plant wastes.

Flue Gas Desulfurization. An entire chapter is devoted to FGD in this book. It is only mentioned briefly in this chapter.

In 1990, the Clean Air Act Amendments included new source performance standards that required a much higher level of sulfur removal from stack gases of coal-fired electric power-generating plants and caused the market for lime used in FGD to increase accordingly. In 1990, 1.673 Mt of lime (9.6% of total sold and used lime) was consumed for FGD in the United States; in 2003, the figure rose to 3.440 Mt of lime (17.9% of total sold and used lime)—an increase of more than 100% or just more than double the amount used prior to the Clean Air Act Amendments.

Coal contains up to 4% sulfur by weight in the form of iron sulfide (iron pyrite; FeS₂), organic sulfur compounds, and inorganic sulfates. When coal is burned, sulfur is oxidized to SO₂ and minor amounts of sulfur trioxide (SO₃). Sulfur dioxide can combine with water in the atmosphere to form H₂SO₄. The application of lime in flue gas scrubber systems removes SO₂ from smokestack gases, which is accomplished by several methods:

- Wet scrubbing with milk-of-lime
- Semidry scrubbing with milk-of-lime using a spray drier or circulating fluidized-bed technology
- High-temperature (>850°C) dry injection of hydrated lime
- Low-temperature (<300°C) injection of hydrated lime
- Low-temperature (<300°C) absorption by hydrated lime in fixed bed

In addition, these methods may be used to remove other acid gases such as hydrogen chloride and hydrogen fluoride, as well as nitrogen oxides.

The United States, Germany, and Japan are the leaders in FGD technology and research, which is in its initial development phase. More recent industrial research has been directed to the task of FGD; for example, the emissions of dioxins, furans, and volatilized heavy metals.

Major problems associated with the processes of FGD include the cost and efficiency of the technologies, as well as the

issue of how to dispose of the reaction products (e.g., landfill versus by-product utilization such as synthetic gypsum for wallboard manufacture).

Construction

Prior to the 20th century, lime was used in construction for such diverse applications as whitewash and masonry mortars.

Soil Treatments. Lime has three major applications for soil treatments: drying wet soils; modifying clay-rich soils; and soil stabilization. Basically, modifying wet soils at construction sites involves the drying of mud. Dry soils provide stable platforms for heavy equipment, an extended working season in wet climates, and stability of soil embankments and engineered fill. Lime is spread on the soil, mixed into the upper 30 cm of soil, and, finally, compacted. When quicklime hydrates on application, lime offers a relatively immediate reaction time (4 to 24 hr). During the hydration process, the quicklime absorbs water and generates heat, providing additional evaporation.

In the modification of clay-rich soils, the desired reaction typically occurs within a time span measured in hours. Specifically, soil modification is an ion exchange between the calcium cation supplied by lime and the sodium and potassium cations contained in the clay. After flocculation and agglomeration of the soil has occurred, plasticity and swelling are reduced, and friability is increased, making the soil easier to work and compact and reducing the ability of soils to retain moisture.

In soil stabilization, lime is mixed with soils to react with siliceous and aluminous soil components, generating long-term increases in soil strength resulting from a pozzolanic effect. Early in the reaction, the formation of hydrous colloids and gels slowly crystallize into calcium silicates and calcium aluminates. The reaction can continue over long periods of time, providing the pH remains high and as long as lime is present. The amount of lime applied to soils for stabilization ranges from 3% to 5% of dry soil weight. When hydrated lime is used, it typically is applied in slurry form. Slaked lime slurries made with pebble quicklime may also be used; however, when using quicklime, it is critical that it be soft-burned, high-calcium lime with less than 10% residue on slaking. Low-residue lime produces higher cure strengths in soils than does lime with large residues. All federal agencies and most state highway departments have recognized the advantages of soil stabilization with lime, and thousands of kilometers of interstate highways in the United States have benefited from this system.

The application of lime for soil stabilization provides soils that are homogeneous, impermeable, and stable. Soil stabilization with lime also reduces soil plasticity and the amount of density changes (shrinking and swelling). In addition, lime applied to soils will increase soil compressibility, tensile strength, and flexural strength. Sites that are good candidates for soil stabilization using lime include roads, runways, parking lots, temporary haul roads, landfills, and building foundations and/or footings.

Lime Fly Ash (Lime Kiln Dust). Lime kiln dust (LKD) mixes were first introduced by the Corson Company in a proprietary process called Poz-O-Pac. Since then, LKD pozzolanic mixes have achieved increased acceptance with their success. In this process, lime is mixed with kiln dust, aggregate, and a small amount of water, usually in a pug mill, at a central mix plant. Controlling moisture is critical for the proper pozzolanic reaction and the resulting level of strength in the subgrade. The product may then be laid down either with standard paving equipment or by utilizing a compaction method.

Mortar. For thousands of years, lime was used in mortar and continues to be used even today. Before the advent of portland cement in the late 19th century, mortars were composed of lime and

sand. Today lime-cement mortars are used with varying proportions, ranging from one-quarter to three parts of lime by volume to one part of cement. Lime is still the most dependable plasticizer for mortar, making it workable and more trowel-able, or cohesive. In the cement-lime mixes, the cement provides the rapid set. These type of masonry mixes, however, encounter severe competition from masonry portland cements.

A similar application for lime is found in plasters. At one time it was used in base plaster coats, but these generally have been replaced with gypsum wallboard. In interior plastering today, lime is still used in the finish, or white coat, and is usually mixed with gypsum. In California and Florida, or other places with warm climates, lime also is used in exterior plaster or stucco as a mixture with portland cement and sand in varying proportions.

Asphalt. The addition of 1% to 1.5% of hydrated lime to asphalt hot mixes has a number of advantages in road construction. Lime acts as an anti-stripping agent, preventing the aggregate from raveling from the bituminous cement binder in the presence of water. In reducing the asphalt's sensitivity to water, cracking and potholes are reduced. In remote areas, lime permits the use of marginal, unwashed aggregates, and, where necessary, it serves as filler. Based on the immersion compression test with some asphalts and aggregates, lime markedly increases the wet/dry strength ratio and reduces volume change (swelling and shrinking). Lime-charged asphalt mixes prevent oxidation of the asphalt binder and the effects of aging, such as brittleness and cracking. In improving the stiffness of the asphalt binder, the tendency toward rutting is reduced.

Hot lime slurry is now being added to the asphalt emulsion in cold in-place recycling of distressed asphalt pavements. This mixture is placed and compacted using conventional paving techniques, providing a smooth base for the new asphalt surface. Lime use in cold in-place recycling adds greater early strength and resistance to moisture damage.

The American Society for Testing and Materials' (ASTM's) committee on lime, Committee C07, has adopted specifications for the use of hydrated lime in asphalt and asphaltic concrete mixtures. Nevertheless, professional biases within the construction industry continue to foster some resistance to the use of lime in asphalt, even though its advantages are well known.

Agriculture

Since Roman times, lime was used in farming. Today the role of lime in agriculture is expanding.

Sugar Refining. Although sugar refining normally is included with most chemical or industrial lime use statistics, in reality it is an agricultural application. Lime is essential for making sugar in both sugar beet and cane sugar refining processes. Sugar beet refining requires a significantly higher volume of lime than does cane sugar. On average, beet sugar requires 200 kg of quicklime per ton of sugar, whereas cane sugar requires only 1.9 to 4.9 kg/t of lime. During sugar refining, milk-of-lime raises the pH of the product stream, precipitating colloidal impurities. These impurities, normally phosphatic and organic acid compounds, are removed from the stream by filtration. Most sugar beet plants have captive lime plants onsite so that CO₂ kiln stack gas resulting from limestone calcination can be captured and used during carbonation in the sugar refining process.

Agricultural Lime. Although most agricultural liming today is achieved with pulverized limestone, some farming still uses ground quicklime or hydrated lime. This is particularly true in truck farming where lime is able to neutralize soil acidity more rapidly and maintain a pH level that allows for three crops to be grown per year. The added cost for lime is easy to justify in higher value

Table 6. U.S. lime industry statistics

Statistic	Year				
	1980	1985	1990	1995	2000
Quicklime sold or used, <i>ktpy</i>	17,200	14,200	15,800	18,500	20,100
Number of lime plants	153	119	113	113	107
Average kilotons per plant	112.4	119.3	139.8	163.7	187.8
Average selling price, \$/t	49.00	57.00	57.10	59.50	60.60
Average selling price, constant 1998 \$/t	97.00	86.40	71.20	63.60	57.37

crops. In some sandy soil areas, only dolomitic lime is used, because of persistent magnesium deficiencies.

Feedlot Applications. Corporate farming and husbandry practices over the past several decades have led to the establishment of large facilities for raising farm animals in rural areas. Attention has been drawn to environmental issues, including the facilities' potential impacts on public water supplies, and the concerns of nearby residents. Federal and state agencies dealing with environmental quality now regulate the effects—mostly from animal waste products—that swine waste lagoons, cattle feedlots, and chicken farms, for example, may have on rural areas. Applying lime to wastewater effluent or feedlot soils increases their pH and temperature to high enough levels to destroy most harmful bacteria and viruses and reduces unpleasant odors associated with animal wastes. In addition, lime applied to areas affected by animal wastes fixes hazardous pollutants and helps to decrease harmful nitrogen (ammonia) levels. Quicklime hydrates when applied to animal waste sludge, resulting in water absorption and heat generation that provides additional evaporation. Lime also imparts strength to the sludge, making it easier for landfill disposal or composting.

Other. Lime is used as a CO₂ absorbent in controlled atmospheric storage for fresh fruit and certain vegetables to extend the freshness of the produce. This prevents CO₂ from building to abnormally high levels, which would accelerate the rotting of produce. Lime is also used to recover glue and gelatin from packing house by-products. In citrus fruit processing, lime is employed to treat the waste pulp, which, after grinding and drying, is sold as cattle feed.

Specifications and Testing

Because of the many types and uses of lime, plus their wide variety of physical and chemical characteristics, there are different specifications for lime products for most major consumers, even for individual companies or plants.

The National Lime Association, along with its member companies and the majority of lime consumers, subscribes to ASTM specifications on lime, promulgated by Committee C07. The specifications cover many uses and testing procedures:

- C25-99: Standard Test Methods for Chemical Analysis of Limestone, Quicklime, and Hydrated Lime
- C50-00: Standard Practice for Sampling, Sample Preparation, Packaging, and Marking of Lime and Limestone Products
- C51-05: Standard Terminology Relating to Lime and Limestone (as used by the industry)
- C110-05: Standard Test Methods for Physical Testing of Quicklime, Hydrated Lime, and Limestone
- C400-98: Standard Test Methods for Quicklime and Hydrated Lime for Neutralization of Waste Acid

- C593-95(2000): Standard Specification for Fly Ash and Other Pozzolans for Use with Lime
- C602-95a(2001): Standard Specification for Agricultural Liming Materials
- C706-02: Standard Specification for Limestone for Animal Feed Use
- C737-02: Standard Specification for Limestone for Dusting of Coal Mines
- C821-78(2000): Standard Specification for Lime for Use with Pozzolans
- C911-99: Standard Specification for Quicklime, Hydrated Lime, and Limestone for Chemical Uses

Although these are some primary tests and specifications for lime, it is not a complete or comprehensive list. For a complete listing, the reader is referred to ASTM in West Conshohocken, Pennsylvania (www.astm.org). For a quick reference on some European (CEN) and British (BS) specifications, see Oates 1998.

Another important lime specification promoted by the American Water Works Association (AWWA; <http://www.awwa.org>) is ANSI/AWWA B202-02 on quicklime and hydrated lime (AWWA 2002). This includes a bonus and penalty arrangement based on available lime content, slaking rate, and slaking residue. It also applies to sewage and industrial waste treatment plants.

ASTM procedures are used in testing lime intended for FGD; however, many specifications are based on U.S. Environmental Protection Agency (EPA) performance standards and apply to a specific utility. Consequently, individual utility customers may have specifications that exceed normal ASTM standards.

Product Pricing

Lime is considered a commodity mineral that has low to moderate unit value and high place value. Table 6 shows the trends in the U.S. lime industry over the last two decades (Krukowski 2004). As the industry took advantage of economies of scale, the number of plants producing lime decreased while increasing domestic production. As a result, the average annual output per plant increased from 112,400 to 187,800 t over the time period 1980 to 2000. In that same period, the actual average selling price rose from \$49.00 to \$60.60/t; however, the average selling price in constant 1998 dollars went from \$97.00 to \$57.37/t, primarily because of overcapacity.

During the period from 1910 to 1970, lime pricing was relatively constant and rarely exceeded \$15/t f.o.b. at the lime plant. Beginning in 1970, lime prices increased steadily because of fuel costs and government-mandated environmental controls. In 1974 the oil embargo initiated a substantial increase in energy costs, which were clearly reflected in the costs of production and, consequently, the cost of lime.

The average values per ton of various types of lime, rounded to three significant figures, are listed in Table 7. The data are reported by type of lime produced: high-calcium quicklime, high-calcium hydrate, dolomitic quicklime, dolomitic hydrate, and dead-burned dolomite. Emphasis is placed on the average value per metric ton of lime sold.

On average, prices rose by 4% in 2003, to \$64.80 for all types of lime sold per metric ton (\$58.80/st). This is the first significant evidence of price increases by major lime companies since 2001 (Miller 2003), which were instituted to compensate for increased costs of raw materials, environmental compliance, labor, and health care. The average value per ton of high-calcium quicklime, dolomitic quicklime, and dolomitic hydrate all increased, but the average value of high-calcium hydrate and dead-burned dolomite decreased. It is anticipated that a rise in fuel costs may lead to higher lime prices, especially when natural gas is burned; for

example, some lime plants stopped operating in 2001 when natural gas prices peaked.

Lime prices can be affected by whether contracts between buyers and sellers are long or short term. Long-term contracts tend to give the buyer an advantage if the seller is guaranteed demand for the product. Many factors can influence the price of a commodity, including the following:

- Economic climate (e.g., times of economic growth versus recession)
- Oversupply (e.g., when markets are saturated after new plants come on-line)
- Cost of production (e.g., when fuel costs increase)
- Competition from product substitutes
- Customer product specifications
- Distances to points of consumption

Substitutes

Limestone is a substitute for lime in many applications, such as agriculture, fluxing, and sulfur removal (e.g., in FGD). The advantage of limestone is its lower cost, but it is less reactive in terms of time and material (tonnage). In many chemical applications, NaOH may substitute for lime, especially in cases where pH control is concerned; however, hydrated lime is a diacid base, so smaller quantities are needed in some applications (e.g., acid neutralization).

Ground calcium carbonate (GCC) is a substitute for PCC in paper, PVC plastic products, and paint and other pigments.

Calcined gypsum is an alternative material in industrial plasters and mortars. Cement and LKD and fly ash are potential substitutes for some construction uses of lime; for example, in soil stabilization and hot-mix asphalt. Some organic compounds also may take the place of lime in soil treatment roles. Portland cement mortars have been a traditional alternative to lime in its use as masonry cement.

Magnesium hydroxide is a substitute for lime in pH control, and magnesium oxide is an alternative for dolomitic lime as a flux in steelmaking.

Recycling

Large quantities of lime (90% to 96%) are regenerated by pulp paper mills. Some municipal water treatment plants recycle lime from softening sludge. In the carbide industry, quicklime is regenerated from waste hydrated lime. In the production of caustic soda, lime is recycled for use in the chemical process.

Packaging and Transportation

Because of their large particle sizes, lump, crushed, pebble, or pelletized limes are rarely handled in bags. Therefore, most quicklime is shipped in bulk. Bags are made of multiwall paper with capacities of 22.7 kg (50 lb) or 36.4 kg (80 lb), and bulk bags up to 1.8 t (2 st). The finer sizes of quicklime (fine, granular, and pulverized) are shipped in bulk or in bags.

For many years, railroads were the primary carrier for bulk lime in the United States. The convenience of truck transport on U.S. interstate highways, however, reduced significantly the volume of bulk lime delivered by rail. Trucks used for shipping bulk lime are typically pneumatic tank carriers that can provide both an enclosed container and a safe handling system so the operator can avoid direct contact with the product. While truck and rail shipments are used to ship most bulk lime, an increasing amount is moved by barge on inland waterways.

In a number of locations, intermodal shipments of lime take advantage of barge and rail rates with low unit costs over long dis-

Table 7. Lime prices*

Type	2002		2003	
	\$/t	\$/st†	\$/t	\$/st†
Sold and used				
Quicklime	59.20	53.70	61.30	55.70
Hydrate	88.50	80.30	84.80	77.00
Dead-burned dolomite	86.70	78.70	90.80	82.30
Average all types	62.60	56.80	64.90	58.80
Sold				
High-calcium quicklime	58.50	53.10	61.00	55.40
Dolomite quicklime	59.80	54.20	62.10	56.30
Average quicklime	58.70	53.30	61.20	55.50
High-calcium hydrate	86.20	78.20	81.20	73.70
Dolomite hydrate	97.40	88.40	102.70	93.20
Average hydrate	88.60	80.40	84.90	77.00
Dead-burned dolomite	94.30	85.50	92.10	83.50
Average all types	62.30	56.50	64.80	58.80

Source: Miller 2003.

* Average value per ton, on an f.o.b. plant basis, including cost of containers.

† Conversions were made from unrounded metric ton values and may not be conversions of the rounded values.

tances. In these systems, bulk lime cargoes are unloaded at barge or rail terminals, stored in silos, then later transferred to pneumatic tank trucks for local delivery. For small customers located beyond the railroad or waterway, these systems allow them to take advantage of bulk transportation rates.

Although most lime is transported in bulk, hydrated lime frequently is packaged and shipped in bags or bulk bags. Paper bags weighing 22.7 kg (50.0 lb) normally contain a polyethylene liner to protect the lime from moisture and to ensure its satisfactory performance for the consumer. Bulk bags weighing 900 kg (1 st) lack the flexibility of sizing to customer requirements and may be larger or smaller in capacity. A variety of bulk containers include one-way and returnable bulk bags, cardboard "gaylords," and reusable metal containers.

Because of quicklime's affinity for water, and because it may slake by absorbing moisture from ambient humidity (air slaked), lime is considered a perishable product. It is recommended that quicklime not be stored in bags for more than 3 months, although it can be held for as much as 6 months. To protect quicklime from moisture, storage containers and transport media must be watertight. Bulletin 213 from the National Lime Association (1995) provides excellent discussions on the handling and storage of lime.

Economic Factors

Tariffs and Duties; Depletion Allowance

In the United States, the depletion allowance for limestone produced and used for lime from both domestic and foreign production is 14%. Under normal trade relations, there are no tariffs on quicklime, slaked lime, and hydraulic lime; however, there is a 3% ad valorem tariff on calcined dolomite. There is no U.S. government stockpile.

By-products

LKD is composed of very fine particulates trapped in air pollution control systems of rotary kilns used to manufacture lime. It is a mixture of dust from finely ground limestone kiln feed and fly ash from fuel (coal, fuel oil, natural gas) used for combustion in kilns.

If it contains a minimum amount of calcium oxide, LKD can be successfully employed in asphalt hot mix and for soil stabilization. Although it also has been used as an agricultural soil amendment, a complete chemical analysis is necessary before it is applied to agricultural soils to ensure the absence of any harmful elements. LKD may also be used for lightweight aggregates or as fill material.

Carbon dioxide generated from the dissociation of calcium carbonate in lime kilns is captured and used in the production of PCC. It is also captured from lime kilns in the sugar industry and used in the carbonation process in refining sugar from sugar beets.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Health and Safety

All mining and related activities in the United States are regulated by and come under the jurisdiction of the Mine Safety and Health Administration (MSHA). MSHA administers the provisions of the Federal Mine Safety and Health Act and enforces compliance with mandatory safety and health standards for the following purposes:

- Eliminating fatal accidents
- Reducing the frequency and severity of nonfatal accidents
- Minimizing health hazards
- Promoting improved safety and health conditions in the nation's mines

Persons working in mining operations, including the lime industry, must complete required health and safety MSHA training followed by annual refresher courses.

Short-term goals for MSHA include the reduction of respirable silica dust exposure in metal and nonmetal mines and the reduction of noise exposures. To maintain compliance, lime operators must monitor their plants and personnel. For these reasons, federal and state mine inspectors are required to visit mining operations on a regular basis and may arrive unannounced.

When water is applied to quicklime, its reaction may generate enough heat to cause paper, wood, or cloth to combust. Quicklime is classified as a Class E corrosive material that can destroy the skin and/or eat through metals. Additionally, it can cause severe eye and skin irritation on contact; cause severe tissue damage with prolonged contact; and may be harmful if inhaled. Proper personal protection equipment must be used in appropriate situations when close contact is anticipated.

Mining Regulation

Federal and state governments in the United States regulate the mining industry. This includes issuing mining permits that comply with statutes and regulations of the governing body. A permit is issued when the mine operator submits an acceptable application and posts adequate bond to cover reclamation costs. The mining permit application must include the requirements for legal and financial compliance, the safeguard of environmental resources, and an operations and reclamation plan. Bonds are not released until mine reclamation is complete.

Part of the permitting process typically allows for public notification and participation; the latter may include filing a protest against a pending permit or revision. Public meetings, usually held at a location close to the permit area, may be part of the process that includes participation of the public, the permit-issuing government agency, and the mine permit applicant. The first responsibility of the issuing agency is to ensure both statutory and regulatory compliance by the permit applicant; however, mine operators generally work with their neighbors and are willing to address their concerns. Nevertheless, it is the obligation and responsibility of prospective mine operators to know the laws and regulations under which they

must operate. See the section on Evaluation of Limestone Deposits in this chapter as well as the Limestone and Dolomite chapter in this book.

Air Quality Considerations

On August 25, 2003, the EPA issued a final rule to reduce toxic air pollutant emissions from new and existing lime plants. The rule was authorized by Section 112(c) of the Clean Air Act and set limits on hazardous air pollutants (HAPs) from commercial lime plants, captive lime plants at steel mills, captive lime plants at non-ferrous metal production facilities, and producers of dead-burned dolomite. The EPA has identified the lime industry as a source of HAP emissions that include hydrochloric acid and the metals antimony, arsenic, beryllium, cadmium, chromium, lead, manganese, mercury, nickel, and selenium.

The final rule set particulate matter (PM) emission limits for lime kilns, lime coolers, and mineral-processing operations with stacks. PM is not a HAP but is considered a permissible surrogate for HAP metals. The PM emission limit for kilns and lime coolers is 0.10 lb/st of stone feed at a new lime plant, 0.10 lb/st at existing lime plants, and 0.60 lb/st of stone feed at lime plants with wet scrubbers (EPA 2003). The final rule went into effect with its publication in the *Federal Register* on January 5, 2004. Although the compliance date for existing lime plants will be January 5, 2007, new plants will have to comply immediately (Miller 2003).

OUTLOOK AND FUTURE TRENDS

Because lime is a commodity chemical with a myriad of applications in many industries, the long-term forecast is excellent. The U.S. lime industry is currently at production capacity and lime prices are increasing, a trend that began in 2001. Future success will depend on the ability of the industry to develop new markets.

Johnson and Roden (2003) recognized that environmental applications will continue to be the major growth area for lime in the future. Since passage of the 1990 Clean Air Act Amendments, the focus over the last 10 to 15 years has been on FGD. The EPA's Maximum Achievable Control Technology (MACT) program will likely continue to identify and implement tighter regulation of air pollutant emissions, including sulfur dioxide. This will especially be true for coal-fired electrical power-generating plants, but a broader base of pollutant emitters will be targeted beyond the utility companies. As the technology of smokestack scrubbing advances over time, the demand for lime and its application in this field should increase. The use of lime for the mitigation of stack pollution may be supplanted by other substances (unknown at present), but it still may find application in other sectors of the process (e.g., sludge treatment and control). Alternatively, Johnson and Roden (2003) speculate that lime may replace existing environmental treatment solutions that use more expensive and/or less effective reagents (e.g., caustic and magnesium hydroxide).

Environmental applications are not restricted to air pollution applications such as FGD. The Clean Water Act and enforcement efforts by both federal and state water quality departments will put tighter restrictions on municipal and industrial sewage and wastewater treatment plants as point-source polluters, thus expanding lime markets for environmental application. Additionally, lime's neutralizing effect can be used to control pH in acid lakes and reservoirs, which will positively affect aquatic life and make these bodies of water safe for recreation.

In solid waste management, lime will have a larger role in treating sewage biosolids and animal wastes, along with industrial sludge and solid hazardous wastes. Although its use in sewage treatment is well known, lime also is applied to biomedical, or hospital,

waste. (See the Environmental and Agriculture subsections in this chapter.) In the treatment of solid hazardous waste, lime stabilizes most metals to prevent their leaching into groundwater. The EPA has identified lime as suitable for pretreatment of hazardous wastes prior to landfill disposal. Stabilization and precipitation often are required of metals contained therein, and the EPA has endorsed lime for the task.

The lime industry is marketing its product for construction uses more aggressively. Two primary areas of focus are in soil stabilization and modification and in asphalt hot mix for highway construction. If the Transportation Equity Act for the 21st Century (TEA-21) is extended by the U.S. Congress, federal highway funding will be available for construction of U.S. highway systems. This means that increased amounts of lime will be necessary for road base stabilization and for the use of lime in asphalt hot mix for asphalt concrete.

In *Industrial Minerals and Rocks*, 6th edition, Freas (1994) discussed the implementation of statistical process control (SPC) and integrated process control (IPC) on the production side of lime manufacture. Much of the upgrades achieved in the 1990s in the industry included these concepts. The lime industry continues to upgrade its production facilities through refinements in software packages, which should lead to increased energy efficiency, reduced personnel, and a more consistent quality product.

Tables 8 and 9 illustrate additional trends in the U.S. lime industry. In the past, the means of production was domestically owned and dominated by family-run companies, while now it is dominated by large, foreign-owned, international corporations. In 1900, many small lime plants produced low tonnages, but today, the industry produces lime from a few large plants producing large tonnages. In the past, the plants were located as close to the consumer as possible, but today, although still relatively close to consumers, plants are closer to the resource, mainly because of advances in transportation.

Although the United States lagged behind the rest of the industrialized world in these trends, in the last 20 years the U.S. lime industry has learned to take advantage of economies of scale (the bottom line) and has seen more international ownership.

The consolidation within the lime industry and expanded foreign ownership of U.S. lime producers will probably continue, but at a slower pace.

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ADDITIONAL RESOURCES

Because lime is one of the oldest materials known to humans, and its end-use pattern is diverse, the literature on lime is so extensive that it is impossible to give a complete bibliography. Many earlier bibliographical references can be found in the Lime chapters in the 5th and 6th editions of *Industrial Minerals and Rocks*. The following list of sources presents some general references as well as specific citations in the text. For the latest and up-to-date information on the industry, the following trade periodicals are excellent resources: *Rock Products*; *Pit and Quarry*; *Global Cement and Lime*; *Gypsum Lime and Building Products*; *Zement-Kalk Gipps*; and various USGS publications.

Table 8. U.S. lime production in the 20th century

Year	Production, t	Number of Plants	Major Uses	Major Producing States
1900	1,800,000	>1,000	Construction and building trades	Ohio and Pennsylvania
2000	19,600,000	107	Steel, environmental, chemical	Kentucky and Missouri

Table 9. U.S. lime industry trends during the 20th century

	Early 20th Century	Late 20th Century
Ownership	Family-owned or U.S.-owned	Large corporations, owned internationally
Plants	Numerous and small	Few and large
Production	Low tonnage	High tonnage
Plant capacity	Small	Large
Location	Near user	Near resource
Price, 1998 \$	Increasing	Decreasing*

* Lime prices began to increase in 2001.

Today, the Internet serves as the primary reference tool for many. The National Lime Association (NLA) maintains a Web site that lists many references for lime and its uses. Many NLA publications can be downloaded from the Web site, and interested readers are encouraged to do so. The NLA lists several excellent Web sites belonging to members that assist lime customers and inform the general public about lime products and their uses. A list of pertinent Web sites follows.

- American Water Works Association, Denver, CO: <http://www.awwa.org>
- Asphalt Institute, Lexington, KY: <http://www.asphaltinstitute.org>
- European Asphalt Pavement Association, Breukelen, the Netherlands: <http://www.eapa.org>
- National Lime Association, Arlington, VA: <http://www.lime.org>
- U.S. Department of Agriculture National Soil Survey Center (Natural Resources Conservation Service), Washington, DC: <http://soils.usda.gov>
- U.S. Department of Energy, Washington, DC: <http://www.energy.gov>
- U.S. Department of Labor, Mine Safety and Health Administration, Washington, DC: <http://msha.gov>
- U.S. Environmental Protection Agency, Washington, DC: <http://www.epa.gov>
- U.S. Geological Survey, Minerals Information Home, Commodities, Lime, Washington, DC: <http://minerals.usgs.gov/minerals/pubs/commodity/lime>

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Limestone and Dolomite

Robert C. Freas, John S. Hayden, and Charles A. Pryor Jr.

Limestone and dolomite constitute a group of raw materials commonly referred to as carbonate rocks. They represent the basic materials from which cement, lime, most building stone, and a significant percentage of crushed stone are produced. Carbonate rocks, and their derived products, are used as aggregates, fluxes, glass raw material, refractories, fillers, reactive agents in sulfur-oxide removal, abrasives, soil conditioners, and in a variety of other market applications, many of which are covered in this edition.

Carbonate rocks form about 15% of the earth's sedimentary crust and are widely available for exploitation. Found extensively on all continents, they are quarried and mined from formations that range in age from Precambrian to Holocene. Reserves of carbonate rock are large and will last indefinitely, although high-purity deposits may be absent or have limited availability in certain states and regions.

Limestone and dolomite are so useful and so abundant that in 2002 about 1.6 billion t were produced in the United States. In fact, about 71% of all stone quarried or mined in the United States was carbonate rock. Sand and gravel was the only mineral commodity produced in greater quantity.

This chapter is an overview of carbonate rocks and their composition, distribution, production, and uses. The literature on limestone and dolomite resources of the United States and Canada is so vast and diverse that one can easily become mired in print. The authors have tried to list those references that are easily accessible and serve as a starting point for more intensive study. Additionally,

the selected references on limestone and dolomite resources in Canada and the United States reflect the effort to be selective rather than exhaustive and to direct the reader to the best sources of detailed information. The reader is also referred to other chapters in this volume that provide additional information on limestone and its uses, including the chapters on Lime and various chapters on Construction Uses.

GEOLOGY

Mineralogy

Limestone and dolomite are the principal carbonate rocks used by industry. Limestones are sedimentary rocks composed mostly of the mineral calcite (CaCO_3), and dolomites are sedimentary rocks composed mostly of the mineral dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$). Aragonite (CaCO_3), which has the same chemical composition as calcite but a different crystal structure, is economically important only in modern deposits such as oyster shells and oolites. Aragonite is metastable and alters to calcite in time. Some other carbonate minerals, notably siderite (FeCO_3), ankerite ($\text{Ca}_2\text{MgFe}(\text{CO}_3)_4$), and magnesite (MgCO_3), are commonly found associated with limestones and dolomites but generally in minor amounts.

Because of their similar physical properties, the carbonate minerals are not easily distinguished from one another. Specific gravity, color, crystal form, and other physical properties (see Table 1) are aids to mineral identification if the rock is relatively monomineralic and compact. Further information on the chemical,

Table 1. Physical properties of some common carbonate minerals

Mineral	Physical Properties	Common Color
Calcite (CaCO_3)	Hexagonal crystal system, commonly good rhombohedral cleavage. Mohs hardness, 3; specific gravity, 2.72.	Colorless or white but may be other colors because of impurities
Dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$)	Hexagonal crystal system, commonly good rhombohedral crystals with curved faces. Mohs hardness, 3.5–4.0; specific gravity, 2.87.	White or pink
Aragonite (CaCO_3)	Orthorhombic crystal system. Mohs hardness 3.5–4.0; specific gravity, 2.93–2.95.	Colorless, white, or yellow, but may be other colors because of impurities
Siderite (FeCO_3)	Hexagonal crystal system, commonly distorted rhombohedral crystals. Mohs hardness, 3.5–4.0; specific gravity, 3.7–3.9.	Brown or black
Ankerite ($\text{Ca}_2\text{MgFe}(\text{CO}_3)_4$)	Hexagonal system, commonly rhombohedral crystals. Mohs hardness, 3.5–4.0; specific gravity, 2.9.	White, pink, or gray
Magnesite (MgCO_3)	Hexagonal, usually in granular or earthy masses. Mohs hardness, 3.5–4.5; specific gravity, 2.96–3.1.	White or yellowish but may be other colors because of impurities.

mineralogical, and physical properties of carbonate minerals can be found in Graf and Lamar (1955) and Tucker and Wright (1990).

The rate of solubility of the different carbonate minerals in dilute hydrochloric acid is perhaps the most useful technique to identify them in the field. Calcite is much more soluble in dilute acid than dolomite; hence, if a fresh rock surface is etched, the amount of dolomite left standing in relief can be estimated using a hand lens. Some staining techniques are based on differences in solubility of the carbonate minerals (in decreasing order of solubility: aragonite, calcite, and dolomite). These staining techniques are useful in the laboratory but have limited application in the field (Friedman 1959; Warner 1962). Thin-section staining is particularly effective in the laboratory (Dickson 1965, 1966).

The x-ray diffractometer is commonly used in the laboratory for determining carbonate mineralogy of bulk samples. Cullity (1956), Azaroff and Buerger (1958), Gulbrandsen (1960), Graf and Goldsmith (1963), Muller (1967), and Runnells (1970) describe techniques for determining calcite and dolomite ratios or the percentage of these minerals based on comparison of their diffraction intensities with those of known standards.

Thin-section analysis may be a helpful adjunct to binocular examination of carbonate rocks. Although it is difficult to distinguish between calcite, dolomite, and ankerite in thin section unless staining techniques are used, identification of other minerals, types of carbonate grains, fabrics, textures, and structures is sometimes facilitated by this method (see also section on Physical Properties in this chapter). Appropriate parts of Carozzi (1960) and Hatch and Rastall (1971) introduce microscopic investigation of carbonate rocks, as does the review by Gubler et al. (1967), and Adams and MacKenzie (1998). Good references for assistance in identifying fossils and fossil fragments in thin section are Horowitz and Potter (1971) and Scholle (1978).

Color, an important property of carbonate rocks, can be a rough guide to purity, but it also can be misleading. Only a small amount of noncarbonate material is necessary to produce a marked change in color. The famous building stone called Indiana Limestone, for example, with its distinct gray and buff colors, commonly contains less than 0.2% Fe_2O_3 (iron oxide). Carthage Marble, a fossiliferous dimension limestone from Missouri in shades of gray, generally has a total iron and aluminum oxide content of less than 0.2%. Limestones in shades of gray or green generally indicate the presence of minerals containing iron oxides or carbonaceous matter. As the state of oxidation increases, the colors change to yellows, browns, or reds. A color reference chart is useful in maintaining uniformity of rock descriptions, and one of the most useful is available from the Geological Society of America (Goddard et al. 1963).

Impurities in carbonate rocks vary considerably in type and amount but are important from an economic standpoint only if they affect the usefulness of the rock. Generally, the two most important considerations of each impurity are how much is present and how it is distributed. A considerable amount of some impurities is tolerable in carbonate rock for some uses if the impurity is disseminated throughout the rock. But if the impurity is concentrated in laminae, it may form planes of weakness that seriously affect the performance of the rock.

Clay is perhaps the most common impurity in carbonate rocks. The clay minerals, mainly kaolinite, illite, chlorite, smectite, and mixed-lattice types, may be either disseminated throughout the rock or concentrated in laminae or thin partings. The basic molecular building blocks of clay minerals are silica tetrahedra (a silicon atom and four oxygen atoms) and alumina or magnesium octahedra (an aluminum or magnesium atom and six hydroxyl ions). Other

chemical elements are incorporated into the structure, however, so it is difficult to determine the type of clay mineral by chemical analysis alone. If clay mineral identification is important, other analysis techniques such as x-ray diffraction, differential thermal analysis, and electron microscopy can be used. The clay chapters of this volume give a comprehensive review of clay minerals.

Chert is another common impurity in carbonate rocks and can be disseminated as grains throughout the rock or concentrated in nodules, lenses, or beds. It is composed mainly of very fine grained quartz (SiO_2) that may appear under the microscope as minute sub-equant crystals, usually 1 to 10 μm in diameter (microcrystalline quartz), or as radiating fibers (chalcedonic quartz). Chert easily incorporates impurities, including water, into its structure so that it can be found in almost all colors; its surface texture can range from dense or porcelainous to porous or earthy. Dense cherts have a Mohs hardness of 7 and high impact toughness, which make them particularly abrasive to crushers and other processing equipment. Porous cherts, mainly because of their large surface area available for chemical reaction and moderate solubility in alkalies, are considered deleterious components in aggregates used in concrete. Dunn and Ozol (1962) give comprehensive coverage of the deleterious properties of cherts.

Silica is also found in carbonate rocks as discrete silt- or sand-size grains of the mineral quartz. These grains may be disseminated throughout the rock or concentrated in laminae and beds. Detrital limestone especially may contain a considerable percentage of quartz silt and sand. These grains can act as the nuclei for coated carbonate grains, such as some oolites and pisoliths.

Finely disseminated organic matter is a common constituent of limestones and dolomites and can give the rock a pronounced brown or black color. Bituminous material, an organic derivative of petroleum and residue of former pore fluids, can be present in sufficient quantity to make the rock undesirable for some uses.

Thin-section and insoluble-residue studies reveal trace amounts of a wide variety of other minerals in most carbonate rocks. Although these trace minerals may affect the economic usefulness of rocks used for chemical purposes, such as glass manufacture, they have little effect on rocks used principally because of their physical properties, as in construction materials.

Origin

Most limestones of economic importance were partly or wholly biologically derived from seawater and accumulated in a relatively shallow marine environment. The obvious skeletal material in limestones speaks of a biologic origin, but even nondescript, fine-grained material may derive from the life of organisms. Pellets in many instances are fecal material, and silt- and clay-size particles may be aragonitic-sheath crystals released upon the death of algae. Oolites, which in the past have largely been thought to be the inorganic accumulation of calcium carbonate around a nucleus, may also depend in part on algal activity.

In some places, lime-secreting organisms such as corals, calcareous algae, and mollusks erect large, wave-resistant structures called reefs. The biologically active parts of these structures are generally near the edge of shallow marine shelves where upwelling currents supply nutrients for the growth of the organisms. In other places along such shelves, small skeletal particles or other material can become coated by concentric layers of calcium carbonate to form oolites. Oolites develop best in the high-energy zone of shelves where water currents agitate the grains, and as the oolites build up the y form elongate lenticular bars that nearly reach the water surface. Very fine grained carbonate muds (micritic limestone) derived from the comminution of coarse skeletal material

or precipitated directly from seawater, accumulate in low-energy environments such as lagoons or deep water.

The depositional environment is significant because it determines the size, shape, purity, and other economically significant characteristics of the carbonate rock deposit. Limestones that form in high-energy zones generally contain little noncarbonate material and hence may be the source of high-purity carbonate material. Micrite, which accumulates in zones of low energy, is more likely to be diluted by clay and silt-size noncarbonate material.

Carbonate sediments are highly susceptible to postdepositional alteration and modification. The origin of dolomite is especially significant to the geologist. Although some dolomite may be precipitated directly from seawater, most dolomite is a result of the alteration of calcium carbonate sediments or rocks by hypersaline brines. Good examples are the almost-pure dolomite Silurian reefs in northern Illinois, Indiana, and Ohio, and in southern Michigan.

The depositional environment and postdepositional history of carbonate rocks are best understood by studying modern carbonate deposition. The general reviews by Baars (1963), Ginsburg et al. (1963), and Milliman (1974) are good references for this information. For further information on locations and distributions of modern carbonate sediments, the summaries by Graf (1960a, 1960b, 1963) are useful; the comprehensive discussions of the origin and occurrence of carbonate rock in the papers compiled by Jordan (1978) and Scholle, Bebout, and Moore (1983); in the book by Wilson (1975); and the reviews of limestone by Sanders and Friedman (1967) and of dolomites by Friedman and Sanders (1967) fill the gaps of the other coverages. Tucker and Wright (1990) provide good coverage of carbonate sedimentology.

Classification

The explosive growth in the study of modern carbonate sedimentation from the late 1950s to the present has had a notable effect on carbonate rock classification. Numerous classification schemes have emerged based on this new-found information, such that carbonate rock descriptions are now more explicit and more conducive to genetic interpretation than ever before.

Many aspects of carbonate rocks can be used as the basis of a classification scheme, but perhaps the most useful are composition and texture. Composition can be thought of in terms of mineralogy, types of fossils or grains, or chemical constituents. Texture refers to both depositional and postdepositional features such as relative proportions of framework grains and lime mud, grain size, cement, and pores.

Carbonate rocks are rarely monomineralic in nature; thus, a mineralogical classification of these rocks needs to consider variation in amounts of calcite, dolomite, and noncarbonate materials (see Figure 1). Such a classification is useful in rock descriptions, especially when combined with textural parameters, but it commonly is not sufficient for industrial purposes. Although limestone and dolomite can be used equally well for many purposes, certain uses have special chemical requirements. These special requirements are stated in terms of chemical composition rather than mineralogical composition and specify the quantity of CaCO_3 (or CaO , calcium oxide) and MgCO_3 (or MgO , magnesium oxide) or both in the rock along with the maximum percentage of impurities that can be tolerated. A practical chemical classification considers that ultra-high calcium limestone is more than 97.5% CaCO_3 , high-calcium limestone is more than 95% CaCO_3 , high-purity carbonate rock is more than 95% combined CaCO_3 and MgCO_3 , and high-magnesium dolomite is more than 43% MgCO_3 (theoretically pure dolomite is 45.7% MgCO_3).

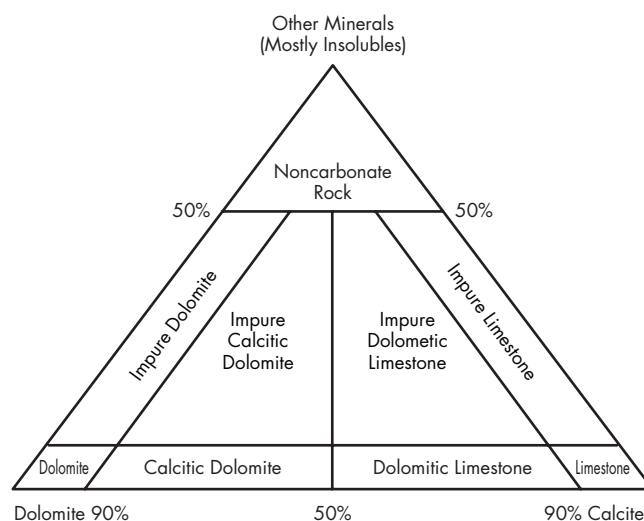


Figure 1. Mineralogical classification of carbonate rocks

A textural classification as well as a mineralogical classification is fundamental to geologic studies to determine the origin of carbonate rocks. One such classification by Leighton and Pendexter (1962) considered that most limestones can be characterized by the types and relative amounts of four textural components: grains, lime mud (micrite), cement, and pores. The ratio of relative proportions of grains to micritic material, which is the basis of their nomenclature system (Table 2), gives some indication of water turbulence because muds cannot be deposited in areas with strong bottom currents. Other classifications, such as the ones by Folk (1962; see Table 3) and Dunham (1962; see Table 4) make use of framework grains to mud ratios and have practical applications.

Dolomite presents a special problem in classification and may require separate handling from limestone. The textural classification can be used for secondary dolomite if the original depositional texture is preserved. Some dolomites, however, show only faint traces of original texture, called ghosts or relics, and others may have had their original texture completely obliterated. For these cases, and for dolomite of primary origin, a classification based on crystal size may be required.

Distribution of Deposits

Carbonate rocks have been deposited from Precambrian to Holocene time, and although they compose only about 0.25% of the volume of the crust of the earth (Parker 1967), they comprise about 15% of the sedimentary rocks. In 2002, limestone and/or dolomite were quarried or mined in all of the 50 states except Delaware, Louisiana, New Hampshire, and North Dakota; they were mined in all Canadian provinces except Saskatchewan.

Because carbonate rocks are widely distributed and differ in their geologic characteristics, each deposit must be considered on its own attributes. The best source of information for carbonate rock deposits is the state geological surveys, or their equivalents. Most state publications are oriented toward aerial geology, commodities, or the two combined, rather than uses or methods. The U.S. Geological Survey (USGS) publishes information on limestone and dolomite. The annotated bibliographies of Gazdik and Tagg (1957) on high-calcium limestone deposits and of Davis (1957) on some high-magnesium dolomite deposits are helpful guides to the older literature, as is the report on high-grade

Table 2. Classification of limestone according to the scheme of Leighton and Pendexter (1962)

Grain: Micrite Ratio	% Grains	Grain Type					Organic Frame Builders	No Organic Frame-Builders
		Detrital Grains	Skeletal Grains	Pellets	Lumps	Coated Grains		
9:1	~90%	Detrital	Skeletal	Pellet	Lump	Oolitic; pisolitic; algae-encrusted	Coralline; algal	Caliche; travertine; tufa
1:1	~50%	Detrital-micritic	Skeletal-micritic	Pellet micritic	Lump-micritic	Oolitic; pisolitic; micritic	Coralline-micritic; algal-micritic	
1:9	~10%	Micritic-detrital	Micritic-skeletal	Micritic-pellet	Micritic-lump	Micritic-oolitic; pisolitic	Micritic-coralline; micritic-algal	
← Micritic Limestone →								

Table 3. Classification of limestone using the texture scheme of Folk (1962)

More than 2/3 Lime Mud Matrix					Subequal Spar and Lime Mud	More than 2/3 Spar Cement		
% Allochems	0-1	1-10	10-50	>50		Sorting poor	Sorting good	Rounded and abraded
Rock terms	Micrite and dismicrite	Fossiliferous micrite	Sparse biomicrite	Packed biomicrite	Poorly washed biosparite	Unsorted biosparite	Sorted biosparite	Rounded biosparite
1959 terminology	Micrite and dismicrite	Fossiliferous micrite	Biomicrite		Biosparite			
Terrigenous analogues	Claystone		Sandy claystone	Clayey or immature sandstone		Submature sandstone	Mature sandstone	Super-mature sandstone

Table 4. Classification of limestones according to the scheme of Dunham (1962)

Depositional Texture				
Original components not bound together during deposition				Original components were bound together during deposition, as shown by intergrown skeletal matter, lamination contrary to gravity, or sediment-floored cavities that are roofed over by organic or questionably organic matter and are too large to be interstices
Contains mud (particles of clay and fine silt size)			Lacks mud and is grain supported	
Mud supported		Grain supported		
<10% grains	>10% grains			
Mudstone	Wackestone	Packstone	Grainstone	Boundstone

dolomite deposits by Weitz (1942) and a more recent report by Freas and Horne (1982).

Although high-purity carbonate rock deposits are not overly abundant, they are by no means rare. All of the states except Delaware, Hawaii, Louisiana, Mississippi, New Hampshire, and Rhode Island, and all of the Canadian provinces, report potentially commercial deposits of high-calcium limestone or high-magnesium dolomite. A complete list of publications is available on the Web sites of all the state geological surveys; these Web sites are given later in this chapter and in the bibliography. Twenty-one of the 31 Mexican states produced high-calcium limestone or high-magnesium dolomite in 2000, and 5 of the Canadian provinces have commercial production of high-calcium limestone. Because deposits are present, however, does not necessarily mean that they can be exploited. In many areas, competition is intense for potential mineral lands for construction sites, recreation areas, nature preserves, and highways; even nature has its own requirements for flowing streams and soil development. Society has also imposed environmental controls, now firmly established in state and federal statutes, which prohibit or restrict mineral production in areas where it might significantly affect the quality of the environment.

Exploration

Exploration for limestone and dolomite in North America is largely the detailed examination of known deposits. Because most limestone is a sedimentary rock, it occurs in strata generally of consid-

erable extent. Some data on chemical composition and physical characteristics are available for most such strata in the published reports or files of state, provincial, and national geological surveys. Exploration for a new limestone deposit, therefore, in most instances begins with a search of these records to find the locations of deposits that satisfy the various economic factors, and proceeds to a sampling program of favorable deposits. Geophysical techniques, if used at all, are performed to determine the thickness of overburden. Geochemical techniques are not used.

All aspects of exploration are important, but the one most likely to be slighted is sampling. Yet it determines the validity of further study and may become the basis for hundreds of thousands and sometimes millions of dollars' worth of developmental work. The goal of sampling must be the accurate representation of the limestone deposit. The most common sampling methods are coring, rock biting, and surface (ledge) sampling, and the choice among these depends on such matters as the geology of the deposit, the proposed use of the material, and the availability of equipment.

Special care should be taken when sampling weathered outcrops. In humid regions, the surface layer of a carbonate rock can be leached of calcite and dolomite and hence be less pure than the rest of the unit. On the other hand, in arid and semiarid regions, where evaporation exceeds precipitation for long periods of time, the surface layer may be enriched in calcite and dolomite. Thus, if surface samples must be taken under these conditions, the geologist should be aware of a potential bias.

Coring

Coring is generally the best method of exploring a new deposit. A single core may not always be more representative than a section sampled in a quarry or in a natural exposure, where some judgment may be used as to what is representative, but cores taken on a grid pattern constitute a more representative and unbiased sample of a deposit than an equal number of surface sections. Coring avoids contamination by soil and weathered material, and disproportionate sampling of different parts of a single unit, yet retains the surface material that may have worked downward into solution cavities.

Initial drilling is generally widely spaced, both to help locate a potential deposit and to determine its potential size. Once an apparently large and suitable deposit is discovered, it should be drilled in a more or less regular pattern. The core grid and type of drilling depend largely on the proposed use of the limestone, although other factors such as the homogeneity of the deposit, geologic complexity, topography, and cost of drilling are significant. In areas of steeply dipping strata, the grid spacing must take into account whether vertical or inclined drilling will be used. If the stone is to be used as cement raw material and the magnesium content of the rocks is believed to be marginal and unpredictable, no greater than 30-m centers would be required. If the deposit is relatively homogeneous in one direction and not in another, a rectangular rather than a square grid might be used. If the stone is to be used as aggregate and is relatively uniform in other deposits, generally only a few cores need to be taken in several hundred hectares. For most deposits of flat-lying strata in which the chemical composition of the rocks is important, cores should be spaced on 30-m centers until a pattern of uniformity indicates that the spacing can be increased safely. The authors know of one lime company, quarrying in a structurally complex area of Pennsylvania, that found coring on 15-m centers necessary for adequate quality control.

For most limestone exploration, a BX core (4.13 cm in diameter) suffices, but if physical tests are required, a core of larger diameter must be used. NX core (5.4 cm in diameter) is adequate for chemical analyses and limited physical testing but too small for some physical tests. If the core is stored for a significant period of time, it may be necessary to use plastic or wooden core boxes rather than the common corrugated cardboard boxes normally supplied by the core drilling contractor (Figure 2).

Each common physical test of rock used for aggregate requires about 5 kg of rock. Tests for absorption, abrasion, and soundness require more than 14 kg of rock. Testing stone for use as highway materials (ASTM 2004, Volume 04.02; AASHTO 2004) requires a minimum of 23 kg of rock. Highway commissions in some states do not perform physical testing of cores and accept only ledge samples. Testing agencies in other states will run physical tests on cores.

Rock Bitting

Used alone, drill cuttings are probably the least reliable samples in exploration, but if used to supplement cores or information obtained from nearby quarries or outcrops, they are an inexpensive, rapid method of acquiring much information. If the drilling is done in a carefully cased hole to prevent contamination by overburden, if the cuttings are collected carefully, and if the geologist is experienced in interpreting well cuttings, these samples can be as reliable as core and surface sampling for some purposes. In fact, the percussion air drill is probably the fastest and least expensive method for preliminary sampling.

Because of the large amount of drilling for oil and gas during the past few decades, cuttings of thousands of wells are on file in government and other sample libraries. Although not intentionally



Figure 2. NX core being placed in a plastic core box

so, these cuttings constitute the largest exploration program for industrial minerals ever undertaken. Cuttings cannot be interpreted properly unless the interpreter understands drilling techniques, and the best interpretation of the well cuttings requires considerable well-site experience. In addition, the explorationist should be skeptical of these cuttings without prior knowledge of the drilling conditions and the competency of the personnel logging samples from these wells. Stein and Starkweather (1996) is a good reference on drilling and coring.

Surface Sampling

Chip samples taken carefully on a quarry face can provide a good representation of the limestone deposit. The geologist should first inspect the quarry face, divide the face into units of uniform lithology, and then mark tops of units with paint or flags. Thick homogeneous beds should be arbitrarily subdivided, so that no sample is more than about 1.5 m thick. Starting at the base of the unit, one should take chips of uniform size as nearly as possible along a selected vertical line to the top of each unit. (The geologist might start at the top and work down, but it is easier to work up than down.) This method of sampling is sometimes called channel sampling. Chip samples should be taken from unweathered surfaces even if the weathered rind must be chipped away. Samples should be washed to remove contaminants such as lichens or soil, but care should be taken not to wash out thin, interbedded shales.

Many channel or core samples weigh 5 to 10 kg, and this amount must be crushed, thoroughly mixed, and quartered several times in the laboratory to reduce the sample to the few grams needed for chemical determination.

EVALUATION AND TESTING

If given sufficient cores or exposures of rock, an experienced industrial minerals geologist can evaluate a limestone deposit largely just by visual inspection, using a hand lens, hammer, and weak hydrochloric acid as the only tools. The geologist can generally appraise whether a stone will make class A aggregate or cement raw material. They may not, however, be able to determine whether the stone is of sufficient purity for other uses. Final evaluation of rocks suitable for aggregate, dimension stone, and similar uses requires physical testing. Rocks used for making lime, cement, or other products that depend on chemical purity should be chemically analyzed.

Table 5. Physical properties of selected carbonate rocks

Age	Formation	Location	Rock Type	Apparent Specific Gravity	Apparent Porosity, %	Compressive Strength, MPa	Modulus of Impact, MPa	Toughness, cm/cm ²	Reference
Miocene	Unspecified	Eniwetok	Limestone (fossiliferous)	2.39	4.0	97.2	16.5	0.4	Blair (1956)
Eocene	Unspecified	Eniwetok	Limestone (dense)	2.53		122.0	22.0	0.8	Blair (1956)
Cretaceous	Niobrara	S. Dakota	Limestone (chalky)	1.81	8.3	25.5	4.1	0.5	Blair (1955)
Mississippian	St. Louis	Missouri	Limestone (oolitic, fossiliferous)	2.56		115.8	15.9	1.1	Blair (1956)
Mississippian	Maxville	Ohio	Limestone (fine-grained)	2.41		108.9	17.2	1.2	Blair (1956)
Mississippian	Salem (Spergen)	Indiana	Limestone (fossiliferous)	2.37	11.0	75.2	11.0	0.7	Windes (1949)
Devonian	Columbus	Ohio	Limestone (very fine-grained)	2.60	5.4	123.4		1.4	Blair (1956)
Devonian	Columbus	Ohio	Limestone (fine-grained)	2.69	0.7	196.5	20.0	3.4	Windes (1949)
Silurian	Brassfield	Ohio	Limestone (dolomitic)	2.8	1.3	179.2	193.1	1.6	Windes (1950)
Silurian	Niagara	Ohio	Dolomite (fine-grained)	2.4	8.6	89.6	75.8	0.7	Windes (1950)
Silurian	Clinton	Alabama	Limestone (coarse-grained)	2.83	0.9	165.5		2.6	Windes (1949)
Ordovician	Chickamauga	Tennessee	Limestone	2.73	3.4	>173.0	5.5	2.2	Blair (1956)
Ordovician	Lenoir	W. Virginia	Limestone (siliceous)	2.68	6.0	158.6	13.1	1.0	Windes (1950)
Ordovician	Knox	Tennessee	Dolomite (fine-grained)	2.84	0.7	322.0	26.2	2.3	Windes (1949)
Cambrian	Bonne Terre	Missouri	Limestone (dolomitic)	2.66	3.3	175.1	12.4	1.9	Blair (1955)
Cambrian	Oro Grande	California	Marble	2.72	0.2	165.5	16.5	0.7	Blair (1955)
Precambrian	Cockeysville	Maryland	Marble	2.87	0.6	212.4	19.3	1.1	Windes (1949)

The American Society for Testing and Materials (ASTM) *Directory of Testing Laboratories, Commercial-Institutional* (2005) lists laboratories capable of making chemical and physical determinations on rocks.

Physical Properties

Procedures for physical testing can be obtained from two main sources: ASTM and the American Association of State Highway and Transportation Officials (AASHTO). Both organizations describe explicit procedures, in cookbook fashion, for testing limestone and dolomite. State highway commissions may specify slightly different procedures and should be consulted if stone is to be used as aggregate in those states. In earlier years, several federal organizations developed physical tests for building stone, such as those reported by the U.S. Census Office and the U.S. Bureau of Standards; however, current building-stone testing generally follows procedures outlined by ASTM.

Physical tests are designed to test how well a rock will perform for a particular use. As might be expected, many tests have been developed corresponding to the many uses for which the carbonate may be designated. Table 5 shows selected physical properties of carbonate rock. The *Handbook of Physical Constants* (Birch et al. 1950) and a book by Barksdale (1991) describe a large number of physical properties of limestones and other rocks. These references contain data on bulk density, compressive strength, compressibility at high and low temperature, dielectric constant, electrical resistivity, porosity, thermal conductivity, thermal expansion, and other properties that are especially useful to the geophysicist. Manger (1963) published a tabulation of porosity and bulk density determinations of carbonate rock, as reported in the accessible American, British, German, and Swiss literature.

A great many physical tests of carbonate rock used for aggregate have been performed in connection with state and federal road-building programs, but much of this information is unpublished. Unfortunately, most data from testing of aggregate in the federal highway program have not been tabulated. Marek (1991) gives a

useful overview of sampling and testing principles. Unfortunately, much of that material is dated relative to changing highway construction methods and materials requirements. The International Center for Aggregates Research (ICAR) is now the focal point of current aggregate research. ICAR is a collaborative effort of the University of Texas at Austin and Texas A&M University and has very strong ties to the National Stone, Sand, and Gravel Association (NSSGA). ICAR publishes a free reference library of information on their Web site at www.ce.utexas.edu/org/icar. AASHTO, a nonprofit association representing the transportation departments of all 50 states, the District of Columbia, and Puerto Rico, publishes an excellent two-volume book on aggregate material standards (AASHTO 2004).

Through the years, the U.S. Army Corps of Engineers (USACE) has tested carbonate rock from many quarries in the continental United States to evaluate their potential use in constructing locks, dams, and other structures. Technical Report No. 6-370, *Test Data Concrete Aggregates in Continental United States* from the USACE Waterways Experimental Station (1953) gives a summary of this testing, which includes the standard tests for sulfate soundness, abrasion resistance, specific gravity, and absorption. This compilation, which occupies nearly a meter of shelf space, cannot be purchased but is available for inspection at USA CE libraries. Other, more accessible publications that give physical test values and results of USACE extensive research relating to the use of carbonate rock as aggregates in portland cement concrete include one by Curry and Buck (1966). The most current list of USACE publications is available from the Engineer Research and Development Center Professional Library Services, an online library at <http://www.edrc.usace.army.mil/library/publications>.

Some manufacturers of pulverized limestone, defined as limestone or dolomite having a minimum fineness of 97% passing a 325-mesh sieve, established standards and test methods through the Pulverized Minerals Division of NSSGA. Recommended test methods include those for particle size, pH, dry brightness, water demand, and calcium and magnesium carbonate content.

Petrographic examination of carbonate rock can foretell its physical properties and subsequent suitability for certain uses, but too few people use this method. The definitive reference for this type of applied petrography is ASTM Standard C295, which is based on work from the 1950s. Techniques of petrographic examination and some of its applications can be found in Mielenz (1954, 1955), and Scholle (1978).

Rippability is a physical property of rock that concerns mainly the construction industry. Limestones that are thinly bedded, low in compressive strength, or sufficiently inhomogeneous so as to contain horizontal planes of weakness can generally be ripped easily. Empirical testing by the Caterpillar Tractor Co. (1972) found a relationship between seismic wave velocities and rock rippability: the higher the wave velocity, the more difficult it is to rip the rock.

Various research workers have examined the relationships between different physical and chemical properties of carbonate rocks. These attempts have not met with much success because of the inhomogeneity of the rocks. Further information can be found in Judd and Huber (1961), West and Johnson (1965), Baxter and Harvey (1969), and Barksdale (1991).

Chemical Properties

The chemical and physical properties of carbonate rocks are interdependent. Pure calcite in the form of poorly cemented chalk is not only unique in its low strength and high absorption among the carbonate rocks but is also highly reactive chemically because of the large surface area of its component grains. Pure calcitic marble of the same chemical composition as chalk is relatively strong, unabsorptive, and unreactive. Dolomite that contains quartz sand grains can have the same overall composition as dolomite that contains chert, but its suitability as aggregate differs widely because of the difference in reactivity of the two forms of silica. Processing also affects the degree of fracturing of stone and thus its surface area and chemical reactivity. Therefore, physical and mineralogic descriptions of carbonate rocks are of importance in predicting the chemical properties of the products that may be produced from a deposit.

For some uses of carbonate rocks, chemical analysis may be of little or no help in estimating the suitability of a rock unit; for other uses chemistry is of utmost importance. For example, in stone used for chemical purposes, such as glass raw material, flux, or cement, the percentage of certain elements must fall within specified limits or ranges. On the other hand, the chemical content may or may not be important for stone that is used because of its physical properties, such as aggregate, building stone, or riprap. A thick section of rock that is almost pure dolomite is likely to be well-cemented reefal dolomite, and it can be predicted generally to make good aggregate (Ault 1989). Rock that is pure calcite, however, may be a skeletal or oolitic limestone that is either well cemented or poorly cemented and thus might make excellent or only fair aggregate.

The proportion of alumina (Al_2O_3) and silica (SiO_2) in the rock may be helpful in determining the value of a carbonate rock for a use in which physical properties are important. Most silica in a carbonate rock is likely clay, silt- and sand-size quartz, or chert. For the common clay minerals found in limestones and dolomites, as much as 2% silica may be present for each 1% of alumina. The higher the alumina content, the more argillaceous the sample is likely to be. The alumina content can be multiplied by two to obtain an estimate of the amount of silica tied up in the clay.

The chemical analysis of a carbonate rock is essential for estimating the neutralizing value of agricultural limestone, which is usually expressed in terms of calcium carbonate equivalent (CCE).

Pure calcite ($CaCO_3$) is assigned a CCE value of 100. Pure dolomite ($CaCO_3 \cdot MgCO_3$) has a theoretical CCE value of 108.6; that is, it is 8.6% more effective than pure limestone as a neutralizer. Such interpretation assumes that a molecule of $MgCO_3$ with a molecular weight of 84.32 is as effective a neutralizer as one molecule of $CaCO_3$ with a molecular weight of 100.09. Thus, a given weight of $MgCO_3$ is 1.19 times as effective as the same weight of $CaCO_3$. Because of differences in solubility, however, a dolomitic liming material will take longer to neutralize a given amount of acid than a pure limestone, even though the CCE of both is the same. Goodwin (1979) is a useful guide to selecting agricultural limestone materials, as is information available from several state agency Web sites (see Additional Resources section in this chapter).

Many published chemical analyses of carbonate rocks show the varied compositions of limestones and dolomites (Clarke 1924; Graf 1960b; Siegel 1967), but these may not always be typical of the formation from which they were taken. Most sedimentary carbonate rocks vary in their impurities—including clay minerals, resistant minerals such as quartz, and organic material—because they were deposited in different environments. In addition, the rocks have evolved chemically as well as physically during compaction, dehydration, and lithification. Subsequent processes, including burial and exposure to percolation of water, provide for synthesis of authigenic minerals and alteration, such as oxidation of organic matter. Because of the limited extent of identical environments of deposition and subsequent postdepositional conditions, composition of any given rock unit is likely to be variable. Analyses of many samples taken at different sites are required to reveal the approximate composition of a particular rock unit.

Good sources of chemical data on carbonate rocks are the state geological surveys or their equivalents. Many state surveys have files of chemical data obtained from quarry sampling and coring programs. The USGS has published 1,131 analyses of carbonate rocks from Colorado, Kansas, Montana, Nebraska, North Dakota, South Dakota, and Wyoming (Hill, Werner, and Horton 1967) and 3,585 analyses of carbonate rocks from Alaska, Idaho, Oregon, and Washington (Hill and Werner 1972).

Specifications

Limestone specifications vary with end use of the stone. These specifications can be either physical or chemical, but frequently they include both. Physical specifications such as durability and gradation are more important if the stone is to be used as mined, such as for construction aggregate. Chemical properties are more important if the stone is to be subject to calcination, as in the production of lime or cement. Most industrial and agricultural applications require adherence to both a physical and a chemical specification. For example, glass-batch raw materials might have both a rigid chemical specification and a narrow gradation requirement.

Physical specifications focus on both the natural properties of the rock and the properties imparted during processing. Natural properties are intrinsic, such as hardness, composition, texture, color, porosity, and density, and processing properties are derived from the physical gradations and result from crushing, screening, washing, and air classification. Obviously the results of processing are directly related to the natural characteristics of the stone.

Physical specifications relating to gradation and durability are by far the most common when the rock is used as an aggregate material. These specifications are based on standardized testing and practices developed through ASTM. ASTM-specified grading requirements for coarse aggregate are shown in Table 6. Other related ASTM physical specifications can be found in ASTM 2004 (Section 4—Construction).

Table 6. Grading requirements for coarse aggregates

		Amounts Finer than Each Laboratory Sieve (Square-Openings), wt %												
Size Number	Normal Size Range (Sieves with Square Openings)	4 in. (100 mm)	3½ in. (90 mm)	3 in. (75 mm)	2½ in. (90 mm)	2 in. (50 mm)	1½ in. (37.5 mm)	1 in. (25 mm)	¾ in. (19 mm)	½ in. (12.5 mm)	⅜ in. (9.5 mm)	No. 4 (4.75 mm)	No. 8 (2.36 mm)	No. 16 (1.18 mm)
1	3½–1½ in. (90–37.5 mm)	100	90–100		25–60		0–15		0–5					
2	2½–1½ in. (63–37.5mm)			100	90–100	35–70	0–15	0–15	0–5	0–5				
3	2–1 in. (50–25.0 mm)					90–100	35–70	35–75		10–30		0–5		
357	1½–¾ in. (37.5–19.0 mm)					95–100								
4	1½ in.—No. 4 (37.5–4.75 mm)					100	90–100	20–55	0–15		0–5			
467	1–½ in. (37.5–4.75 mm)					100	95–100		35–70		10–30	0–5		
5	1–½ in. (25.0 to 12.5 mm)						100	90–100	20–55	0–10	0–5			
56	1–⅜ in. (25.0–9.5 mm)						100	90–100	40–85	10–40	0–15	0–5		
57	1 in.—No. 4 (25.0–4.75 mm)						100	95–100		25–60		0–10	0–5	
6	¾–⅜ in. (19.0–9.5 mm)							100	90–100	20–55	0–15	0–5		
67	¾ in.—No. 4 (19.0–4.75 mm)							100	up to 100		20–55	0–10	0–5	
7	½ in.—No. 4 (12.5–4.75 mm)								100	90–100	40–70	0–15	0–5	
8	⅜ in.—No. 8 (9.5–2.36 mm)									100	85–100	10–30	0–10	0–5

Source: ASTM 2004.

Table 7. Comparison of size gradations no. 8 stone screen size % passing

State Specifications	1 in.	1/4 in.	1/2 in.	3/8 in.	No. 4	No. 8	No. 10	No. 16
ASTM		NA*	100	85–100	10–30	0–10	NA	0–5
Ohio	NA	NA	100	85–100	10–30	0–10	NA	0–5
Indiana	100	85–100	20–60	NA	0–5	0–2	NA	NA
Kentucky	NA	100	85–95	40–65	5–20	0–5	NA	NA

* NA = not applicable.

ASTM standards provide guidelines for both required gradations and test methods employed in evaluating materials for use as construction aggregates. The specific gradation requirements may vary to some degree by individual state as a result of specific regional application or generally accepted practices. As an example, Table 7 compares gradations for an ASTM No. 8 specification with gradation for a No. 8 stone from Ohio, Indiana, and Kentucky.

Although there may be state-to-state modifications or variations in physical gradations of specific stone sizes, most states generally have durability requirements that are fairly consistent across the United States for aggregates for use as highway surface materials. The most common specifications for durability relate to abrasion, soundness, and freeze-thaw, all of which are covered by an ASTM standard procedure. These tests are a measure of the rock's

ability to withstand repeated cycles of weathering and continued impact of traffic. Several states have also included skid resistance for aggregate to be used in surface-course paving and bridge decks. As a consequence, several states have excluded carbonate rocks for these uses because they polish easily.

Frequently, the specifications for rock used in projects not funded by states or the federal government are modified for economic reasons such as lower transportation costs. This type of project could include nonsensitive uses such as subgrade material for driveway or other nonload-bearing purposes. Conversely, a higher transportation cost might be justified to achieve a specific appearance, as in some exposed-aggregate applications where architectural requirements are more important than economic considerations.

Chemical specifications for carbonate rocks generally are industry or application specific. In any consideration of chemical specifications of a limestone or dolomite, it is important to understand that chemical properties are not necessarily related to physical properties. For example, high-purity limestone from the Mosheim Formation in Virginia is very hard, whereas equally pure limestone from the Ocala Formation in Florida is very soft. The marble from the Franklin Formation in New Jersey has both high-brightness and high-carbonate values, yet the dark gray, almost black, marble from Michigan's Dundee Formation has a higher calcium-carbonate value.

Limestone and dolomite specifications can be developed in a variety of ways, including rigid testing and evaluation, mutual consent between the buyer and seller, common practice in an area, or even as a compromise to offset some other item such as high freight cost. A specification may also be written to describe a particular limestone source, such as when the buyer is not sure which components are important for a particular application. In these instances of uncertainty, the final specification results from testing several different limestones; selection is based on best performance.

Some specifications may be unique to a particular industry and require testing properties based on an industry standard or procedure. Thermal decrepitation, odor, taste, and crystallinity are examples of such properties. In some instances, these requirements may be related to a specific company and be unique to the specific application. For instance, when a limestone is used in rice polishing, it may be subjected to a taste test to ensure that the limestone does not impart an unpleasant taste to the rice during polishing.

As noted previously, it is not at all uncommon for a limestone specification to incorporate both physical and chemical requirements. This is particularly true of industrial uses such as glass manufacturing, where limestone is one component of the glass-batch raw materials. In this example, particle size, gradation, chemical degradation, and chemistry are equally important. Additionally, batch-to-batch uniformity of composition, both in chemistry and physical properties, is important and may require statistical process control (SPC). The importance of SPC should not be underestimated. For example, Tier One automotive glass producers require all glass-batch suppliers of raw materials to employ audited SPC in their process technology to qualify as an acceptable vendor. Several manufacturers also require ISO 9000 certification, although this is not consistently applied to the limestone and dolomite industry.

Table 8 shows typical specifications for limestone to be used in glass-batch raw materials. Industry-specific specifications such as those required for limestone or dolomite used in the production of lime or cement, in flue-gas desulfurization, and filler and extender specifications are included in the chapters on these materials. Any industrial or agricultural application, however, can have a unique specification predicated on specific performance requirements. Individual publications on specifications and uses are available at <http://www.nssga.org>.

PRODUCTION AND USES

The USGS reports that 1,130 t of limestone, dolomite, and related materials were sold or used in the United States in 2001 (Table 9) for construction purposes, including the production of lime and cement. As in previous years, carbonate rock was produced in 48 of the 50 states, with only Delaware and North Dakota not reporting any limestone or dolomite production. The top five producing states in descending order were Texas, Florida, Missouri, Illinois, and Ohio. These five states accounted for 40.8% of total U.S. production.

The tonnage is consumed in hundreds of applications, but the predominate markets for limestone and dolomite can be divided

Table 8. Physical and chemical specifications for glass-grade limestone

Typical Physical Analysis			
Size, mm	% Retained	Cumulative % Retained	Cumulative % Passing
1.68 (12 mesh)	0.00	0.00	100.00
1.19 (16 mesh)	0.35	0.17	99.83
0.84 (20 mesh)	5.06	5.20	94.80
0.30 (50 mesh)	57.05	62.25	37.75
0.15 (100 mesh)	26.26	88.90	11.10
0.07 (200 mesh)	9.98	98.40	1.60
pan	1.60	100.00	0.00
Moisture content 0.09%			
Typical Chemical Analysis			
Chemical	Reported as	%	
Calcium carbonate	CaCO ₃	97.80	
Magnesium carbonate	MgCO ₃	1.25	
Iron oxide	Fe ₂ O ₃	0.095	
Silica	SiO ₂	0.56	
Alumina	Al ₂ O ₃	0.23	
Nickel	Ni	<0.002	
Chromium	Cr ₂ O ₃	<0.001	
Strontium oxide	SrO	0.03	
Manganese oxide	MnO	<0.01	

Table 9. Crushed carbonate rock sold or used in the United States in 2001, by type

Type	Number of Quarries	Quantity, kt	Value, \$1,000	Unit Value, \$
Limestone	1,967	1,030,000	5,330,000	5.19
Dolomite	188	101,000	570,000	5.64
Marble	25	9,050	54,400	6.00
Calcareous marl	8	4,470	17,500	3.92
Shell	10	1,420	7,360	5.19
Totals weighted (average)	2,198	1,145,930	5,979,260	4.55

Source: Tepordei 2002.

into 9 major categories and 39 primary uses (Table 10). The first five major categories are related to the use of carbonate rocks as construction materials. A total of 430,613,000 t, or 38% of all crushed carbonate rock produced in the United States in 2001 was produced for aggregate markets. Limestone and dolomite thus represent 54% of the total 790 t of an aggregate material sold or used. Agricultural applications consumed 11.7 t of limestone and dolomite, of which agricultural liming materials made up 83% of this category. Chemical and metallurgical uses account for about 99.3 t, or about 8.8% of all the limestone and dolomite produced each year. Tegethoff (2001) gives additional information on the use and applications of limestone.

Special uses cover a host of applications, the largest of which are fillers, extenders, and whitening materials. Because of the unique applications and value of these products, they are covered in a separate chapter. Mine dusting and acid water treatment are a unique category unto themselves. High-calcium limestone (more than 95% calcium carbonate) is used as rock dust in coal mines as an explosion suppressant. This product must contain less than 2% silica and

Table 10. Crushed limestone and dolomite sold or used by producers in the United States in 2002, by use*

	Limestone Use [†]		Dolomite Use	
	Quantity, kt	Value, \$1,000	Quantity, kt	Value, \$1,000
Construction				
Coarse aggregate (+37.5 mm) (+ 1/2 in.)				
Macadam	2,350	14,700	140	1,040
Riprap and jetty stone	9,880	59,500	296	2,720
Filter stone	3,120	18,900	73	522
Other coarse aggregate	11,300	78,900	667	3,870
Coarse aggregate, graded				
Concrete aggregate, coarse	34,600	229,000	3,400	20,700
Bituminous aggregate, coarse	26,200	180,000	3,960	23,800
Bituminous surface-treatment aggregate	5,800	41,900	1,090	5,610
Railroad ballast	1,690	8,880	544	3,680
Other graded coarse aggregate	65,700	423,000	1,930	15,800
Fine aggregate (-3/8 in.)				
Stone sand, concrete	6,740	42,600	415	2,110
Stone sand, bituminous mix or seal	3,890	23,900	868	5,800
Screening, undesignated	10,900	57,900	639	3,270
Other fine aggregate	22,500	150,000	954	6,910
Coarse and fine aggregates				
Graded road base or sub-base	64,600	326,000	5,700	27,600
Unpaved road surfacing	10,600	60,300	807	4,090
Terrazzo and exposed aggregate	168	1,280	0	0
Crusher run or fill or waste	17,400	84,500	1,150	7,240
Roofing granules	214	1,720	0	0
Other coarse and fine aggregates	49,200	275,000	8,500	43,400
Other construction materials [‡]	5,880	37,900	488	2,700
Agricultural				
Agricultural limestone	9,660	57,300	848	5,560
Poultry grit and mineral food	932	9,980	0	0
Other agricultural uses	271	2,980	67	316
Chemical and metallurgical				
Cement manufacture	67,100	299,000	95	341
Lime manufacture	18,700	99,600	1,480	6,160
Dead-burned dolomite manufacture	W [§]	W	W	W
Flux stone	1,440	7,940	811	3,630
Chemical stone	313	2,700		
Glass manufacture	W	W		
Sulfur oxide removal	2,990	20,100		
Special				
Mine dusting or acid water treatment	168	1,850		
Asphalt fillers or extenders	730	5,430	W	W
Whiting or whiting substitute	126	1,830	W	W
Other fillers or extenders	1,550	21,200	15	171
Other miscellaneous uses				
Refractory stone	1,070	4,730		
Sugar refining	W	W		
Other specified uses not listed	6,930	34,800	123	639
Unspecified**				
Reported	306,000	1,550,000	49,300	282,000
Estimated	210,000	1,000,000	13,000	69,000
Total	978,000	5,230,000	97,400	549,000

Source: Tepordei 2002.

* Data are rounded to no more than three significant digits; may not add to totals shown.

† Includes a minor amount of limestone-dolomite reported without a distinction between the two.

‡ Includes building products, drain fields, and pipe bedding.

§ Withheld to avoid disclosing company proprietary data; included in "Total."

** Reported and estimated production without a breakdown by end use.

is normally ground to 95% less than 325 mesh. Limestone or dolomite used in acid-water treatment can be specified with a variety of sizes depending on both the pH of the water to be treated and available residence time. In some instances, limestone may be injected as a 325-mesh powder into a low-pH effluent stream, or it might be used as boulders in acid streams not suitable for continuous treatment with finer-grained materials.

Dimension stone is the one category not included in Table 9. Dimension stone production is closely tied to commercial construction; in 2002 about 1.26 Mt were produced in the United States. Limestone and marble together account for approximately 33% of total U.S. dimension-stone production. Indiana was the leading state in dimension limestone production, and Georgia was the leading state for dimension marble production, followed by Vermont.

When granite production is included with limestone and marble production, the United States is the fourth largest producer of dimension stone in the world. Nevertheless, total U.S. dimension-stone production has historically been one fourth that of Italy and one half that of Spain (Harries-Rees 1991). Italy, Spain, and Greece produce more dimension stone than the United States; each is a net exporter and the United States is a net importer of dimension stone.

Interestingly, dimension stone production is reported in tons, but sales and prices are normally based on the cost per cubic foot. These prices have remained fairly constant over the last several years; increases in profitability realized by producers have come from increases in productivity.

PREPARATION FOR MARKET

Mining

Limestone and dolomite are high-volume, low-value commodities. This segment of the industrial minerals industry is highly competitive and is characterized by thousands of operations serving local and regional markets. Thus a competitive environment dictates that production cost control is the critical element in any stone operation.

Most limestone and dolomite are mined from open quarries, although in many areas economic and environmental considerations favor large-scale production by underground mining. The only carbonate materials not consistently recovered by surface or underground mining are shell products that are dredged from parts of U.S. coastal waterways, and this is coming to an end with increased environmental pressure in conventional areas of shell production.

Surface Mining

The basic elements of surface mining are overburden removal (stripping), drilling, blasting, and hauling ore to the crushing and processing plant. Ultimately the surface mine must also contend with reclamation requirements. The selection of surface mining equipment varies with the particular requirements at each operation, including production capacity required, size and shape of the deposit, haul distances, estimated life of the operation, location relative to urban centers, and other social and economic factors. Other factors that must be considered in surface mining are the value of the products produced, location of competitive operations, and environmental and safety requirements associated with a particular deposit.

Frequently, a surface mine or quarry will contract for the drilling or blasting part of the production cycle. The specialized nature of this aspect of production, combined with the unique regulatory and safety requirements associated with the handling and use of explosives, may make the use of an outside contractor economically attractive, particularly for quarries close to densely populated urban environments. The contractor is responsible for the maintenance of an explosives magazine and all record and reporting requirements and may arrange for seismic monitoring of each blast.

The issue of explosives handling and storage has become much more highly regulated since September 11, 2001, adding considerable incentive to using an outside contractor.

Overburden removal is a key element in the cost of any surface mining operation and consequently its ability to compete with other mines in its market area. For example, if 3 m of overburden must be removed to recover 30 m of limestone, a mine with 15 m of overburden for the same 30 m of rock will not be competitive. If a mine is unique to its particular area, however, a high overburden ratio may be economically justified. Additionally, the production of high-value end products may support mining operations that would not be economical for low-value products. For example, in East Tennessee, as much as 90 m of overburden has been removed from a 30-m-thick, steeply dipping deposit of chemical-grade limestone for use in the production of lime. This high overburden ratio would probably not be justified if this were a conventional aggregate operation.

Underground Mining

In 2002, 83 underground limestone mines were operating in the United States. In 1900, total production of limestone from all underground mines was 95 kt, or 0.37% of the total limestone production. In 1924, production was 520 kt, or 4.5% of the total production. In 1965, it was 31,200 kt or about 6% of the total limestone production. In 2002, it was 60,000 kt or about 5.3% of the total production. Many of the mines are in the Midwest, however, and this reflects the abundance of high-quality limestone in horizontal beds in that part of the country as much as a concentration of population. This distribution pattern will change gradually as more mines are built to serve urban centers (Carr and Ault 1983; Baxter 1989).

The basic operations in underground mining are drilling, blasting, loading and hauling, scaling, and roof bolting. Drilling equipment includes horizontal drill jumbos and downhole track drills. This equipment is generally quite different from that used for surface mining and results in much smaller blast holes and a lower volume of rock pulled with each blast. Other equipment required in the underground mine includes powder loaders, which are used to blow ammonium nitrate-fuel oil mixtures into the blast holes. Scaling rigs, which are used to remove loose rocks from the ribs and roof of the mine, and roof-bolting equipment may also be required in an underground mine.

Most underground limestone and dolomite mines are room-and-pillar-type operations, and many recover rock from both headings and benches. It is not uncommon for an underground limestone mine to have several benches and an overall mine height up to 30 m. Whereas the thickness of the deposit being mined is directly controlled by the thickness of the rock and related roof conditions, it is not uncommon for an individual heading to be 7.5 to 10.5 m high, and in some instances to reach as high as 15 m. Rooms are generally 13.5 to 15 m wide, which, depending on the type of drilling jumbo used, normally can be mined with one- or two-drill setups. A V-type drill pattern is commonly used to maximize the amount of rock pulled with each shot to reduce the number of boots or unbroken rock in the shot face. Scaling is normally required as a safety measure; roof bolting may or may not be required, depending on roof conditions at the individual mine. Loading and hauling equipment may include standard 22 to 45 Mt haul trucks and correspondingly sized front-end loaders. In some mines, the loading equipment may be more typical of underground hard-rock operations, and may include load-haul-dump units or other types of tramming equipment. For more detailed information on both surface and underground mines, the reader is referred to Kennedy (1990), Bise (1986), and Hartman (1992).

Processing

Limestone processing varies with the end product and targeted consuming industry but of necessity includes several basic similarities. These similarities relate primarily to sizing and include crushing and screening. Depending on such factors as the volume of rock processed, type of mine, haulage distance, and surface topography, primary crushing may be done either at or near the mining face or at the primary processing plant. When primary crushing is done in the quarry or mine, the rock is normally reduced to a less than 15-cm diameter and is moved via conveyor to the main processing plant.

Selection of crushing equipment depends on plant size, physical properties of the rock, and the product produced. In general, primary crushing is by a jaw or gyratory crusher, but an impact crusher or other specialized equipment may be used. Several underground limestone mines use Stamler feeder-breakers as the primary crusher, which is a low-profile piece of equipment. Secondary crushing is usually by cone or gyratory crushers, although impact and roll crushers and hammer mills may be used.

Screening is one of the most critical steps in the processing cycle, particularly in the production of crushed stone. The selection from a wide variety of screen types and screen cloth depends on the requirements for the end product. Most screens incorporate some form of inclined vibratory equipment. Screen cloth can range from a rod, a deck, or punctured steel plates for larger product sizes down through woven wire, welded wire cloth, rubber, plastic, and polyurethane for smaller product sizes. Screens must be checked regularly for holes and tears because oversized material can quickly contaminate a significant volume of product. Stainless steel is frequently used for the screen cloth to reduce wear and increase screen life.

Quarried stone usually has some moisture associated with it, and, as a consequence, fines may adhere to larger pieces of rock. Many crushed stone facilities include washing equipment in the production line to remove these fines and thus ensure gradation specifications and the removal of clay or soft shale. Where washing facilities are included in the processing cycle, settling ponds are also required to eliminate the discharge of silt-laden water to neighboring streams. Where stone washing is not practical and when moisture cannot be tolerated in either subsequent processing steps or the final product, a dryer may be required. The dryer is normally installed ahead of the screening equipment. These dryers are usually counterflow rotary dryers that operate at 120°C to 150°C. Fluidized-bed dryers may also be used and are particularly applicable where flash calcination of fines might be a problem.

Limestone and dolomite processing for industrial and agricultural applications may also require air classification and milling equipment, particularly when products are smaller than 10 mesh and must have a clean bottom cut (usually at 100 or 200 mesh). Air classifiers are easily adjusted and have the flexibility to make a wide range of products. Cage mills, roller mills, and ball mills are used in the production of varying particle sizes ranging from 20 mesh to 2 µm. Wet processing is usually required to produce products smaller than 2 µm.

Once processed, the stone products must be stored before shipment. Most crushed stone products are stored in open areas or in a combination of open areas and loading bins. The volume of material produced and the variety of products generally dictate the design of the storage area. In many larger aggregate operations, a series of radial stackers distribute stone from the screening plant. Alternatively, a plant may have several stone bins to facilitate truck or rail loadout. Storage of industrial and agricultural products requires enclosed silos and bins to protect them from moisture and contamination by other products. These bins and associated loadout

devices require positive dust control, including adequately sized baghouses. They may also include pneumatic conveying equipment or bucket elevators in the product-handling system.

Programmable controllers or computers are finding increased use in the processing of limestone and dolomite. As process plants become larger and more complex, computer-controlled processing systems are an invaluable tool in achieving improved production efficiencies and improved product quality. This equipment can be incorporated into the statistical process-control program of the plant and can be interactive with loadout and scale computers. Where interactive systems are used, they can provide on-line inventory control, bills of lading, and input directly from loadout scales to computer-generated invoicing. Several software packages available today are particularly well adapted to aggregate operations. A useful reference is the NSSGA publication *Guidelines for the Successful Automation in the Crushed Stone Industry*, which can be supplemented with the proceedings from the NSSGA annual Automation Conference (NSSGA 1990). The annual proceedings can be purchased through the NSSGA Web site (<http://www.nssga.org>).

Transportation

Transportation is a major factor in the delivered price of limestone and dolomite products. In very general terms, the lower the value of the processed product, the shorter the distance it can be transported. Stated another way, construction aggregates are less likely to move long distances to the marketplace than are 2-µm carbonate filler/extender materials. In many places, the cost of transportation equals or exceeds the free on board (f.o.b.) plant value of the stone. Thus, limestone and dolomite aggregates generally are marketed locally.

In the limestone and dolomite chapter in the 6th edition of *Industrial Minerals and Rocks*, it was reported that trucking accounted for 82% of the transportation of limestone and dolomite products in the United States. The remainder of the material was transported about equally by rail or waterway. This distribution has not changed appreciably in the last 10 years; however, many factors related to the cost of transportation have changed. Both rail and trucking rates have been deregulated, and competition functions openly in the marketplace. As a consequence, it is frequently possible for a stone processing company to negotiate rates for specific jobs or contracts. This competition also has fostered a number of unit train and intermodal transportation arrangements that have allowed aggregate products to be delivered to more remote locations than previously thought possible.

In evaluating the cost of trucking limestone and dolomite products, the trucking costs associated with aggregate and crushed stone materials must be considered separately from the cost of transporting higher value industrial and agricultural products. The specifics of trucking vary from area to area; however, in very general terms, approximately half the trucking of crushed stone is done by a contractor purchasing and using the aggregate as opposed to owner/operators or commercial haulers. Many state and local governments also have their own trucking equipment and can be grouped with those contractors hauling for their own purposes or jobs. For them, the actual cost of trucking is extremely difficult to determine because each values and costs transportation somewhat differently. For owner/operators or contract haulers using open dump trucks for hauls of less than 40 km, a charge of \$0.06 to \$0.10 per metric ton-km is not uncommon. These rates are subject to negotiation and may be cut significantly on very large construction projects; they also do not include fuel surcharges.

In many places, trucking of industrial and agricultural products is handled differently from the hauling of limestone and dolomite aggregates. The equipment normally used includes pneumatic

tankers, bottom-dumping grain trucks, and vans and flatbeds for bagged products. Where bottom-dump grain haulers can be used, back-haul freight rates may be possible, thus allowing the producer to reach customers whose geographical location is far more remote than would otherwise be economical with normal tariff rates. Contamination by foreign matter is a major concern for many industrial customers; consequently, some carbonate producers operate their own equipment or contract with a specific hauler for dedicated equipment. Even then, it may be necessary to use rigorous clean-out procedures to prevent contamination, particularly when bulk micrometer-sized product is being trucked. Because of the specialized nature of equipment used for industrial and agricultural purposes, trucking rates tend to be slightly higher than those for aggregate products and may be in the \$0.10 to \$0.20/t-km range. These rates may also be subject to negotiation when a consistent haul can be established and several units can be dedicated to a specific customer.

Railroads continue to be a major factor in the transportation of limestone and dolomite products, whether aggregate materials or industrial and agricultural products. For aggregates, rail movement may use intermodal facilities at the receiving end where the stone is either transferred to a stockpile or directly to a truck for delivery to the customer. Such facilities are used successfully in selected markets and most recently were employed by one Pennsylvania producer to move aggregates into the Baltimore-Washington market area. On a single line haul with 60 to 90 car unit trains, it is possible to ship aggregate products at a cost of \$0.02 to \$0.06/t-km. In many places, agricultural and industrial customers are large-volume users and require the use of covered-hopper equipment. In these instances it is possible to negotiate very favorable rail freight rates if a single-line haul can be used. The negotiation of favorable rail rates, however, becomes far more difficult when two or more rail lines are involved and when short-line rail carriers impose switching charges. Nevertheless, even in multiline hauls, when the competition is a straight truck movement, the volumes of stone to be transported may justify a very competitive bid from the combined rail effort. The downside to rail utilization is that the railroads have become quite aggressive in assessing service fees, including demurrage, switching fees, and surcharges, which can greatly increase the cost of rail freight.

Waterway transportation continues to handle about the same volume of stone products that it has for the past 10 years. Most of the stone moved via waterway is either construction aggregate or chemical-grade limestone or dolomite used in the production of lime or cement. Transportation by barge normally requires a shipment of 1.4 kt per barge and generally is not attempted on movements shorter than 480 km. Freight quotations of \$0.01/t-km are not uncommon. Barges are not the only means of waterway transportation. Self-unloading ore carriers on the Great Lakes, oceangoing barges, and 27- to 54-kt bulk ship movements on the ocean are also being used to move crushed stone. Ocean freight and Great Lakes shipment rates can be very economical when this mode of transportation is feasible, but it is clearly restricted to large-volume movements.

LEGISLATIVE AND ENVIRONMENTAL ISSUES

Limestone and dolomite producers, along with the rest of the mining industry, are faced with an ever-increasing array of regulatory and environmental legislation. The average U.S. citizen today is far more environmentally conscious than just 10 years ago. As a consequence, the public expects a positive and responsible commitment from the mining industry to environmental, health, and safety concerns. These concerns separate into two basic groups: local community sensitivities, and state and federal mandates.

At the local level, the limestone industry is faced with zoning and community relations requirements, the response to which will dictate the success or failure of each quarry or mine in the years ahead. The response by stone producers must include long- and short-range reclamation plans, aggressive dust and noise control, attention to the aesthetics of plant entrances and other street-appeal items, and a willingness to listen to community concerns. In some instances, restrictions may be imposed on the hours that blasting can take place or on the hours a quarry may operate. One of the major concerns of many communities is the traffic associated with quarry or mine operations. In some places, trucks moving to and from a limestone producer's operations must travel through neighboring residential areas. As a consequence, additional driver safety and courtesy training may be required, and speed restrictions must be aggressively enforced.

State and federal regulations include a number of items of critical interest to the limestone and dolomite industry. As previously noted, reclamation plans may be a critical part of the permit process and should be developed well in advance of mining. In years past, limestone producers could view reclamation requirements as a future issue not needing current planning or engineering. Today, many local communities, and some states, require long-range operating plans that include the reclamation of abandoned areas concurrent with active mining or quarrying. Reclamation plans need to specifically address several items, including long-term land use decisions, health and safety of the community, and elimination of hazardous wastes and other potentially toxic discharges.

State and federal legislation under debate—such as the USACE and U.S. Environmental Protection Agency (EPA) federal wetlands regulations found in Section 404 of the Clean Water Act and associated legislation—will likely have a significant impact on the mining industry. Given the current federal guidelines of no net wetlands loss and the location of many limestone and dolomite resources, conflict appears to be inevitable, although mitigation guidelines can be found at www.mitigationactionplan.gov. Industrial, environmental, and political factions are currently debating the definition of wetlands, and it may be some time before what is and what is not a regulated wetland can be clearly defined. This issue is being litigated in the federal court system, along with questions of jurisdiction between federal and state agencies.

Other critical issues receiving public attention include respirable crystalline silica, storm-water runoff, underground fuel storage tanks, Phase II of the Clean Air Act Amendments of 1990, and potential revisions to the Endangered Species Act. The crystalline-silica issue is of particular concern since silica has been declared a carcinogen by the National Institute for Occupational Safety and Health, and tort claims are being filed even though the specifics for updated Occupational Safety and Health Administration and Mine Safety and Health Administration regulation have yet to be adopted. Several environmental groups and labor unions have challenged current regulations on silica (30 CFR, part 71.01), saying that they are too low. This issue is being both debated and litigated.

Storm-water runoff is another environmental issue that the quarry operator must address. The EPA requires storm-water discharge permits for all mining operations, and requires that the permit applicant consider potential ground water contamination resulting from quarry or mining activities. The NSSGA is working extensively with state and federal regulatory agencies and stone producers to assist in the development of and compliance with these regulations. The NSSGA Web site maintains regular updates on regulatory issues and governmental actions affecting the crushed stone industry (<http://www.nssga.org>).

Federal mandates to eliminate underground fuel storage tanks have been in place for many years. These tanks could potentially contaminate groundwater as they age and develop leaks. Because it is extremely difficult to monitor the integrity of these underground tanks, their removal has been strongly encouraged. In addition, it is also necessary to provide adequate containment structures around surface tanks to mitigate potential environmental issues that could result from a spill.

FUTURE TRENDS

Looking ahead to the next decade, the demand for limestone and dolomite is expected to grow at an average annual rate of about 2.0% to 2.5%. Limestone is the primary raw material for crushed stone, and its demand is expected to match the demand for new construction. In recent years, particular attention has been focused on the nation's deteriorating infrastructure and the need for repair and replacement. Although the specifics of federal funding initiatives may change from year to year, the fact remains that the federal and state governments annually allocate hundreds of billions of dollars to infrastructure repair and replacement.

The demand for chemical-grade carbonate rock used in industrial and agricultural applications is expected to equal, at a minimum, the growth of the U.S. population. In addition, Phase II of the Clean Air Act Amendments of 1990 could greatly expand the demand for both lime and limestone for utility stack-gas scrubbing. Lime is a primary reagent material for both wet and dry scrubbing, and limestone is used in both wet scrubbing and fluidized-bed combustion. These uses are covered in more detail elsewhere in this volume.

Although the demand for limestone and dolomite is expected to remain strong throughout the twenty-first century, the structure of the U.S. stone industry is changing. The most pronounced changes relate to consolidation within the industry and the increasing role played by foreign owners. In the 1990s and continuing into the early years of the twenty-first century, foreign and domestic companies completed mergers, acquisitions, and joint ventures that have resulted in a continuing change in the names on the front gates of many limestone and dolomite operations. Data from the USGS (Tepordei 2002) lists the U.S. top 10 crushed stone producers as follows

1. Vulcan Materials, Birmingham, Alabama
2. Martin Marietta Aggregates, Raleigh, North Carolina
3. Hanson Building Materials—America, Neptune, New Jersey
4. Oldcastle, Inc., Washington, D.C.
5. Lafarge North America, Inc., Herndon, Virginia
6. CSR, Ltd., dba Rinker Materials Corp., West Palm Beach, Florida
7. Cemex, Inc., Houston, Texas
8. Rogers Group, Nashville, Tennessee
9. Florida Rock Industries, Inc., Jacksonville, Florida
10. APAC, Inc., Atlanta, Georgia

A second trend having an increasing impact on U.S. limestone production is the role of imported crushed stone materials. Offshore limestone operations located in Canada, the Bahamas, and Mexico have been able to take advantage of low-cost ocean freight to reach markets along the east, west, and Gulf coasts of the United States. Newfoundland Resources and Mining Company, Ltd., initiated its first shipments of limestone to the United States in May 1990, from a \$30 million plant specifically designed for exporting crushed stone by ship along the eastern coast of the United States. Canada is only one of the countries exporting crushed limestone to domestic U.S.

markets. Martin Marietta's quarry near Freeport, Bahamas, and Vulcan Materials' Mexican imports from the Yucatan have had significant impact on aggregate markets in Florida and along the U.S. Gulf Coast. Martin Marietta's Bahamian quarry ships more 1.4 Mt annually, and Vulcan reports that their operations near Cancun have a capacity of more than 3.6 Mt per year. The efforts of Vulcan Materials, Martin Marietta, and Newfoundland Resources and Mining Company have been directed at the importation of crushed stone for aggregate materials, but they are not the only operations bringing limestone into the United States. On a much smaller scale, white, chemically pure, industrial-grade limestone has also been imported from the Caribbean and China for use in filler/extender materials. These products, however, have thus far represented only a fraction of 1% of total high-calcium filler/extender material produced and sold in the United States. Additionally, both aggregate and chemical-grade limestone is exported from Vancouver Island, British Columbia, Canada, to Pacific coastal ports.

In summary, limestone and dolomite have been and continue to be one of the most important raw materials in the United States. Demand will increase, albeit at a modest rate, and new uses and applications will be found. But limestone and dolomite will continue to be commodities produced and sold in a highly competitive marketplace. Competitive pressure will dictate that limestone and dolomite producers be attentive to cost control and apply improvements in technology to increase productivity. Producers will also have to adapt to a social and political climate that will demand no deterioration in the environment, and thus costs for limestone and dolomite products will increase.

ADDITIONAL RESOURCES

The Web sites of the geological surveys for each U.S. state and Canadian province offer a wealth of information about limestone and dolomite. The URLs are given in Table 11.

ACKNOWLEDGMENTS

This chapter draws heavily on the chapter in the 6th edition of *Industrial Minerals and Rocks*, written by D.D. Carr, L.F. Rooney, and R.C. Freas. The authors of this chapter updated the data and information and revised selected material while leaving much of the chapter as originally written. Because limestone and dolomite are the basic raw materials of a large segment of the construction industry, the majority of material presented in the 6th edition remains current.

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Table 11. Website addresses of U.S. state and Canadian provincial geological surveys

State/Province	Website	State/Province	Website
United States		New York	http://www.nysm.nysed.gov/research/geology
National	http://www.usgs.gov	North Carolina	http://www.geology.enr.state.nc.us
Alabama	http://www.gsa.state.al.us	North Dakota	http://www.state.nd.us/ndgs
Alaska	http://www.dggs.dnr.state.ak.us	Ohio	http://www.ohiodnr.com/geosurvey
Arizona	http://www.azgs.az.gov	Oklahoma	http://www.ou.edu/special/ogs-pttc
Arkansas	http://www.state.ar.us/agc/agc.htm	Oregon	http://www.oregongeology.com
California	http://www.consrv.ca.gov/cgs	Pennsylvania	http://www.dcnr.state.pa.us/topogeo
Colorado	http://geosurvey.state.co.us	Rhode Island	http://www.uri.edu/cels/gel_home/ri_geological_survey.htm
Connecticut	http://dep.state.ct.us/cgnhs/index.htm	South Carolina	http://www.dnr.state.sc.us/geology
Delaware	http://www.udel.edu/dgs/index.html	South Dakota	http://www.sdgs.usd.edu
Florida	http://www.dep.state.fl.us/geology	Tennessee	http://www.state.tn.us/environment/tdg/index.html
Georgia	http://www.dnr.state.ga.us/dnr/enviro/aboutepd_files/branches_files/gsb.htm	Texas	http://www.beg.utexas.edu
Hawaii	http://www.state/hi.us/dlnr/cwrm	Utah	http://geology.utah.gov
Idaho	http://www.idahogeology.org	Vermont	http://www.anr.state.vt.us/dec/geo/vgs.htm
Illinois	http://www.isgs.uiuc.edu/isgshome.html	Virginia	http://www.mme.state.va.us/Dmr/home.dmr.html
Indiana	http://igs.indiana.edu	Washington	http://www.dnr.wa.gov/geology
Iowa	http://www.igsb.uiowa.edu	West Virginia	http://www.wvgs.wvnet.edu
Kansas	http://www.kgs.ku.edu/kgs.html	Wisconsin	http://www.uwex.edu/wgnhs
Kentucky	http://www.uky.edu/KGS/home.htm	Wyoming	http://www.wsgs.uwyo.edu
Louisiana	http://www.lgs.lsu.edu	Canada	
Maine	http://www.state.me.us/doc/nrimc/nrimc.htm	Alberta	http://www.ags.gov.ab.ca
Maryland	http://www.mgs.md.gov	British Columbia	http://www.em.gov.bc.ca/geology
Massachusetts	http://www.geo.umass.edu/newsite/stategeologist	Manitoba	http://www.gov.mb.ca/itm/mrd/index.html
Michigan	http://www.michigan.gov/deq/0,1607,7-135-3306_28607---,00.html	New Brunswick	http://www.gnb.ca/0078
Minnesota	http://www.geo.umn.edu/mgs/index.html	Newfoundland and Labrador	http://www.geosurv.gov.nf.ca
Mississippi	http://www.deq.state.ms.us/MDEQ.nsf/page/Geology_home	Northwest Territories	http://www.nwtgeoscience.ca
Missouri	http://www.dnr.mo.gov/geology/homegsrad.htm	Nova Scotia	http://www.gov.ns.ca/natr/meb
Montana	http://www.mbmng.mtech.edu	Prince Edward Island	http://www.gov.pe.ca/enveng/eam-info
Nebraska	http://csd.unl.edu	Ontario	http://www.mndm.gov.on.ca/MNDM/MINES/ogs/default_e.asp
Nevada	http://www.nbmng.unr.edu	Quebec	http://www.mrnfp.gouv.qc.ca/english/home.jsp
New Hampshire	http://www.des.state.nh.us	Saskatchewan	http://www.ir.gov.sk.ca
New Jersey	http://www.state.nj.us/dep/njgs/index.html	Yukon	http://www.geology.gov.yk.ca
New Mexico	http://geoinfo.nmt.edu		

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Lithium Resources

Ihor Kunasz

INTRODUCTION

The second half of the 20th century saw a dramatic shift in lithium carbonate (and some lithium chloride) production from the usual pegmatite sources to brines. Today, all lithium carbonate, which is the basis of various downstream lithium chemicals, comes from the brines of the Salar de Atacama, Chile, and Clayton Valley, Nevada (United States). Lithium chloride is also produced from the Salar del Hombre Muerto, Argentina. Various other salars and playas such as those of China, Bolivia, Argentina, and Tibet are being evaluated for future lithium chemical production. The industry was once dominated by two major U.S. producers, until a third producer from Chile started production of various salts, including lithium carbonate. This shift in sources led to the shutdown of both U.S. pegmatite operations. Australia, Canada, and Zimbabwe have continued to supply lithium mineral concentrates for the ceramic and glass industry and other applications. Minor producers in Brazil, Portugal, Russia, and the People's Republic of China mine various lithium minerals. One new U.S. supplier of lithium chemicals came on stream using the depleted lithium hydroxide government stockpile.

When it was first recognized, lithium was an oddity that became an important commodity owing to its unusual properties. In 1854 in Germany, R. Bunsen and A. Mathiessen used an electrolytic process to prepare lithium as a free metal from molten lithium chloride. They prepared lithium carbonate, lithium chloride, and then lithium metal from zinnwaldite, a lithium-bearing mica. Lithium-bearing minerals were sometimes used as exotic additives to ceramic compositions.

Not until World War II were the special properties of lithium compounds fully investigated and exploited. A compact, lightweight source of hydrogen was needed for use in emergency-signaling balloons. Lithium hydride was found to be ideal for this purpose. Lithium was also used in alkaline batteries in submarines. Later, greases containing lithium stearate were found to lubricate at both very high and very low temperatures. For the first time, the same grease could be used for multiple purposes over a wide range of operating conditions.

With rocketry came the search for materials that could withstand the extreme temperatures of high-speed travel through the atmosphere. A ceramic composition containing lithium was developed that expanded very little and resisted cracking during rapid extreme temperature change. This lithium-containing material *pyroceram* was the forerunner of modern glass-ceramic cookware

that resists thermal cracking. Perhaps the most recognized application is CorningWare, in which lithium imparts a negative coefficient of expansion when heated, which allows the ceramic to be used from refrigerator to oven without shattering.

In 1953, the Atomic Energy Commission (AEC) required large amounts of lithium hydroxide from which the lithium-6 isotope was separated and reserved for use in producing the hydrogen bomb. For about 5 years, the government was the largest consumer of lithium. After the AEC contracts expired in 1960, the lithium industry, faced with vast overcapacity, sought desperately to develop some commercial markets. Though not an overnight success, it soon became a firmly established supplier to basic industries such as ceramics, lubrication, aluminum reduction, and pharmaceuticals. If certain technical issues are resolved, thermonuclear fusion, which requires lithium as the primary fuel, could solve much of the world's energy requirements.

Today, even though lithium products are widely used in households, factories, and laboratories, lithium's presence often goes unrecognized. Lithium may be as close to the average person as a medicine chest, a television, a swimming pool, or a calculator. Lithium is found in minerals, clays, and brines in various parts of the world. High-grade lithium ores and brines are the present sources for all commercial lithium operations. Economical brine sources of lithium were rare until several salars in South America were discovered to contain significant deposits of lithium.

Lithium was first produced from zinnwaldite in Germany. This was followed by the production of spodumene from the Black Hills of South Dakota, where log-sized spodumene crystals were mined. The WWII exploration for strategic elements (titanium, tantalum, and others) resulted in the discovery of the pegmatite fields in North Carolina (Kesler 1961), where two major lithium mineral and chemical production centers developed. During the 1950s lepidolite from Southern Rhodesia (Zimbabwe) was imported for conversion to lithium hydroxide at a Texas plant for producing the hydrogen bomb. After the depletion of the lepidolite, a spodumene zone was outlined, resulting in the production of high-grade spodumene concentrates. Numerous lithium pegmatites were also discovered in Canada. Spodumene concentrates are produced at the Tanco mine in Manitoba. In the 1980s spodumene was identified during tantalum mining and exploration in Western Australia, resulting in the production of spodumene concentrates at Greenbushes.

Lithium chemical production was shifted when the Silver Peak brine deposit, originally evaluated as a potash source, resulted in the unique production of lithium carbonate in 1966. Although lithium had been identified in 1936 in the brines of Searles Lake, California, the lithium diphosphate scale generated during the boron recovery process was considered more of a hindrance than an economic product. Put into production in 1966, the Silver Peak brine was, for almost 20 years, the only brine source of lithium carbonate production in the world. In 1969, the Chilean Instituto de Investigaciones Geológicas (IIG) identified unusually high concentrations of potassium and lithium at the periphery of the Salar de Atacama in Northern Chile (Moraga et al. 1974). After confirming the high concentrations, Foote Mineral initiated a feasibility study in 1975, and the Sociedad Chilena de Litio (SCL) began producing lithium carbonate from the southern sector of the salar in 1986. Several companies attempted to develop the northern portion of the salar. Eventually, Sociedad Química y Minera (Soquimich or SQM) developed the deposit and produced a number of chemicals, including potassium chloride, potassium sulfate, lithium carbonate, and boric acid. From a nonproducer before 1988, Chile has become the world's major supplier of lithium carbonate (Ober 2002).

The Lithium Division of FMC Corporation explored the Salar del Hombre Muerto in the Altiplano of Argentina and produces lithium chloride from the brine via a patented ionic exchange process.

As a result of extensive exploration for brine deposits, prompted by lithium production development in Chile, several chemical-rich deposits were identified and explored in Argentina, Bolivia, the People's Republic of China, and Tibet. The shift in lithium carbonate production from pegmatites to brines closed the two unzoned pegmatite operations of Chemetall Foote Mineral Company and the Lithium Division of FMC in North Carolina. Zoned pegmatites, which contain high-grade spodumene, continue to be important sources of lithium mineral concentrates for the various ceramic and glass industries.

GEOCHEMISTRY OF LITHIUM

Lithium is a silvery-white metal that is slightly harder than sodium but softer than lead. It is the lightest of all the metals, with a density of 0.534 g/cm³, or about half that of water. It has an atomic weight of 6.938, an ionic radius of 0.68 Å, and a charge of +1. Lithium is the third element in the periodic table and the first element in Group I, the alkali metals group. Like the other metals in the group—sodium, potassium, rubidium, and cesium—it is so chemically active that it never occurs as a pure element in nature; it is always bound in stable minerals or salts.

Some lithium compounds show a great resemblance to Group II, the alkaline earth metals. For example, the water solubility of lithium hydroxide is substantially lower than that of other alkali hydroxides. In general, lithium's physical and chemical properties stem from its atomic structure. An atom of lithium consists of a nucleus (three protons and either three or four neutrons) with three electrons orbiting in two shells. The inner shell (the helium shell) contains two electrons and is chemically inert. The outer shell contains only one electron. Lithium, more than any other alkali metal, tends to eject this electron from its outermost shell. The resulting lithium ion carries a positive charge (+1). In solid metal, individual lithium atoms are arranged geometrically in a cubic lattice and can transfer a negative charge from place to place. This electron movement makes lithium metal an excellent electrical conductor.

A Swedish scientist, Johan August Arfwedson, discovered lithium in 1817 in the laboratories of Berzelius. He analyzed the content of a mineral called petalite from Utö Island, Sweden. The results of the analysis left a sizable percentage of the sample's

chemical make-up unaccounted for. Further work resulted in the extraction of a compound with chemical properties, suggesting that an unknown element was present. Since the new element had been found in chunks of petalite, Arfwedson called it "lithium," from the Greek word *lithos*, meaning stone.

The geochemistry of lithium has been extensively studied, and Goldschmidt (1937), Rankama and Sahama (1950), Hortsman (1957), and Cerny (1991) summarized the work.

The distribution of lithium in igneous rocks is controlled by its size and its charge, and by the (MgO+FeO)/Li₂O ratio. In the early stages of crystallization of a magma, that ratio is very large. Consequently, both magnesium and iron are removed by ferromagnesian minerals in preference to lithium, which is then concentrated in the residual magma. The result is an enrichment of lithium in silicic rocks and pegmatites (Strock 1936).

Pegmatites are coarse-grained igneous rocks formed by the crystallization of postmagmatic fluids. Minerals within pegmatites can also form by metasomatism (Jahns 1955). Genetically the pegmatites are associated with neighboring intrusives. Mineralogically, granitic pegmatites contain feldspar, quartz, and mica as the main constituents and a variety of exotic elements such as lithium, beryllium, tantalum, tin, and cesium, which may or may not occur in economically significant concentrations.

Detailed studies by numerous investigators (Cameron et al. 1949, 1954; Hanley, Heinrich, and Page 1950; Jahns 1952, 1955; Page et al. 1953; Norton and Schlegel 1955; Cerny 1991) indicate that many pegmatites exhibit an internal zonal arrangement, with each zone containing a specific suite of minerals. The lithium minerals are usually found in the intermediate zones, and, although as many as 13 zones have been recognized (Cameron et al. 1949), a complete zonal arrangement is rarely found. Zoning of pegmatite bodies has also been observed regionally. The regionally zoned pegmatite sequences exhibit mineral assemblages and complexity according to their respective distance from the granitic bodies to which they are genetically related. Various theories have been proposed for the genesis of pegmatites. Cerny (1991) offered convincing evidence that rare metal pegmatites are essentially magmatic phenomena. Although pegmatites exhibit a broad diversity of paragenetic, geochemical, and structural styles, pegmatites have crystallized from a volatile-rich melt enriched to various degrees in lithophile elements. From a practical exploration standpoint, Cerny concluded that Late Archean and Early Proterozoic fields are possibly the most productive, and that lower amphibole facies of volcano-sedimentary rocks are the main hosts for pegmatites.

Lithium is also found in small proportions in a variety of rocks. The average lithium content of igneous rocks is estimated at about 28 ppm Li. Sedimentary rocks contain an average of 53 ppm Li, and the highest concentrations are recorded in shale (Hortsman 1957). Volcanic rocks, particularly obsidian, contain high concentrations of lithium (Shawe, Mountjoy and Duke, 1964; Price et al. 2000). Unusual amounts of lithium are found in the clay mineral hectorite, which is expandable and belongs to the magnesian end member of the smectite (montmorillonite) group.

Lithium is also present in significant amounts in waters associated with geothermal areas (White 1957) in Iceland (Reykjavik), New Zealand (Waikare), California (Imperial Valley), and Mexico (Agua Prieta geothermal field). Very high concentrations (up to 47 ppm Li) have been recorded in the El Tatio geothermal field, located north of the Salar de Atacama (Ide and Kunasz 1989). It is also associated with certain oil well brines (Mayhew and Heylman 1966). Lithium occurred in higher concentrations in certain desert basin brines of California (Searles Lake), Nevada (Clayton Valley), and Utah (Great Salt Lake), and in a number of salars in Chile (Atacama, Pedernales,

and others), of which the Salar de Atacama is the richest; Bolivia (Salar de Uyuni); Argentina (Salar del Hombre Muerto, El Rincon, and others); Tibet (Lake Zabuye), where natural lithium carbonate was discovered (Holland et al. 1991); and the People's Republic of China (Qinghai Basin).

LITHIUM MINERALS

Although lithium occurs in some 145 minerals, only spodumene, lepidolite, petalite, and some other minerals such as amblygonite and eucryptite have been commercial sources of lithium. Today, the principal sources of lithium ores and chemicals are spodumene and petalite.

Spodumene

Spodumene, a lithium aluminum silicate ($\text{LiAlSi}_2\text{O}_6$), is a monoclinic member of the pyroxene group. It has a very pronounced cleavage plane (110), which results in typically lath-shaped particles on breaking. The color of spodumene is variable, being nearly white in the low-iron variety and dark green in iron-rich crystals. When clear, spodumene is considered a gemstone. Three varieties are known: hiddenite, the green variety from Alexander County, North Carolina, first discovered in Brazil; triphane, the yellow variety also from Alexander County; and the lilac-colored kunzite from the Pala District in California, and in Brazil and Afghanistan.

Spodumene undergoes pseudomorphic alteration to a variety of minerals. Norton and Schlegel (1955) described spodumene replacement by quartz, albite, perthite, muscovite, beryl, amblygonite, apatite, and tourmaline. Weathering commonly alters spodumene to kaolinite and to montmorillonite.

Spodumene constitutes the most abundant commercial source of lithium minerals. Theoretically it may contain up to 3.7% Li, but the actual lithium concentration ranges from 1.35% to 3.56%, probably as a result of sodium and potassium substitution for lithium. Spodumene concentrates typically contain 1.9% to 3.3% Li. Spodumene occurs in many pegmatite belts around the world and was the conventional source of lithium concentrates and chemicals in the United States (North Carolina) until the discovery of brines closed the only two spodumene mines in North Carolina. Spodumene occurs in many countries: Sweden (Utö), Austria (Koralpe), Brazil (Minas Gerais), Argentina, Canada (Manitoba, Quebec, and Northwest Territories), Zimbabwe (Bikita), Democratic Republic of the Congo (Manono and Kittolo), Australia (Greenbushes), the Russian Federation (Chita region), and the People's Republic of China (Altai Mountains).

Lepidolite

Lepidolite is a phyllosilicate with the general formula $\text{K}_2(\text{Li,Al})_{5-6}[\text{Si}_{6-7}\text{Al}_{2-1}\text{O}_{20}](\text{OH,F})_4$. The chemical variability expressed in the formula stems from a structural complexity attributed to a mixture of polymorphs, which include muscovite, lithium muscovite, and polyolithionite (Winchell 1942). On the other hand, Foster (1960) and Deer, Howie, and Zussman (1962) suggested that there is a continuous series between muscovite with a 2M1 structure to lepidolite with 1M, 2M2, and 3T structures. The structural transition takes place when the lithium oxide content in the mica reaches 1.53%.

The lithium concentration in lepidolite ranges from 1.53% to a possible theoretical maximum of 3.6%. In commercial deposits the concentrations are more normally 1.4% to 1.9% Li. In addition to lithium, lepidolites also carry substantial concentrations of rubidium and cesium (Deer, Howie, and Zussman 1962).

The major commercial deposits of lepidolite are in Zimbabwe (Bikita), Namibia (Karibib), Canada (Bernic Lake, Manitoba), Brazil (Minas Gerais), Portugal, and Spain.

Petalite

Petalite, $\text{LiAlSi}_4\text{O}_{10}$, is a monoclinic mineral with a framework silicate structure. Its color is grayish white and more rarely pinkish. It has two cleavage directions, which form an angle of 38.5° . The basal cleavage is perfect.

The theoretical lithium content of petalite is 2.27%. In commercial deposits it ranges from 1.6% to 2.1% Li. Sizable deposits of petalite occur with lepidolite in Zimbabwe (Bikita), Namibia (Karibib), Brazil (Aracuai), Australia (Londonderry), the former U.S.S.R. (eastern Transbaikalia), Sweden (Utö), and Canada (Bernic Lake).

In certain pegmatites there is evidence that petalite alters to a mixture of spodumene and quartz. For the Bernic Lake pegmatites of Manitoba, Cerny and Turnock (1971) described pseudomorphs of spodumene and quartz after petalite, commonly referred to as SQI, according to the following reaction: petalite (spodumene + 2quartz).

Eucryptite

Eucryptite is also a lithium aluminum silicate that is deficient in silica. It has a formula LiAlSiO_4 and can contain 5.53% Li. The only large deposit of eucryptite is found in Zimbabwe (Bikita), where its occurrence with quartz suggests spodumene origin (Westenberger 1963). The grade of the eucryptite is 2.34% Li. Eucryptite has also been reported in Connecticut (Branchville mica mine); New Mexico (Harding mine); Manitoba (Tanco mine); Ontario (Nakima mine); and North Carolina (Foote mine).

Amblygonite

Amblygonite, with the generalized formula $\text{LiAl}(\text{PO}_4)(\text{F,OH})$, is the fluorine-rich end member of a phosphate series and montebrasite represents the hydroxyl-rich end member. It occurs in white to gray masses. Most cleavage planes are pearly; others are vitreous. Amblygonite weathers to earthy apatite, wavellite, and other lithium-deficient phosphates. Although amblygonite may contain as much as 4.74% Li, most commercial ores carry 3.5% to 4.2%. Amblygonite has been mined in Canada, Brazil, Surinam, Zimbabwe, Rwanda, Mozambique, Namibia, and the Republic of South Africa.

Hectorite

Lithium also occurs in significant concentrations in the mineral hectorite, a trioctahedral smectite. The purest deposit is found at Hector, California, where the white clay is exploited for its swelling characteristics in cosmetic applications. The lithium concentration in the hectorite is 0.53% Li. Hectorite has also been identified in Clayton Valley (Kunasz 1970) and McDermitt, Nevada (Glanzman, McCarthy, and Rytuba 1978).

CONTINENTAL BRINES

Lithium is found in commercial quantities in certain continental brine deposits. The brines, volcanic in origin, are present in desert areas and occur in playas and saline lakes where dilute lithium solutions have been concentrated by solar evaporation. In Seares Lake, where production of dilithium phosphate began in 1938, the lithium concentration is 70 ppm Li. In Clayton Valley, Nevada, the lithium concentration in brines varies from 100 to 300 ppm. Lesser concentrations of lithium (28 to 60 ppm Li) are found in the Great Salt Lake of Utah.

Following the discovery of lithium in the brines of the Clayton Valley, Nevada, exploration revealed the presence of lithium in other playas and salars in the world (Kunasz 1994). High concentrations of lithium have been recorded in several salars in Argentina (Salar del Hombre Muerto, 200 to 2,000 ppm Li); Bolivia (Salar de Uyuni,

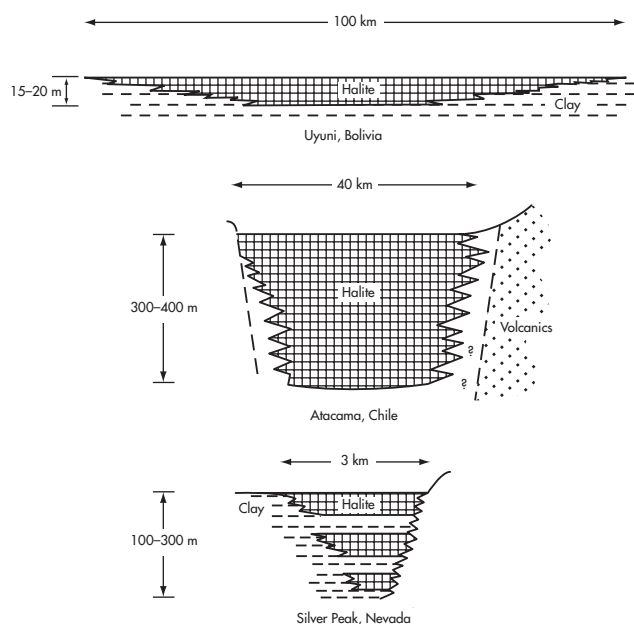


Figure 1. Idealized cross sections of three basins

100 to 700 ppm Li); Chile (Salar de Atacama, 1,000 to 7,000 ppm Li); Tibet (Lake Zabuye, 700 to 1,000 ppm Li); and the People's Republic of China (Qinghai, 100 ppm Li; Yiliping, 300 ppm; Tajiner, 350 to 400 ppm Li).

Brines are the predominant sources of lithium carbonate in the world today. Much has been done on the chemistry of these brines, revealing that although playas and salars are similar in many respects, they nevertheless exhibit individual characteristics (Kunasz 1980). Lithium-bearing salars or desert basins have the following similar characteristics: they occur within Tertiary or Recent volcanic belts, they are closed structural depressions, and they occur within the desert areas of the earth. These may then be considered the fundamental requirements for the occurrence of economic lithium brines.

The first requirement simply establishes the source of lithium. The volcanic environment supplies the lithium either directly through hot springs or geothermal solutions or indirectly through the leaching of lithium-bearing volcanic or clastic sediments or by the recycling of trapped lithium-bearing solutions. This condition is met by all three major salars: Clayton Valley, Salar de Atacama, and Salar de Uyuni all occur in areas with abundant volcanic rocks. The second requirement provides the necessary mechanism for retaining the dilute solutions introduced into the basin. Strong structural control is evident in Clayton Valley, Nevada, and in the Atacama Area, Chile. Direct structural control is not obvious for the Salar de Uyuni. Finally, all potentially commercial lithium concentrations are the result of concentration by solar evaporation. With the exception of the Imperial Valley geothermal field and oil-field brines where lithium concentrations as high as 280 ppm have been recorded, high lithium concentrations are not primary but secondary phenomena, caused by concentration under proper climatological factors. Although the fundamental character of the salars is similar, cursory examination of the three lithium-rich basins that are described in the following sections reveals great variability in size, surface character, stratigraphy, structure, and chemistry.

The salars or playas fall within three general types, as illustrated in Figure 1. Clayton Valley is the smallest of the three. Its total surface area covers approximately 100 km². The Salar de Atacama basin has an approximate surface area of 3,000 km², whereas the salt nucleus proper covers an area of approximately 1,400 km². The Salar de Uyuni, on the other hand, occupies a very large surface area of approximately 10,000 km², and thus represents the largest such desert basin in the world. The idealized stratigraphic column of each of the three basins indicates significant differences between them as well and reveals their individual historical evolution. Clayton Valley underwent alternating dry-wet climatic cycles under conditions of structural instability. The Salar de Atacama formed under an intense evaporative cycle with associated major subsidence. The Salar de Uyuni appears to have undergone a single evaporitic cycle with little associated subsidence. When the basin surfaces are predominantly composed of silts and clays with some salt incrustation, they are referred to as playas. If the surface is predominantly salt (with or without polygonal cracks), they are called salars (English) or *salar*es (Spanish).

Clayton Valley, Nevada

The Silver Peak playa in Clayton Valley is known to be a complex system (Zampirro 2004), possibly because it has been extensively studied, having produced lithium for some 35 years. It can be considered an intermediate between the Salar de Uyuni and the Salar de Atacama because it incorporates the structural elements of the Salar de Atacama but underwent fluctuating arid and wet climatic cycles. The basin consists of interbedded fine-grained sediments and halite, some volcanic ash layers, and some tufas. This is consistent with the paleohydrologic regimes in the southwestern Great Basin, although obvious breaks such as those reported by G.I. Smith (1966) at Searles Lake have not yet been recognized. Although the halite layers in the section contain large lithium reserves, production comes mainly from an unconsolidated volcanic ash aquifer and additional reservoirs identified by subsequent exploration. Structure maps of the main volcanic ash indicate that some portions of the basin subsided as much as 150 m during sedimentation. Several sources have been identified for the lithium contained in the Quaternary playa sediments (Figure 2) and in the lithium-bearing aquifers (Figure 3):

- Geothermal fluids issuing from faults on the eastern side of the playa; sampling along a fault zone show a substantial lithium enrichment (Kunasz 1970)
- Increased lithium concentrations in the Tertiary lacustrine sediments exposed on the eastern side of the basin compared to the northern sediments (Kunasz 1970)
- Rhyolitic rocks with high lithium contents on the east side of the basin (Price et al. 2000)
- Concentration of lithium in the Quaternary basin by natural solar evaporation

These conditions resulted in the accumulation of lithium-rich sediments and enriched brine in the southeastern portion of the present playa. This sector is the principal source of the brine fed to the 4,000 acres of solar evaporation ponds in which the lithium chloride is concentrated (Zampirro 2004).

Salar de Atacama, Chile

The Salar de Atacama is in northern Chile at an elevation of 2,300 m, where it straddles the Tropic of Capricorn. The basin proper has a surface area of approximately 3,000 km², and the salt nucleus proper covers approximately 1,100 km². The salar is bounded on the eastern

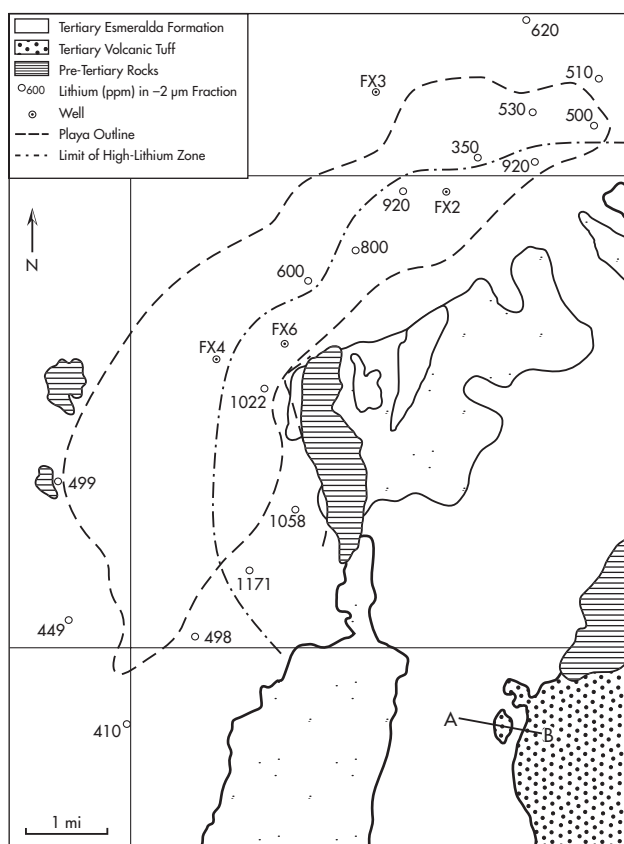


Figure 2. Lithium content (ppm) of surface sediment samples, Clayton Valley, Nevada (A–B sampling location is in Figure 3)

side by Andean Cordillera and on the western side by the Cordillera Domeyko (Figure 4).

The salt nucleus consists almost exclusively of a halite facies with a development of very narrow marginal facies of sulfate and carbonate. The surface of the salar is extremely rugged because of extensive development of polygonal cracks (Figure 5). It is similar in many respects to the Devils Golf Course in Death Valley, California.

During the early exploration phase in 1975, access to the salar was limited to trails and a 37-km gravel road, so much of the geochemical work was conducted by helicopter. Numerous roads have since been built for the two brine operations. The Salar de Atacama basin is a graben in a tectonically quite active area with numerous fault scarps. The extensive thickness of salt in the basin indicates that saturation with respect to sodium chloride was predominant during most of the subsidence history of the basin. No beaches or algal reef complexes are present, which suggests desiccation from a much larger body of water. The ancestral chemical system was probably very high in solutes. The source of the lithium in the basin is volcanic in origin (Ide and Kunasz 1989). It enters the basin from two principal directions. One is from the north where the liquid from the El Tatio geothermal field (with lithium concentrations of 47 ppm) discharges via the San Pedro River. The other source is very likely from saline lakes in the Andean Cordillera east of the salar. Structural interpretations by Frutos (1972) suggest the presence of numerous east–west lineaments, which are the conduits through which lithium-bearing solutions discharge into the salar.

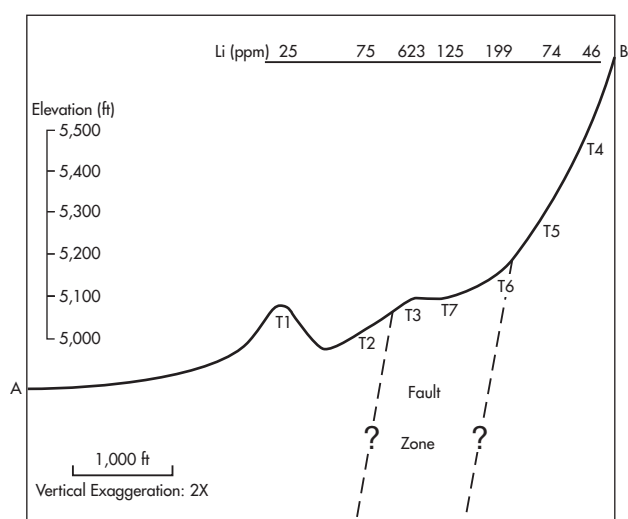


Figure 3. Lithium enrichment along Fault Zone 1, Clayton Valley, Nevada



Figure 4. Aerial photo of Salar de Atacama (Chile) salt nucleus and pond operating systems—SQL (southeast) and SQM (two pond systems)



Figure 5. Surface crust of Salar de Atacama (Chile)

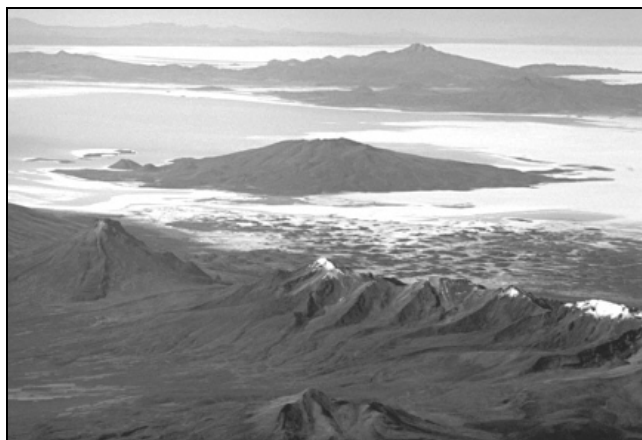


Figure 6. Aerial view of Salar de Uyuni (Bolivia)



Figure 7. Surface of the Salar de Uyuni (Bolivia)

The deltaic sediments of the San Pedro River bind the salt nucleus to the north. The surface of the salar is inaccessible because of extensive polygonal cracking. Preliminary drilling by CORFO (Corporación de Fomento; a Chilean state development agency) over various parts of the basin indicated a minimum thickness of 360 m of halite near the center of the basin, diminishing to about 40 m near the southern margin. Drilling by the Hunt Oil Company indicates that the salt thickness may exceed 1,000 m. Salt cores show that only the near-surface portion of the halite crust has high porosity and permeability. A 10-km-long seismic survey revealed that the highest porosity extends to a depth of 20 to 25 m and that some additional lower-porosity halite may exist at depths from 25 to 35 m. Below this depth, salt cores show complete recrystallization of the halite into a solid mass, devoid of any pores. The yield characteristics of the upper halite layer were determined by drilling and testing shallow wells to 30 m and 60 m. The wells, pumped for 3 months at 64 L/sec, stabilized at drawdowns of 20 cm/sec and 7.9 m, respectively, corroborating that only the upper 30 m have a high transmissivity.

Salar de Uyuni, Bolivia

The Salar de Uyuni is in southwestern Bolivia at an elevation of 3,653 m. The salar represents an immense body of salt, with a maximum

Table 1. Partial cation chemical analyses, wt %

Cation	Silver Peak, Nevada	Salar de Atacama, Chile	Salar de Uyuni, Bolivia
Li	0.023	0.14	0.025
K	0.53	1.87	0.62
Na	4.43	6.92	9.1
Mg	0.033	0.91	0.54
Mg:Li	1.5	6.6	21.5

surface dimension reaching 120 km (Figure 6). The surface of the salar is smooth (Figure 7).

Meager subsurface data suggest that the salt crust is about 15 to 20 m thick. Extensive development of algal reefs some 75 m above the present surface of the salar attests to the existence of a much larger and less saline ancestral body of water—Lake Minchin (quite reminiscent of the ancestral Lake Lahontan and the present Great Salt Lake in Utah). The presence of several algal terraces suggests lowering of the lake level in several stages. The ultimate stage represents saturation with respect to sodium chloride and resulted in the precipitation of present crust. A sample collected from a depth of 15 cm beneath the surface of the salt crust by W.D. Carter (Ericksen, Vine, and Ballou 1978) gave a radiocarbon date of $3,520 \pm 600$ years, suggesting that salt precipitation may have begun some 350,000 years ago. Comprehensive reports on the studies conducted on the Salar at the request of the Bolivian Government have been prepared by Ericksen, Vine, and Ballou (1978) and by the Servicio Geológico de Bolivia (Ballou and Risacher 1981).

All three basins contain abnormal lithium concentrations. As mentioned previously, the lithium must be attributed directly or indirectly to volcanic geothermal activity of Recent or older age. There is no doubt, however, that the strength recorded today in the brine is the direct result of an intense concentration mechanism resulting from natural solar evaporation.

Table 1 shows some partial chemical analyses of the major cations contained in the three brines. All analyses represent the averages of several samples collected in each of the basins and early production averages from the well field for Silver Peak.

The Salar de Atacama contains the highest lithium, potassium, and magnesium concentrations (Table 1). Concentrations up to 7,000 ppm Li have been recorded in the Salar de Atacama brines. Several sources of lithium have been identified, but the most important was from the leaching of the volcanic rocks surrounding the salar. A second source was the weathering and leaching of exposed lacustrine sediments predating the formation of the salar. Geothermal fluids such as those of the El Tatio (28 to 47 ppm Li) represent a third source (Ide and Kunasz 1989). Of the three basins, however, there is no question that the evaporation-concentration mechanism was most intense for the Atacama Basin. Table 1 also indicates that ratios between various cations in the brine are different between the three basins, which strongly argues for different compositional inputs. The chemistry, specifically the Mg:Li ratios, also illustrates one of the important aspects controlling the production of lithium from different brines. In systems with high Mg:Li ratios, the phase chemistry prevents the formation of lithium chloride brine unless the magnesium is removed at the start of the process. This has been achieved in Clayton Valley (Barrett and O'Neill 1970) and at the Salar de Atacama. The exceedingly high Mg:Li ratio has prevented the development of the Salar de Uyuni (and the Great Salt Lake) as an economic source of lithium.

PRODUCTION FROM BRINE DEPOSITS

Historically, lithium chemicals and mineral concentrates were produced from pegmatites. The most important was the Kings Mountain Belt of North Carolina, where the two major producers (Chemtall Foote Corporation and FMC Lithium Division) mined and produced lithium concentrates, mineral concentrate by-products, and lithium chemicals.

In the early 1960s, Foote Mineral Company started developing the Silver Peak, Nevada, brine operation (Barrett and O'Neill 1970). Although the American Potash Corporation produced some lithium as a by-product at Searles Lake, California (1938–1978), Silver Peak was unique because it represented a primary source of lithium carbonate from a brine deposit. Its uniqueness led to the investigation and identification of lithium in numerous other salars around the world and the eventual new production from Chile (Salar de Atacama) and Argentina (Salar del Hombre Muerto).

Clayton Valley, Nevada

Foote Mineral Company traces its origins to A.E. Foote, who founded the company in 1876 as a purveyor of rare minerals. It became a major producer of lithium chemicals when it acquired the right to mine spodumene at Kings Mountain, North Carolina, in the early 1950s. In the 1960s, Foote pioneered the production of lithium carbonate from brine with the opening of the Silver Peak plant (Clayton Valley). It was acquired by Cyprus Minerals Company, then by Chemetall of Germany and more recently by Rockwood Specialties.

The Clayton Valley salt marsh was first investigated during the World War II effort to locate sources of strategic minerals, one of which was potash. The salt marsh area was leased by the American Potash Corp., which let the leases lapse. The leases were picked up by the Leprechaun Mining Company (Clyde Kegel), which conducted some exploration on the subsurface brines and identified lithium in addition to potassium. An agreement was later negotiated with Foote Mineral Company, which developed the brines of the basin as a source of lithium carbonate (Barrett and O'Neill 1970).

In Clayton Valley, lithium-bearing brines occur in an asymmetric, undrained structural depression filled with Quaternary sediments composed mainly of clay minerals, including hectorite, volcanic sands, and alluvial gravels, and saline minerals consisting of gypsum and halite (Kunasz 1970). The brine that saturates the sediments is chemically simple. It is a concentrated sodium chloride solution containing subordinate amounts of potassium and minor amounts of magnesium and calcium. The lithium concentration is variable and decreases with pumping; the lithium concentration in the brine varies from 100 to 300 ppm Li. The dominant source of lithium has been a volcanic ash that extends across the basin. Exploration has identified additional aquifers and they supply additional volumes of lithium-bearing brine.

An extensive well field supplies the brine into some 4,000 acres of solar evaporation ponds (Zampirro 2004). Over 12 to 18 months, concentration of the brine increases to 6,000 ppm Li through solar evaporation. When the lithium chloride reaches optimum concentration, the liquid is pumped to a recovery plant and treated with soda ash, precipitating lithium carbonate, which is then filtrated out, dried, and shipped. Domestic production of lithium carbonate from brine is limited to Chemetall Foote's operation in Nevada. At this time, the Silver Peak operation is one of the world's leading producers of lithium hydroxide. Chemetall Foote also produces normal and secondary butyl-lithium at its New Johnsonville, Tennessee, facility and a number of downstream products (lithium chloride, bromide, and sulfate; U.S. Pharmacopeia- [USP-] grade lithium carbonate and high-purity

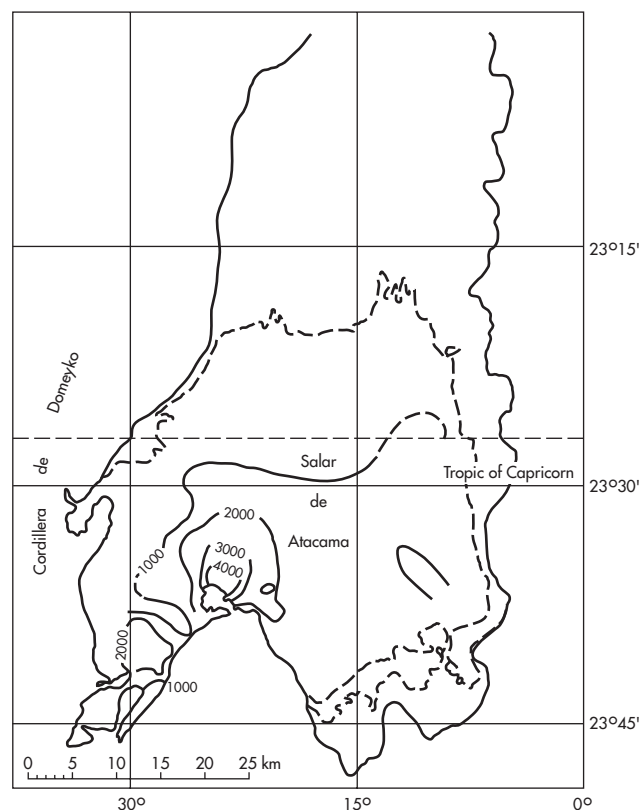


Figure 8. Salar de Atacama—lithium, ppm

lithium carbonate; lithium metal ingots and foils for the primary battery industry) at Kings Mountain, North Carolina.

Salar de Atacama, Chile

Two companies produce lithium carbonate and other salts from the brines of the Salar de Atacama: SCL, wholly owned by Chemetall Foote, and SQM.

In the 1990s large-scale production of lithium carbonate shifted from the United States to South America (Chile and Argentina). IIG made the first published reference on the occurrence of lithium in Chile in 1969 when it undertook an extensive survey of the Salar de Atacama. The institute published its findings in 1974 (Moraga et al. 1974). Subsequent studies by CORFO showed that the salt nucleus contains a resource of 4.3 Mt of lithium (Penner 1978). In April 1974, Foote Mineral Company (Cyprus Foote Mineral Company) verified the high lithium concentrations in the shallow brines below the saline crust. In January 1975, an agreement was signed with CORFO to initiate a 4-year feasibility study to assess the potential of producing lithium carbonate from the brine. The results of an exploration program based on test holes drilled on 5-km centers revealed very high lithium concentrations (Figure 8) over most of the salar (1,000–7,000 ppm Li).

SCL, a subsidiary of Chemetall Foote, has been exploiting the brines from the southern portion of the salar since 1984. The saturated brine is found 50 cm below the salt crust in a porous upper salt layer that reaches a thickness of about 30 m. It is pumped via standard wells to a series of extensive, plastic-lined, solar evaporation ponds (Figure 4). The initial phase chemistry is controlled by mixing brines from separate sectors of the salar to

remove the magnesium and sulfate at the early stages of evaporation. The final brine, concentrated to about 6% LiCl, is then transported by rail to the port city of Antofagasta, where it is converted to Li_2CO_3 by reaction with sodium carbonate. The combined SCL production between the Silver Peak, Nevada, and the Salar de Atacama operations is approximately 20,500 tpy. SCL also harvests KCl as a by-product at the salar.

Exploration by a number of companies over the northern portion of the Salar de Atacama led to its development as a second chemical production center. SQM, the Chilean nitrate producer, acquired the development rights and started the production of potassium chloride, potassium sulfate, and lithium carbonate in 1997.

SQM is the world leader in specialty fertilizers, iodine, and lithium carbonate. Created in 1968 as part of a plan to reorganize the Chilean caliche (sodium nitrate) industry, SQM is today the lowest cost producer worldwide of potassium chloride, lithium carbonate, potassium sulfate, and boric acid. Between 1994 and 1998 the company developed the largest nonmetallic project in Chile: the Salar de Atacama project. The three stages of the project required an investment of US\$300 million. The first stage was to build a 300,000-tpy potassium chloride plant, which currently produces about 170,000 tpy KCl. The entire output is consumed internally, supplying raw material to SQM's potassium nitrate production. The second stage was to produce lithium carbonate with a design capacity of 23,000 tpy from brines obtained from the potassium chloride production process. The last stage, begun in 1998, was the construction of a potassium sulfate plant that now also produces boric acid as a by-product. The company also produces boron chemicals. SQM avoided the issue of the high magnesium concentration by mixing brines of different compositions, resulting in a phase chemistry that led to the precipitation and subsequent harvesting of various salts (sylvinite, potassium sulfate, and boric acid). The excess residual brines are reinjected into the salar. Trucks carry the saturated solution of lithium chloride from the Salar de Atacama to the plant at the Salar del Carmen, east of Antofagasta, where it is purified by removing the remaining boron and magnesium through extraction and filtering processes. Finally, the purified lithium brine is reacted with sodium carbonate to produce lithium carbonate, which is filtered, washed, dried, and packed into different kinds of products. The production of lithium carbonate started at 22,000 tpy. SQM now produces 40% of the world's lithium carbonate. The company has also started production of butyl-lithium at its Bayport, Texas, plant and has acquired LithChem, a producer of lithium carbonate and lithium hydroxide.

Salar del Hombre Muerto, Argentina

Several lithium occurrences have been documented in the Argentinian Altiplano (Poppi 1981). Discovered as a result of an Earth Resources Technology Satellite (ERTS) collaborative project (Nicolli et al. 1980), several salares (Hombre Muerto, Rincon, Pastos Grandes, and others) were explored. In 1995, FMC Lithium purchased the rights to the Salar del Hombre Muerto, a salar containing high, uniform concentrations of lithium with low levels of other contaminants. The Salar del Hombre Muerto is in the high Andes at about 4,025 m above sea level, about 1,400 km northwest of Buenos Aires. The location is convenient to major rail lines and seaports. Covering a smaller area than most salars of the region, it contains lithium brines at depths much greater than its neighbors. The site investigation involved core drilling, testing, sampling, and hydrological studies. Reserves were estimated using geostatistical techniques and a three-dimensional flow model with coupled solute transport, which indicate a reserve of 75 years. The concentrations

of lithium in these brine deposits range from 200 to 2,000 ppm and can be further concentrated using solar evaporation. Contributing to efficient solar evaporation and concentration of the brines are the low rainfall and humidity, high winds and elevations, and relatively warm days in the area of the salars. When such conditions are present, highly concentrated brines can be produced at reasonable cost and used as feedstock for a lithium carbonate plant.

While mining spodumene in North Carolina, FMC perfected and commercialized a selective purification process extracting nearly pure lithium chloride from the salar brine with minimal processing (*North American Mineral News* 1995). The Salar del Hombre Muerto area also contains plentiful fresh water needed by the selective purification process. Selective purification uses low-cost raw materials housed in modular units. FMC has installed production facilities for both lithium chloride and lithium carbonate from the Salar del Hombre Muerto. Between 1999 and 2003, FMC produced an average of 4,800 tpy (Ober 2003), well short of the planned production capacity. With its market position in soda ash, FMC planned to produce lithium carbonate at a competitive cost. The company recently announced, however, that it will source its carbonate requirements from Chile under a supply contract with SQM (Ober 2000). FMC also produces downstream lithium products at Bessemer City, North Carolina, and at Bayport, Texas.

Potential Brine-Producing Districts

Argentina—Salar del Rincon and Others

Equity-1 Resources of Australia has been involved in developing Salar del Rincon. In addition to significant lithium, the brine contains high concentrations of sulfates, resulting in a complex phase chemistry that must be resolved before lithium can be economically recovered.

Qinghai Basin, People's Republic of China

As a result of the shift of lithium carbonate production from pegmatite source to brines, the Chinese spent much effort to identify and exploit brine deposits in the Qaidam Basin of northwestern China. A number of playas (salt lakes) have been identified. In the Golmud Area, brines have been exploited for potash and Chinese researchers have undertaken renewed efforts to produce lithium from the salt lakes of Tajinar and Yiliping, where high lithium concentrations have been recorded. The Mg:Li ratio is, however, very high and thus is a key to solving the process flowsheet (Peihua and Pengxi 2000).

The Qaidam Basin is in northwestern China's Qinghai Province. Several playas have been explored, and some could quite possibly become centers of lithium chemical production. A group of scientists from the Qinghai Institute of Salt Lakes of the Chinese Academy of Sciences has successfully solved the problem of separating lithium from the brine solution, which contains a high concentration of magnesium. The province will set up a company capable of producing 100 tpy of lithium chloride, near the Dong Tajinar Lake. The Qaidam Basin has about 33 salt lakes with a reported resource estimated at nearly 14 Mt of lithium chloride. At present, the basin is China's largest production base for potash fertilizer (*People's Daily* 2000).

Tibet

Lake Zabuye is one of 352 salt lakes on the Qinghai-Xizang (Tibetan) Plateau. The lake lies in a closed basin at an elevation of 4,421 m. The evaporation of these alkaline chloride-sulfate waters has led to a complex set of evaporitic minerals. Of importance is the occurrence of zabuyelite, which precipitates from the lake waters as natural lithium carbonate. The source of the rather extraordinary

high levels of lithium (800 ppm) is most likely of geothermal origin, because the springs that feed the lake are abnormally high in lithium (Holland et al. 1991). A recent announcement (*China News* 2005) indicated that 240 million yuan (US\$29 million) have been invested in 2003 to build the Baiyin lithium carbonate plant in Lake Zabuye. The plant capacity is reported to be 5,000 tpy of lithium carbonate.

PRODUCTION FROM PEGMATITE DISTRICTS

Following the shift to lithium carbonate to Chile, the pegmatite-mining district of North Carolina was no longer able to compete economically. The two mining operations closed down, although the sites continue to produce downstream lithium chemicals. Similarly, the two major producers no longer produce spodumene and other mineral concentrates. The slack was picked up by the three dominant producers in Canada (Tanco), Australia (Greenbushes), and Zimbabwe (Bikita).

Australia

Spodumene is mined from a zoned pegmatite in the southwest of Western Australia, approximately 300 km south of Perth and 80 km east of the Port of Bunbury. Sons of Gwalia acquired a 100% interest in the Greenbushes mine in 1998.

The Greenbushes pegmatite is the largest hard-rock tantalum resource and the largest and highest-grade lithium mineral resource in the world. The deposit is a zoned pegmatite with a strike length of more than 3 km. It contains zones of tantalite, spodumene, sodium, and potassium feldspars with some overburden of very white, high-grade kaolin.

Mining in the area has continued almost uninterrupted since tin was first discovered in 1888. The spodumene deposit was identified in 1980 during the extensive drilling program for tantalum. By 1983, initial development of the spodumene ore body commenced and, by 1985, a 30,000-tpy spodumene concentrator was commissioned. This was later increased to 100,000 tpy capacity in 1993–1994 and again to 150,000 tpy capacity in 1996–1997. The ore reserve and resource are >13 Mt, that is, sufficient to supply high-grade products for several decades.

The Minerals Processing Plant, constructed in 1980 as a tantalum pilot plant, was converted to the Lithium Minerals Processing Plant in 1983. The plant was expanded several times, the latest in 1995, to meet increased demand for spodumene. This plant liberates and recovers the spodumene into several spodumene minerals by milling, screening, flotation, gravity, and magnetic separation processes to meet the requirements of the various product applications.

The Greenbushes operation produces about 60,000 tpy of spodumene concentrates. It supplies about 60% of the world market. The highest quality concentrate has a grade of 7.5% Li_2O . The company also produces several other concentrates. A chemical plant was constructed but was mothballed after a fall in the world price of lithium (ACTED 1997).

Canada

Tantalum Mining Corporation of Canada is part of Cabot Specialty Fluids, a division of Cabot Corporation, Boston, Massachusetts. It produces spodumene from a zoned pegmatite and operates a concentrating plant at Bernic Lake, Manitoba, Canada. The site is about 130 km northeast of Winnipeg.

The Bernic Lake pegmatite is one of a number of subhorizontal pegmatite sheets in the Bird River greenstone belt within the Superior geological province in the Canadian Shield. It was formed during the Kenoran Orogeny of the Late Archean age and is approximately 2.5 billion years old. Internally, the pegmatite is

composed of eight discrete mineralogical zones comprising economic minerals containing tantalum, lithium, cesium, and rubidium, each occurring in separate zones. The various minerals are spodumene, montebrasite, wodgonite, microlite, pollucite, lepidolite, and feldspar. Jack McNutt discovered Bernic Lake in 1929, and the area was first exploited for tin (Vanstone et al. 2000). Commercial production began in 1969 with tantalum concentrates as the major mineral. In 1984, Tanco began producing spodumene concentrates, supplying Corning. Pollucite was also sold to the Soviets. Currently, the mine produces tantalum, cesium, and lithium.

Access is through both a decline and a shaft. Mining is carried out using the room-and-pillar method. Processing consists of crushing to –12 mm, with tantalum and lithium ores stored separately, and pollucite and rubidium are collected into direct-sale stockpiles. Tantalum is recovered via gravity separation and the concentrate is sent directly to Cabot's Bozertown, Pennsylvania, plant. Spodumene is sent to a dense medium circuit where feldspar is removed. Further cleaning is achieved through a series of flotation and gravity separations that remove tantalum, phosphates, mica, feldspars, and quartz. Separation produces an additional lithium concentrate, montebrasite, a lithium aluminum phosphate and spodulite, obtained as the coarse fraction from the spodumene reject circuit. The spodulite concentrate contains 5% Li_2O . Magnetic separation removes any extraneous iron. Pollucite is further processed by leaching to produce cesium chemicals (Hilliard 2002).

Zimbabwe

The largest lithium-bearing area in Zimbabwe is the Bikita tin fields, which is about 60 km east of Masvingo. Important mineralized zones are in the Al Hayat, Bikita, and Southern sectors. The pegmatite is about 1,700 m long, and its width varies from 30 to 70 m. It strikes north-northeast and dips from 14° to 45° east. The pegmatite is asymmetrically zoned and contains a variety of commercially important lithium minerals as well as beryl and pollucite. Bikita Minerals (controlled by AMZIM Minerals, a company in the United Kingdom) produces standard petalite, low-alkali petalite, container-glass petalite, and spodumene concentrate.

Other minor lithium-bearing occurrences are in the Wankie, Salisbury, Umtali, Mtoko, Insizi, Matobo, and Mazoe districts (Toombs 1962).

Production of lithium minerals increased from 18,064 t in 1993 to 49,883 t in 1997 (Mobbs 1998) but declined to 33,000 t in 2002 (Cockley 2002).

Other Producing Regions

Russian Federation

The Russian Federation produces spodumene and other mineral concentrates at the Pervomaisky mine, southeast of Chita. The spodumene occurs in unzoned pegmatites that intrude amphibolites, reminiscent of the Kings Mountain system. The narrower veins are not mined selectively, which requires belt sorting to remove the host rock before processing and production of spodumene concentrates and other minerals recovered. The concentrates are hauled more than 2,000 km to processing facilities in Krasnoyarsk, where the spodumene is converted to lithium hydroxide and metal and then further transported to Novosibirsk, where lithium carbonate and other chemicals are produced (production data unavailable). Low-cost carbonate production from Chile shut down the plant.

Historically, the former Soviet Union obtained its spodumene concentrates from the People's Republic of China from a mine in the Altai Mountains (near Fuyun) in Sinkiang Province. When the Soviets realized that they were going to be ousted, they began an intensive development program of the pegmatite field identified

southeast of Chita and built a self-contained infrastructure at Pervomaisky. After the 1959 events, China took control of the Sinkiang region, and the Soviets were left to their own means. Pervomaisky became the source of the spodumene for the Soviet military-industrial complex.

People's Republic of China

The People's Republic of China produces lithium and other mineral concentrates (beryl, lepidolite, high-purity quartz) from a mine in the Altai Mountains in northwestern China. The lithium concentrates are trucked some 600 km to Urumqi, the capital of Sinkiang Province, where a processing plant produced lithium hydroxide using the old Foose Mineral lime–spodumene process. With the recent information on the production of lithium carbonate, it must be assumed that the plant has been partially converted to the acid-roast process. Low-cost lithium carbonate from Chile may have shut the plant down (Ober 2000).

Minor Producing Districts

Argentina

In Argentina, lithium-bearing pegmatites occur in the western part of the Sierras Pampaneas region, which includes the productive districts of San Luis, Córdoba, and Catamarca. The pegmatites are zoned and contain spodumene. The reserves, considered to be small, total about 18 kt as spodumene (Angelleli and Rinaldi 1963, 1965).

Brazil

In Brazil, lithium-bearing pegmatites occur in the Minas Gerais and in the northeastern part of the country, which includes the states of Paraíba, Rio Grande do Norte, and Ceará (Afghouni 1978).

In the state of Minas Gerais, near Aracuai, several pegmatites have been exploited on a sporadic basis. The pegmatites, which carry spodumene, amblygonite, petalite, and lepidolite, have been traditionally mined for cassiterite, tantalite, and beryl, and lithium minerals have been sporadically recovered. As a result of an increase in demand for lithium minerals (petalite), exploration activities resulted in the discovery of important petalite pegmatites, reported to contain 100 kt of petalite grading 2% Li. Spodumene reserves have been estimated at 300 kt, whereas lepidolite reserves are considered to be nearly exhausted.

The most important producer of lithium minerals is Arqueana de Minerios e Metais (Sao Paulo). The company mines spodumene, petalite, lepidolite, amblygonite, beryl, and cassiterite from the pegmatite bodies near Aracuai in Minas Gerais. The company also supplies spodumene concentrates to Companhia Brasileira do Litio (CBL), a small producer of lithium carbonate and lithium hydroxide (Ober 2003). The processing facilities have been constructed in an economically depressed region several hundred kilometers north of the mining district to benefit from government incentives. The plant is estimated to produce about 1,500 t of lithium carbonate (K. Afghouni, personal communication).

Other Areas

Lithium minerals are also produced in Portugal (lepidolite), Spain (lepidolite), and Argentina (spodumene and amblygonite).

NEW PRODUCERS

Toxco

Toxco, a California company, offers any organization within the U.S. federal government a preapproved battery recycling contract.

It is a company certified in the recycling of various lithium battery types as well as other metal types (Toxco 2003).

In 1995, Toxco won a contract for the purchase of 68 million pounds of depleted lithium hydroxide monohydrate, used in the 1950s and 1960s at Oak Ridge, Tennessee, for the production of lithium isotopes for use in the production of thermonuclear weapons (Frank 1995). LithChem International, a subsidiary of Toxco that produces lithium carbonate and lithium hydroxide in Baltimore, Maryland, was purchased by Soquimich, the Chilean fertilizer and lithium producer. Another subsidiary, Ozark Fluorine Specialties, produces hydrofluoric acid, which is converted to lithium hexafluorophosphate, high-purity lithium fluoride, and other electrolytes used in lithium batteries at its Tulsa, Oklahoma, plant.

Potential Producing Districts

People's Republic of China

The Jiajika pegmatite in Sichuan Province was discovered in 1959 and explored in the period 1959–1992. It is the largest lithium mineral deposit in Asia, with reserves, as defined by China, of 1.03 Mt of 1.28% Li₂O. The deposit is easily accessible by existing infrastructure.

The Lushi pegmatite field, in Henan Province, extends more than 100 km², and numerous veins have been discovered.

Sterling Group Ventures of Australia, through a holding subsidiary, has signed two agreements to develop the Jiajika and Lushi deposits. The joint venture is expected to operate the Jiajika deposit with an initial capacity of 240,000 tpy and produce 47,320 tpy of concentrates (6.09% Li₂O).

On April 10, 2004, Sterling entered into a formal joint-venture agreement with Lushi Guanpo Minerals Development (Lushi) of Henan Province of China to bring the project into production and earn 90% of the interest of the project. According to Chinese geological brigades, the property is estimated to contain about 200,000 t Li₂O grading 1%. The concession covers about 100 km² and has large potential to increase the resources of lithium.

Democratic Republic of the Congo

Probably the largest hard-rock lithium resources in the world are in the Manono and Kittolo in the Democratic Republic of the Congo. Currently Congo-Etain mines only cassiterite and columbite from the Manono pegmatite, which is 5 km long and from 120 to 425 m wide. The adjoining Kittolo pegmatite has similar dimensions. Although the pegmatites are apparently zoned (Varlamoff 1954), their dimensions imply spodumene reserves that dwarf the currently known world reserves. The deposit may not have an economic value for years, however, because of very poor transportation facilities. The deposit is about 2,200 km from the Angolan port of Lobito.

Canada

Avalon Ventures was developing the Separation Rapids rare-metals project in northwestern Ontario not far from the Tanco operation. Avalon was increasing the capacity of its flotation pilot plant to be able to produce large enough volumes to provide potential customers with enough high-grade petalite concentrate for sampling.

AMZIM Minerals, the offshore holding company of Bikita Minerals, the Zimbabwe petalite producer, planned to produce petalite at a site owned by Emerald Fields Resource Corp., a Canadian company, from the same pegmatite body between the Tanco and Avalon operations. This operation was named the Big Mack. If all the tests turned out as expected, construction of a plant with an initial production capacity of 15,000 tpy of petalite concentrate was to

begin by the spring of 2001. Resources at the Big Mack are conservatively estimated at 300,000 t, but only a small portion of Emerald Field's 18,200 ha (45,000 acres) has been drilled (*Industrial Minerals* 2000).

Lithium Metal Technologies (Limtech), a subsidiary of Lithos, both Canadian companies, evaluated options for expanding its high-purity lithium carbonate plant to produce more than its current 300 tpy for sale to specialty-glass manufacturers. Limtech purifies technical-grade lithium carbonate from about 99.3% purity to a high-purity 99.999% product that can sell for \$50 to \$70/kg. The company was considering an additional production line with capacity of 1,000 tpy (*North American Mineral News* 2000).

Raymor Industries announced the successful development of a process to produce lithium metal directly from spodumene (*North American Minerals News* 1999). The process was developed and tested at McGill University's Department of Mining and Metallurgical Engineering under contract with Raymor Industries. The company asserted that the new process would have the lowest production costs and highest purity for lithium metal production. The company was granted exclusive rights to the new technology that was to be patented. For feedstock, Raymor Industries intended to use spodumene mined from its La Motte deposit in Quebec and purchased spodumene (Raymor Industries 2000). A drilling project at the La Motte deposit estimated reserves at 4.55 Mt at 1.07% Li₂O from the surface to a depth of 100 m with an additional 2.5 Mt below 100 m.

FUTURE RAW MATERIALS

Several areas of the world carry potential lithium raw materials in the form of brines, geothermal brines, oil-well brines, and clays.

Among the existing brine deposits, the Great Salt Lake of Utah constitutes an important potential source of lithium chemicals. The lake holds brine formed as a result of concentration by solar evaporation of waters contained in the much larger and more dilute Lake Bonneville (Pleistocene). In the Bear River basin, Great Salt Lake Minerals and Chemicals constructed 5.7 km² of ponds and is producing sodium chloride and potassium and sodium sulfates. The recoverable lithium resources are estimated at 286 kt (Evans 1978).

Lithium is also present in several other salares in Chile (e.g., Punta Negra, Pedernales), in the Altiplano of Argentina (e.g., Pastos Grandes, Rincon), in the People's Republic of China (Qinghai Basin), and in Tibet (Lake Zabuye). Lithium has also been reported in underground brines in Israel (Ober 2000).

A potential geothermal area lies within the Imperial Valley of Southern California. The chemically complex brine contains large concentrations of sodium, calcium, and potassium. It also carries about 0.020% Li. Koenig (1970) indicated that the volume on the brine under an area of 31 to 62 km² is >4 km³. This suggests a potential reserve >840 kt Li. Lithium is also present in significant concentrations in the flashed brines of the Cerro Prieto geothermal field in Baja California, Mexico. The potential exploitation of lithium will depend, however, on whether or not some complex chemical engineering problems are solved.

Other geothermal areas include the Reykanes Field of Iceland, where the visible active sector covers about 5 km². Feasibility studies (Ludviksson and Hermannsson 1970) indicate that a yearly production of 500 t of lithium compounds is possible. The brine contains 8 ppm Li. Additional thermal areas are known at Reykir, Hveragardi, and Drysvik (Karlsson 1961; Prast 1972).

A similar potential source of lithium is the geothermal waters at Wairakei, New Zealand. Potential production from bore waters containing 13 ppm Li are estimated at 2,400 tpy as Li₂CO₃, assuming a discharge rate of 3,785,000 L/hr (Kennedy 1964).

Lithium-bearing clays are known to occur in several localities in the United States. The highest lithium value of 0.53% has been recorded at Hector, California, where the Baroid Division of National Lead Co. mines hectorite for its swelling characteristics (Ames, Sand, and Goldich 1958). Hectorite has been identified in Clayton Valley, where it occurs as an alteration product of volcanic ash along a fault zone and is one of the clay minerals in Tertiary and Quaternary lake sediments (Kunasz 1970). The hectorite contains 0.24% to 0.35% Li. At Spring Mountain, Utah, 0.11% Li has been reported in beryllium-bearing tufts (Shawe 1968), where lithium probably also occurs in hectorite. An important discovery of lithium-bearing clays has been made in the McDermitt caldera in northern Nevada. The occurrence of lithium-bearing clays is also reported (Norton 1965) in Yavapai County, Arizona (0.10% Li), in Tertiary clays at Kramer, California (0.19% Li; Muessig 1966), and in the Turlari playa (0.14% Li) in Argentina (Muessig 1966). An extensive survey by the Lithium Exploration Group of the U.S. Geological Survey (USGS) indicated that vast resources of lithium lie in a great number of sedimentary clays (Vine 1976). The U.S. Bureau of Mines conducted extensive research on the extraction of lithium from clay. Extraction of lithium from clays associated with boron deposits at Begadic in Turkey was recently evaluated (A. Buyukburc and G. Koksall, 2005). Although clays contain lithium concentrations on the same order of magnitude as commercial pegmatites, they are not likely to become lithium sources in the near future because of technological problems associated with the extraction of lithium from the crystal lattice, and also because they cannot compete with the low-cost brine operations in the United States and Chile.

RESERVES

In the 1970s, an accelerated research effort in the field of secondary batteries and thermonuclear power generation prompted the National Research Council to create the Lithium Subpanel charged with evaluating available lithium reserves and resources in the world. The resulting study (Table 2) concluded that the reserves and resources of all classes of lithium occurrences were 10.6 Mt (Evans 1978). At that time the brines of the Salar de Atacama were estimated to contain 4.3 Mt of lithium. Today these reserves are the most significant because they supply the two operations, which produce a substantial amount of the world's lithium carbonate.

According to estimates published by the USGS, Chile holds approximately 73% of the world's lithium resources; followed by China, 13%; Canada, 4.5%; and Australia, with just over 4%. Resource data are not available for some important producing countries, including Argentina, China, and Russia. Lithium resources occur in two distinct categories: lithium minerals and lithium-rich brines. Lithium brine resources, now the dominant feedstock for lithium carbonate production, are produced mainly by Chile. Canada and Australia have the most significant hard-rock lithium resources (Ober 2003).

WORLD MARKETS FOR LITHIUM

The world lithium production has grown from 6,300 t Li equivalent in 1994 to 11,900 t Li equivalent in 2000. Chile, because of the expansion in brine production by SQM in 1996 became the world leader of lithium carbonate (Roskill Information Services 2004).

In descending order of production, the world's largest lithium chemical producers in 1999 were Chile, China, the United States, Russia, and Argentina. Australia, Canada, and Zimbabwe were major producers of lithium ore concentrates.

The United States remains the leading consumer of lithium minerals and compounds. It also led production of value-added

Table 2. World lithium resources

Class	Lithium, t*	
	United States	Other Western Countries
Class A†		
From pegmatites	329,100	366,400
From brines	40,500	1,290,000
From stockpile‡	6,100	na§
Class B		
From pegmatites	47,300	456,800
From brines	na	na
Class C		
From pegmatites	2,780,900	1,969,000
From brines	77,300	3,000,000
Class D		
From brines	283,700	na
Total, Class A	375,700	1,656,400
Total, Classes A and B	423,000	2,113,200
Total, Classes A, B, and C	3,281,200	7,082,200
Total, Classes A, B, C, and D	3,564,900	7,082,200
Combined Totals		
Class A	na	2,032,100
Classes A and B	na	2,536,200
Classes A, B, and C	na	10,363,400
Classes A, B, C, and D	na	10,647,100

* Tonnes to beneficiation and process.

† Classification system:

A: Reserves proved by systematic exploration

B: Reserves indicated by limited exposures and/or exploration

C: Resources inferred on geological evidence

D: Quantities largely known but economic lithium extraction probably dependent on marketing of coproducts

‡ Approximate lithium content of lithium hydroxide currently available for purchase from U.S. government stockpile.

§ na = not available.

lithium materials. Because only two companies produced lithium compounds for domestic consumption and for export to other countries, reported production and value of production data could not be published by USGS.

In 1999, the only active lithium carbonate plant in the United States was at a brine operation in Nevada. Two other mines in North Carolina closed in 1986 and 1998. Subsurface brines have become the primary raw material for lithium carbonate because of lower production costs compared to hard-rock ores. Ore concentrates rather than lithium carbonate and compound feedstock accounted for the majority of mined lithium minerals consumption.

U.S. imports of lithium carbonate from 1999 through 2002 included Chile, 90%; Argentina, 9%; and others, 1%. In 2003, the respective percentages were Chile, 73%, and Argentina, 27% (Ober 2003).

USES

Lithium is marketed in numerous applications. It is used in three basic forms: ore and concentrate, metal, and manufactured chemical compounds.

Ores and concentrates are consumed by the glass, ceramic, and porcelain enamel industries. Petalite, lepidolite, and amblygonite can be used without prior beneficiation, except hand-cobbing, whereas spodumene must be beneficiated by grinding and flotation,

leaching, and magnetic separation. Lithium is useful because it creates favorable internal nucleation conditions. By comparison, sodium favors external crystallization. Because of its small ionic radius and high field strength, lithium imparts high mechanical strength and thermal shock resistance, as well as good chemical resistance (Fishwick 1966). In these applications, lithium is also introduced in the form of lithium carbonate.

In metal form, lithium is the lightest solid element, having an atomic weight of 6.94 and a specific gravity of 0.534 (at 20°C). Lithium metal is used in the synthesis of butyl lithium. In nonferrous metallurgy, the high reactivity of lithium with gases is used for scavenging oxygen and sulfur, converting them into stable compounds. Lithium is also used in lithium aluminum and lithium magnesium alloys, where it imparts high-temperature strength, improves elasticity, and increases the tensile strength. Demand for aluminum lithium alloys in commercial and military aircraft industries, although encouraging, has not met earlier growth forecasts (Alexander 1992).

Lithium carbonate, in addition to its consumption by the ceramic industry, is being used at an increasing rate in the aluminum reduction cells, where it improves the conductivity of the molten bath, reduces operating temperature, and results in higher production. It is also very effective in reducing fluorine emissions by retaining the fluorine as lithium fluoride in the bath. Lithium carbonate consumption has fallen steadily since its peak in the late 1970s, and, although the rate of decline has slowed in recent years, consumption in the aluminum sector is still forecast to decrease further in the next few years (Roskill Information Services 2004).

In purified form, lithium carbonate is being used in the chemotherapeutic treatment of bipolar disorder (Caldwell et al. 1971).

In the United States, Japan, and Europe, development programs have been initiated on molten carbonate fuel cells. Because of the energy efficiency and environmental cleanliness of all types of fuel cells, worldwide financial support for the development of this technology has increased. Molten carbonate fuel cells are expected to use various lithium compounds, principally lithium aluminates and lithium carbonate (Alexander 1992). Lithium carbonate rather than lithium metal has been the focus of recent research for use in batteries for electric vehicles.

In addition to being the lightest metal, lithium is also the most electronegative metal and, therefore, is ideal for use in many battery applications. Lithium battery characteristics include high energy density, high operating voltage, wide operating temperature range, and long shelf life (Grady 1980). Present applications include heart pacemakers, military hardware, cameras, computer memory backup, watches, and measuring equipment in the oil-drilling industry. Future growth in this area may include use in rechargeable lithium batteries for handheld power tools and electronic and communications equipment and even as a power supply for electric vehicles and the total artificial heart. In fact, double-digit growth is forecast for demand for lithium in secondary batteries to 2006–2007 (Roskill Information Services 2004). The highest value application for lithium batteries remains secondary portable consumer products, especially portable computers and cellular phones. This U.S. market was \$500 million in 1997 and should top \$860 million in 2005. Rechargeable, portable, consumer lithium batteries are expected to grow to a \$3.2 billion market in 10 years.

Lithium hydroxide was first employed as an ingredient in alkaline storage batteries where its presence increased the life of the cells (Bach et al. 1981). In the 1940s, Clarence Earl, who developed special grease by reacting lithium hydroxide with fatty acids, discovered a new application. The resulting grease was found to retain its viscosity over a wide temperature range and remain stable in the

presence of water. Lithium-based greases have become a standard product in military, industrial, and automotive lubrication fields.

Anhydrous lithium hydroxide can absorb large quantities of carbon dioxide, a property that has been used in the air regeneration system of the Apollo command and lunar modules, and in new applications in the mining industry for rescue breathing apparatus.

Lithium chloride and lithium bromide brines have low vapor pressures and are used in absorption refrigeration systems. Lithium chloride also constitutes the feed material for the production of lithium metal. Lithium fluoride is used mainly as a flux in enamels, glasses, and glazes, and in welding and brazing.

The most important organic compound is butyl lithium. It serves as a catalyst in the polymerization of butadiene, isoprene, and styrene to produce polymers with special properties. Butyl lithium has applications in the synthesis of pharmaceutical and agricultural intermediates.

Numerous miscellaneous applications of lithium chemicals include sanitation and bleaching, hydrogen generation, oxygen generation, catalysis, and vitamin synthesis.

PRICES

The prices (*Industrial Minerals* 2004) of various lithium ores (in dollars per short ton) are

Ceramic spodumene:	7.25% Li ₂ O	\$330 to \$350 (free on board [f.o.b.] West Virginia)
Glass-grade spodumene:	5% Li ₂ O	\$195 to \$200 (f.o.b. Amsterdam)
Petalite:	4.2% Li ₂ O	\$165 to \$260 (f.o.b. Durban)

The most dramatic change in pricing occurred in lithium carbonate as result of the new production at the Salar de Atacama, Chile. Lithium carbonate commanded prices of nearly \$ 2/lb into 1997; the large production capacity brought on line by SQM led to a nearly 50% decrease in the world price of lithium carbonate. SQM offered lithium carbonate at 90 cents/lb, forcing the two other major producers to follow suit (Ober 2002). World oversupply has kept lithium carbonate prices depressed for the past 3 years (Ober 2003).

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Magnesium Minerals and Compounds

Deborah A. Kramer

INTRODUCTION

Magnesium is the eighth most abundant element and constitutes about 2% of the earth's crust. It is the third most plentiful element dissolved in sea water, with a concentration averaging 0.13%. Although magnesium is found in more than 60 minerals, only a few are of commercial importance. In addition to minerals, seawater and well and lake brines are also important sources of magnesium. One of the more important magnesium minerals is magnesite (MgCO_3), with a theoretical maximum magnesia (MgO) content of 47.6%; this carbonate form represents the world's largest source of magnesia. Other commercially important magnesium-bearing minerals are dolomite, which serves the aggregate industry as well as the chemical industry; brucite, which is used in the production of both caustic-calcined and dead-burned magnesia; olivine, which serves the refractory and heat storage industries; talc, which serves several industries as a filler and as an ingredient in cosmetics; and serpentine. Olivine and talc are discussed in separate chapters of this book. Table 1 shows the composition of these magnesium-containing minerals.

These minerals are the starting raw materials for a wide range of products. These include magnesium metal and several grades of magnesia used for the production of both dead-burned magnesia for refractory manufacture and lighter fired caustic-calcined magnesia. The latter is used in a variety of agricultural, construction, environmental, and industrial applications.

The word *magnesite* literally refers only to the natural mineral, but common usage applies this name to two other types of materials, dead-burned magnesite and caustic-calcined magnesite. For the most part, these are commercial products of magnesia, differing mainly in density and crystal development that results from different levels of heat application. When magnesia produced from seawater or brines first made its appearance on the world market, the products also were called dead-burned or caustic-calcined magnesite, but more recently the technical literature has increasingly referred to the materials as refractory magnesia or refractory-grade magnesia and caustic-calcined magnesia, respectively. These terms are now also increasingly being applied to magnesia products derived from the natural mineral magnesite, especially for those materials with high MgO content. The older terms, however, persist in the trade.

The terms *dead-burned magnesite* or *refractory magnesia* refer to the granular product produced by firing magnesite, magnesium

hydroxide, or another material reducible to magnesia at temperatures exceeding $1,450^\circ\text{C}$. The heat treatment must be of sufficient duration to produce a dense, reasonably weather-stable granule for use in manufacturing refractory materials.

The use of the terms describing magnesia products is somewhat confusing to those not closely connected with the industry. The vagueness of the terminology can lead to misreading of statistics to such a degree that simultaneous shortage and surplus of certain magnesia products is indicated. Confusion has been further amplified by use of such terms as high-purity or super high-purity magnesia; in most cases these terms have been used for magnesia supplied to the refractory industry. They usually refer to the content and relationship of the accessory oxides and density of the material as they affect the refractoriness of the final product rather than any specific MgO content (Duncan and McCracken 1994).

The terms *high grade* and *high purity* generally refer to a refractory magnesia containing more than 96% MgO , a density greater than 3.30 g/cm^3 , preferably 3.40 g/cm^3 , and a proper relationship of auxiliary oxides.

Caustic-calcined magnesia results from 800°C to $1,000^\circ\text{C}$ heat being applied, frequently in a rotary kiln, to magnesite or other material reducible by heat to magnesia. It is heated until less than 10% ignition loss remains and the product displays adsorptive capacity or activity. Caustic-calcined magnesia readily absorbs

Table 1. Chemical composition of selected magnesium-containing minerals

Common Name	Chemical Composition
Brucite	$\text{Mg}(\text{OH})_2$
Carnallite	$\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$
Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Epsomite	$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$
Kainite	$\text{MgSO}_4 \cdot \text{KCl} \cdot 3\text{H}_2\text{O}$
Kieserite	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$
Magnesite	MgCO_3
Olivine	$(\text{MgFe})_2\text{SiO}_2$
Schoenite	$\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$
Serpentine	$\text{Mg}_3(\text{OH})_4\text{Si}_2\text{O}_5$

water vapor or carbon dioxide (CO_2), an action that is referred to as activity. This activity feature then facilitates the production of high-density periclase. This is generally done through briquetting and the application of additional high-temperature heat. The production of caustic magnesia involves less energy than is required to produce dead-burned magnesite.

Fused magnesia is produced by heating high-grade magnesite to a molten state for up to 6 hours in electric arc furnaces to approximately $3,000^\circ\text{C}$. The resulting product, at 96% to 98% MgO , has a high density of 3.50 g/cm^3 and relatively high chemical stability, strength, and resistance to abrasion. World production is approximately 160 ktpy, which is used in refractories and in electrical products.

PRODUCTION, TRADE, RESERVES, AND RESOURCES

The largest magnesite production facilities in the world are in China, North Korea, and Russia. Together, these three countries account for about two thirds of world magnesite production capacity. Japan and the United States account for one half of the world's magnesia production capacity from seawater or brines. Fused magnesia is produced in Australia, Brazil, Canada, China, Israel, Japan, the Republic of Korea, Mexico, Russia, the United Kingdom, and the United States.

United States

Production and Trade

Figures 1 and 2 give a historical perspective of the supply and demand of dead-burned and caustic-calcined magnesia in the United States. Historically, overall U.S. consumption of magnesium compounds has declined, mainly because of a decrease in demand from the refractories industry, the largest consumer of magnesium compounds. U.S. production actually decreased faster than the drop in consumption because imports of low-cost, dead-burned magnesia from China replaced part of the U.S. production. This can be seen in the significant increase in import reliance that occurred beginning in the 1980s. With the recovery in the U.S. economy in the late 1990s, overall consumption of magnesia increased as steel production increased, but this trend was short-lived. The quantity of refractory magnesia consumed per ton of steel produced continued to decline. For example, in the mid-1970s, the electric arc furnace used about 20 kg of refractories per metric ton of steel produced; this quantity has declined to about 4 kg/t (Pearson 2000).

The United States has one producer of dead-burned magnesia—Martin Marietta Magnesia Specialties LLC (Manistee, Michigan). In 2002, the United States produced 123 kt of dead-burned magnesia. Imports totaled 394 kt, of which 73% was from China, and exports were 73 kt, 75% of which was shipped to Canada.

Caustic-calcined and specialty magnesias were produced by Premier Chemicals LLC (Port St. Joe, Florida) from magnesite in Nevada and from seawater in Florida, and by Martin Marietta and Rohm & Haas Co. (both in Manistee, Michigan) from underground brines in Michigan. U.S. production of caustic-calcined magnesia in 2002 was 127 kt; this was the first year that caustic-calcined magnesia production was greater than dead-burned magnesia production. Imports of caustic-calcined and specialty magnesias totaled 166 kt; China (56%) and Canada (31%) were the primary import sources. Exports were 37 kt, distributed among several countries.

Magnesium hydroxide [$\text{Mg}(\text{OH})_2$] is found as the naturally occurring mineral brucite. In addition, it is produced synthetically from seawater or brines. Small quantities of brucite are recovered in

the United States by one firm, Premier Chemicals, as a by-product of magnesite mining in Gabbs, Nevada. Applied Chemical Magnesias Corp. (Fort Collins, Colorado) recovers brucite from a deposit in Bullhead City, Arizona. The deposit is estimated to contain 450 kt of ore grading 90% brucite (Anon. 1998). The company processes this ore and other materials at a 30-ktpy mill in Arizona into products for use in flame retardants, in animal feed, and for acid neutralization.

Several companies in the United States produce magnesium hydroxide synthetically. SPI Pharma Inc. (Lewes, Delaware) and Premier Chemicals recover magnesium hydroxide from seawater. Martin Marietta Magnesia Specialties and Rohm and Haas recover magnesium hydroxide from underground brines. In addition to its Michigan plant, Martin Marietta operates a 30-ktpy plant near Pittsburgh, Pennsylvania, that produces magnesium hydroxide from imported magnesite. Until September 2003, Dow Chemical Co. (Midland, Michigan) produced magnesium hydroxide from underground brines in Manistee. In addition to selling the magnesium hydroxide for water treatment applications, a magnesium hydroxide slurry was supplied to ANH Refractories Inc.'s (Ludington, Michigan) nearby plant for conversion to dead-burned magnesia; this plant closed in September 2003, leaving the United States with one producer of dead-burned magnesia—Martin Marietta Magnesia Specialties. U.S. magnesium hydroxide production in 2002 was 218 kt; this includes some magnesium hydroxide that was used to make dead-burned magnesia. Imports of magnesium hydroxide were only 4 kt, and exports were 14 kt.

In the United States, magnesium chloride is produced and used in two forms—magnesium chloride brines, which are about 30% magnesium chloride in concentration, and magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). Great Salt Lake Minerals Inc. (Ogden, Utah) produces both the brines and the hexahydrate. Reilly Industries Inc. (Wendover, Utah) and Western Salt Inc. (Chula Vista, California) produce magnesium chloride brines. Great Salt Lake Minerals and Reilly Industries recover magnesium chloride from brines of the Great Salt Lake, and Western Salt produces magnesium chloride brines from seawater as a by-product of salt production. Magnesium chloride is recovered from either brines or seawater by solar evaporation and sequential precipitation of the dissolved salts. Because there are only two producers, U.S. magnesium chloride production data are withheld by the U.S. Geological Survey. Imports of magnesium chloride in 2002 were 20 kt—90% from Israel—and exports were 5 kt.

Magnesium sulfate can be found as a naturally occurring mineral or it can be produced synthetically. The two most commonly occurring magnesium sulfate minerals are epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) and kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$). Although these minerals occur in the western United States, they are not mined.

The three U.S. producers of magnesium sulfate are PQ Corp., Giles Chemical Corp., and Southern Ionics Inc. PQ operates a facility in Utica, Illinois, where it produces a magnesium sulfate solution (25% solids) and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ crystal. Giles has two plants that produce magnesium sulfate solutions and magnesium sulfate crystal—in Greendale, Indiana, and Rouses Point, New York. Southern Ionics operates two plants producing 18% to 25% magnesium sulfate solutions in Chickasaw, Alabama, and Baton Rouge, Louisiana.

In 2002, magnesium sulfate production in all forms was 38 kt. Imports of natural kieserite were 13 kt, and imports of synthetic magnesium sulfate were 31 kt. Most of these sulfates were from Germany. Exports of magnesium sulfate in all forms were 18 kt, mainly to Canada.

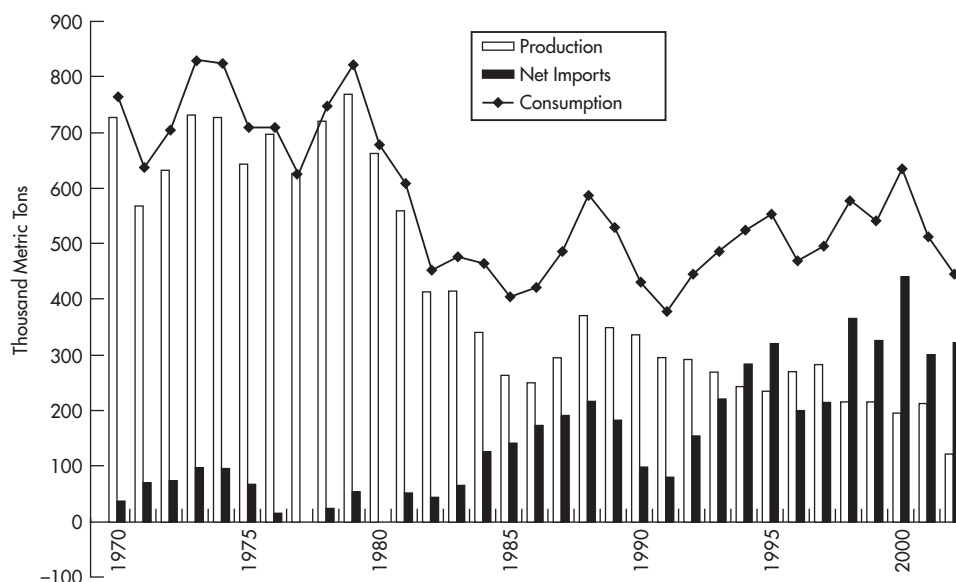


Figure 1. U.S. dead-burned magnesia supply and demand, 1970–2002

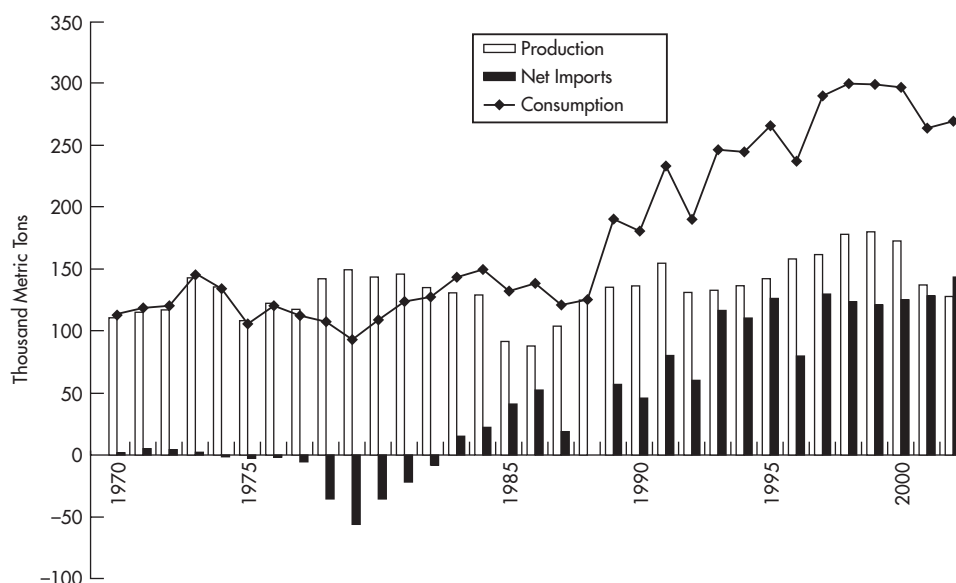


Figure 2. U.S. caustic-calcined magnesia supply and demand, 1970–2002

Reserves and Resources

The reported estimate of 65 Mt of magnesite (15 Mt magnesium) reserve base in the United States is divided as follows: in Nevada, 88%, including 27 Mt of magnesite containing less than 5% calcium oxide (CaO); in Washington, 11%; and in California, the remaining 1%. Magnesite also occurs in Idaho, Maryland, Massachusetts, New Jersey, New Mexico, New York, Pennsylvania, Texas, and Utah, but reserves have not been estimated in these states (Davis 1957).

Brucite reserves are estimated to total 3 Mt in Nevada, associated with the Gabbs magnesite deposit. Walper (1964) reported brucite reserves of more than 2 Mt in the Marble Canyon area,

Culberson County, Texas. This deposit is being mined by Applied Chemical Magnesias.

Reserves of magnesium salts obtained as brines from underground evaporite deposits are difficult to estimate. Available information on magnesium salts in surface evaporites is insufficient to estimate reserves. The Great Salt Lake contains an estimated 630 Mt of magnesium chloride.

World

Total production of magnesite in 2002 was estimated to be 11.2 Mt, with China, Turkey, North Korea, and Russia as the largest producers, together accounting for about two thirds of total world

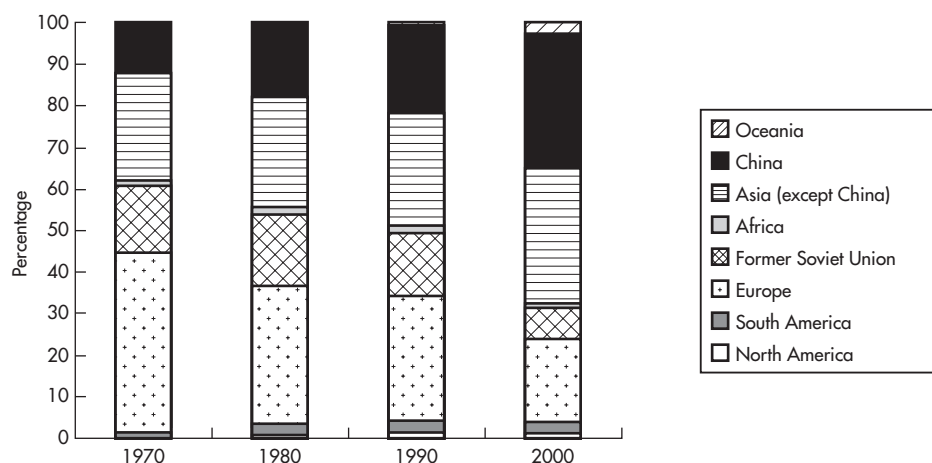


Figure 3. World magnesite production by region

production. Figure 3 shows the regional changes in world production since 1970. In 1970, Europe was the largest magnesite-producing area, accounting for 43% of the total. After 1970, however, production in Europe began to decline, and Asia became the leading producing region. By 2000, Asia represented 65% of the total world production of magnesite. China became the leading producing country and accounted for nearly one third of world production. Some of this reported increase in production in China might result from additional knowledge of production facilities that has been developed in the past 10 years and may not represent as large of an increase as it appears. Specific details of individual producers throughout the world are detailed in the next section.

World reserves and reserve base estimates for magnesite are shown in Table 2. The largest reserves occur in the countries with the largest production—China, North Korea, and Russia. Reserves of evaporite minerals and brines are virtually unlimited. The existing quantities of evaporites and brines provide theoretical resources that are much larger than the quantities that are likely to ever be used.

GEOLOGY

Magnesite, when pure, contains 47.8% MgO and 52.2% CO₂. The pure mineral is found occasionally as transparent crystals resembling calcite. Impurities in magnesite ore are mainly varying quantities of the carbonates, oxides, and silicates of iron, calcium, manganese, and aluminum.

Magnesite dissociates on heating to form magnesia and carbon dioxide. When heated sufficiently, the magnesia develops a crystal structure identified with that of the natural mineral periclase. Periclase occurs only rarely in nature and not in a commercially workable deposit.

Although the genesis of natural magnesite deposits can be complex, it is distinguished in nature in two distinct physical forms, namely crystalline, with a wide range of visible crystal sizes, and cryptocrystalline, sometimes referred to as amorphous, where crystals are not detectable to the eye and range from 1 to 10 μm . The two types not only differ in crystal size but in the sizes of the deposits and in modes of formation.

The crystalline form of magnesite has a Mohs hardness of 3.5 to 4.0. The color ranges from white to black with shades of yellow, blue, red, or gray. The color is not a significant indicator of purity, but in a given deposit, an experienced person can often roughly

Table 2. Magnesite reserves and reserve base (Mt of magnesite)

Location	Reserves	Reserve Base
Australia	366	423
Austria	50	75
Brazil	160	630
Canada	100	140
China	1,310	3,000
Greece	100	120
India	50	245
North Korea	1,500	3,000
Russia	2,200	2,500
Slovakia	150	1,100
Spain	35	100
Turkey	225	550
United States	35	65
Other countries	1,250	1,400
Total (rounded)	7,500	13,300

grade magnesite ore by observing color and crystallinity. Macrocrystalline deposits occur in relatively few, but generally large, deposits on the order of several million tons. The ore shows marble-like crystalline texture and has sedimentary or metasomatic origin. The specific gravity of cryptocrystalline magnesite ranges between 2.90 and 3.00 g/cm³, whereas the value of pure crystalline magnesite is 3.02 g/cm³. In actuality, the specific gravity of magnesite is typically higher than 3.02 g/cm³ because of the presence of iron carbonate.

The cryptocrystalline variety of magnesite typically occurs in many small deposits, although there are exceptions. Cryptocrystalline magnesite is typically massive with no cleavage and is sometimes descriptively called “bone” magnesite. The fracture is usually conchoidal, with a hardness of 3.5 to 5.0. The color is mainly white, but it can have tints of yellow, orange, or buff. Accessory siliceous minerals such as serpentine, quartz, or chalcedony are generally present. Calcium minerals are normally absent or in low concentration; this contrasts with macrocrystalline ore in which calcite and dolomite are the main impurities.

Magnesite occurs mainly in four types of deposits—as crystalline masses replacing dolomite, as impure crystalline masses replacing ultramafic rocks, as cryptocrystalline masses in ultramafic rocks, and as sedimentary beds and lenses.

Crystalline magnesite deposits in dolomite range in size from pockets containing a few tens of thousands of tons to irregular or lenticular bodies containing greater than 100 Mt. Impurities may range from 2% to 20%. In determining the value of this type of deposit, grade is as critical as size, particularly for the magnesite that will be used to manufacture high-purity refractories.

Deposits of cryptocrystalline magnesite are generally smaller than crystalline magnesite deposits. They occur as nodules, veins, and stockworks in serpentinized zones of ultramafic rocks and also can be found as small deposits in tuffs. Magnesite mixed with talc and with or without quartz occurs as lenses replacing dunite or serpentinized dunite. Deposits of this type are as variable in size as those that occur in dolomite.

Sedimentary magnesite is a brown to gray carbonate rock that probably formed by evaporation. Individual beds can cover tens of acres and can range from several centimeters to several meters in thickness. This type of magnesite is interbedded with dolomite, clastic rocks, or strata of volcanic origin. Even though some sedimentary deposits contain high grades of magnesite, the thin beds cannot be mined economically.

Most carbon dioxide that was needed to form magnesite deposits was probably derived from deep-seated igneous sources, although some may have been supplied through thermal dissociation of underlying carbonate rocks. A very small quantity may have been carried by groundwater. Ultramafic rocks supplied the magnesia that is found in their contained magnesite deposits. The source of magnesium in crystalline deposits in dolomite is less certain. One hypothesis suggests that the magnesia was produced during thermal dissociation of underlying dolomite. A second theory suggests that crystalline magnesite deposits are metamorphosed, recrystallized lenses of sedimentary magnesite; however, this hypothesis does not explain the replacement nature of many, if not most, crystalline deposits (Bodenlos and Thayer 1973).

Brucite has been exploited in the past for the production of magnesia but is no longer an important source because minable concentrations of brucite are rarely found. Theoretically, brucite contains 69.1% MgO and 20.9% H₂O. The mineral is often associated with limestone as well as magnesite, is translucent, and is relatively soft and lightweight. Its hardness is 2.5 and specific gravity about 2.4. The color may be white, but blue or green with a gray cast is a more common coloration.

The brine deposits from which magnesium is recovered are brines derived from sea water, wells, and inland salt lakes. The geologic processes that result in these brines are not well understood because they come from different geologic settings. Some of these brines are pore waters in oil fields, some are deep-well brines from marine salines or peripheral rocks, some are from thermal springs or wells, and some are surface or subsurface brines that were associated with Quaternary salt lakes or seas (Smith et al. 1973).

U.S. MAGNESIA DEPOSITS AND RESOURCES

Magnesite

In the United States, the only large deposits of crystalline magnesite are in Gabbs, Nevada, and Stevens County, Washington (Vitaliano and Callaghan 1956; Bennett 1943; Campbell and Loofbourow 1936; Schilling 1968). The only known deposits of crystalline magnesite replacing ultramafic rock are in north-central Vermont. These deposits consist of gray to faintly greenish-gray

rock in which the magnesite occurs as grains or clusters of grains that range from 0.01 to 30.0 mm in a matrix of fine-grained talc (Bodenlos and Thayer 1973). The largest group of cryptocrystalline magnesite deposits occurs at Red Mountain, California; these deposits originally contained about 1 Mt of magnesite. Additional deposits occur in ultramafic rocks in California, with smaller occurrences in Oregon and Pennsylvania (Bodenlos 1950; Davis 1957). Sedimentary magnesite deposits are limited to a few states in the southwest (Rubey and Callaghan 1936; Vitaliano 1950, 1951). Sedimentary magnesite in California and Nevada is thought to have formed in closed basins (Rubey and Callaghan 1936) and therefore is of evaporite origin.

Brucite

Deposits of brucite are associated with the magnesite deposits in Gabbs, Nevada. The mineral occurs as lenses of massive white to light-brown material that is soft enough to scratch with a fingernail. Impurities include veinlets and grains of magnesite, dolomite, talc, forsterite, and periclase. Because the brucite deposition postdated magnesite deposition, it is likely that the associated intrusions of granodiorite drove off the carbon dioxide in magnesite and formed magnesium hydroxide (Schilling 1968).

In addition to the brucite in Nevada, there is a brucitic marble deposit in the Marble Canyon area in Culberson County, Texas, reportedly containing more than 2 Mt with an average brucite content of 38%. Samples of this ore have shown brucite proportions ranging from 23% to 100%.

Brucite was also associated with magnesite in the Stevens County, Washington, deposit. A lens of translucent gray-green brucite about 6 m by 45 m was mined for a short time (from the 1880s until 1905) and manufactured into ornamental objects. These objects, however, tended to develop a white powdery coating of hydromagnesite, and this was most likely one reason that led to the closing of quarrying operations at the deposit (Campbell and Loofbourow 1936).

Brines and Evaporates

Underground brines in Michigan are a source of much of the magnesium compounds produced in the United States. Magnesium-rich brines are found in the Michigan Basin, a structural basin formed of sedimentary rocks of Paleozoic and Jurassic ages. Interstitial natural brines with soluble salts of magnesium, bromine, calcium, potassium, and sodium are confined within the Detroit River Group substrata. The rocks of this group are mainly sandstones and carbonates, often with anhydrite and/or salt lenses. The group is found below lower Michigan, with outcrops or subcrops at the extreme ends of Michigan's lower peninsula (Landes 1951). In the Ludington area, the principal producing aquifer is about 30 m thick and lies about 650 m below the surface. In Manistee, the thickness of the aquifer is estimated to be the same, but it is about 850 m below the surface.

MAJOR DEPOSITS AND RESOURCES OUTSIDE THE UNITED STATES

Australia

Australia has cryptocrystalline magnesite deposits in Queensland, New South Wales (at Fifield, and Young), and in western Australia at Ravensthorpe. In the Kunwarara deposit, 60 km northwest of Rockhampton, Queensland, low iron nodules of cryptocrystalline magnesite cover an area of approximately 63 km² that is entirely overlain by black clay up to 12 m thick. The deposit is thought to have formed by lacustrine deposition of magnesium bicarbonate derived from the

alteration of serpentinite rock. Evaporation caused hydrated magnesium carbonate to precipitate. Deposition of mud over the magnesite caused further evaporation and the formation of hard nodules of dehydrated magnesite (Minerals Council of Australia 2003). Reserves are reported to be in excess of 122.3 Mt containing 34.8 Mt of magnesite, with approximately one half as low iron reserves (Australian Magnesium Corporation 2000). Australian Magnesium Corporation mines this deposit to produce 180 ktpy of dead-burned and caustic-calcined magnesite and 25 ktpy of fused magnesite.

At Thud dungra, northwest of Young in New South Wales, magnesite occurs as veins and nodules formed by the alteration of mafic rocks by magnesium-rich fluids. The magnesite ore contains 95%–99% MgCO_3 and varies in thickness from 2 to 10 m (Minerals Council of Australia 2003). The Thuddungra mine has been in operation since 1935. Ausmag International (Young, New South Wales) produces about 18 ktpy of caustic-calcined magnesite from magnesite from this deposit.

At a now inactive magnesite mine near Fifield, about 30 km northwest of Condobolin, the ore consists of nodules of massive magnesite that occurs as pockets or veins in decomposed ultramafic rock. In western Australia, hard magnesite nodules in dark clayey material crop out 30 km east of Ravensthorpe. Magnesite also occurs in the Kalgoorlie region (Minerals Council of Australia 2003).

Austria

Austria, one of the oldest magnesite producers in western Europe, has a narrow belt of breunnerite magnesite ($[\text{Mg,Fe}]\text{CO}_3$) extending westward from Semmering. The most important deposits are located at Breitenau, Dietin, Radentheim, Semmering, Trieben, and Veitsch. RHI AG (Vienna) operates two dead-burned magnesite plants at Breitenau and Hochfilzen that have a combined capacity of 300 ktpy. About 800 ktpy of magnesite are mined from the company's deposits as feed material (Kendall 1996).

Brazil

Brazil has substantial reserves of crystalline magnesite. The two major areas are located in the Iguatu area of Ceara Province and in the Eguas range near the town of Brumado in southwestern Bahia. Resources are reported to be in excess of 500 Mt (Bodenlos 1954). Magnesita SA (Contagem, Brazil) is the largest producer of dead-burned magnesite in Brazil, with an annual production of approximately 3 Mt of crude magnesite, 285 kt of dead-burned magnesite, 67 kt of caustic-calcined magnesite, and 12 kt of fused magnesite. It produces three chemically similar grades, M-10, M-20, and M-30B, with MgO contents of 94%, 95%, and 98%, respectively, depending on the degree of sinter. The company increased capacity by 65 ktpy in 2004 with the installation of a new kiln for the production of M-30B grade material (O'Driscoll 2003a).

Canada

There are several magnesite deposits in British Columbia (Grant 1987), but the only one being commercially operated is the Mount Brissolof deposit. This open-pit mine is operated by Baymag (Calgary, Alberta) with a capacity to produce 150 ktpy of caustic-calcined magnesite in two rotary kilns and 14 ktpy of fused magnesite in two electric arc furnaces. Minimum grade of the magnesite is maintained at 96.5% MgO . Because the markets to which Baymag sells do not give a premium for product exceeding this grade, the company mines the ore selectively and blends the varying grades to extend the ore life. Other deposits in British Columbia are beds of crystalline magnesite interlayered with sedimentary rocks in the Kootenays region,

the cryptocrystalline magnesite in the Clinton and Bridge River areas of central British Columbia, and the vein deposits in the fault zones along the Yalakom River and the Pinchi Mountains.

China

The explored magnesite resources in China comprise about 30 Gt in 28 mining areas (Bo and Yuilan 1998). About 85% of these resources are concentrated in the eastern Liaoning Province. The majority of Chinese magnesite ores are macrocrystalline, with a crystal grain size from 5 to 50 mm. In the Haicheng area of Liaoning, the magnesite deposits occur as conformable in intermediate strata between 40 and 500 m thick in host rocks of dolomite and schist; the color of the ore ranges from pink to gray. The main accompanying minerals are dolomite, talc, chlorite, graphite, and pyrite, of which dolomite and talc are the most common. There are also cryptocrystalline magnesite deposits in Inner Mongolia, where the main accessory mineral is opal (Schmid 1984; Bo and Yuilan 1998).

Magnesite mining in Liaoning began in 1913, and China has become the largest producer of magnesite in the world. There are six or seven major producers of dead-burned magnesite in Liaoning, with a total production capacity of 3.5 Mtpy. The Chinese market for dead-burned magnesite, mainly for its steel industry, was estimated to be about 1.5 Mtpy; the remainder is exported primarily to the United States and Europe. China also has about 100 ktpy of capacity to produce caustic-calcined magnesite.

Greece

Greece has deposits of cryptocrystalline magnesite. A deposit located at Vavdos in Khalkidiki region in the southwest Thessalonika was first worked in 1957 and operated until 1987. Other deposits, which have been mined commercially, are located on the island of Euboea and in Ormylia in Khalkidiki. The Euboea operations, which once produced 300 ktpy, have been closed.

The Greek deposits are low in iron and boron and produce a grade of sinter suitable for refractories used in basic oxygen furnaces (BOFs). The magnesite is of high quality but tends to be mixed with some siliceous gangue; beneficiation of all ore is necessary for the production of commercial sinter. Most of the magnesite occurs as veins or small lenses, resulting in high mining costs. The removal of about 80 t of waste and overburden is required to obtain 1 t of magnesite (Hatjilazaridou, Chalkiopolou, and Grossou-Valta 1998).

Grecian Magnesite SA (Athens) operates mines and plants at Gerakini and Kalives, Khalkidiki: three rotary and three shaft kilns at Gerakini that produce caustic-calcined magnesite; and a refractory plant at Kalives. Production capacity is 120 ktpy of caustic-calcined magnesite, grading between 88% and 95% MgO , and 100 ktpy of dead-burned magnesite, grading from 85% to 96% MgO .

India

India, a traditional supplier of crude and caustic-calcined magnesite, now produces mainly dead-burned magnesite for its own refractory industry, although small quantities of caustic-calcined magnesite are still produced. Deposits in the southern Salem district of Madras State are cryptocrystalline. The magnesite is of high quality but is mixed with serpentine and requires beneficiation to obtain optimum purity. Deposits in northern India in the Almora district, Uttar Pradesh, are crystalline. Here the ore is white to yellowish in color and produces a sinter in the range of 90% MgO . The Almora deposits are becoming depleted and beneficiation has become more necessary; hand sorting alone does not produce commercial tonnages

or quality (Clark 1983). Approximately 10 companies operate magnesite mining and calcining facilities in India with a total capacity of 270 ktpy; most of this is dead-burned magnesite, but it includes 25 ktpy of caustic-calcined production capacity.

Iran

In eastern Iran, more than 1 Mt of cryptocrystalline magnesite has been reportedly identified in a 20-km-long series of deposits located 50 km southeast of Birjand. Iranian Refractories Procurement and Production Co. operates a 30-ktpy dead-burned magnesite plant in Sarbisheh. Total reserves of magnesite in Iran have been estimated at 5 Mt (Sargheini 2003).

Nepal

According to the Nepal Department of Mines and Geology, ore reserves at the Kharidhunga deposit in Dolkha District, about 110 km northeast of Kathmandu, the national capital, were estimated at 180 Mt, of which 66 Mt was refractory-grade magnesite. Of this 66 Mt, 25 Mt was high-grade recoverable reserves. The Kharidhunga deposit is a crystalline type. The MgO content of ore averages 88% with a maximum 4.5% each for silicon dioxide (SiO_2) and ferric oxide (Fe_2O_3), and 1% each for aluminum oxide (Al_2O_3) and CaO. Mining at Kharidhunga stopped in 1990 because of technical problems at a processing plant producing dead-burned magnesite.

North Korea

Little information is available about the geology of North Korean magnesite deposits, but annual production of crude magnesite has been reported to be in excess of 1 Mt. The principal magnesite deposits are located in Hamgyŏng-namdo and average, on a crude basis, 45% MgO. Korea Magnesia Clinker Industry Group operates three mines and plants in Hamgyŏng-namdo that produce primarily dead-burned magnesite, although small quantities of caustic-calcined magnesite are produced. An open-pit mine has a capacity of 1.3 Mtpy, and two underground mines have a combined capacity of 1.2 Mtpy. The combined capacity of the three plants is estimated to be 1.15 Mtpy. The company produces four grades of dead-burned magnesite. The Grade A product contains a minimum of 90% MgO and maximums of 4.5% SiO_2 and 2% CaO (Anon. 2003b). A small portion is exported, but the majority is used by the country's steel industry.

Russia

Russia has the largest share of magnesite in the Commonwealth of Independent States (CIS), estimated to be about 90% of the total. Resources for the CIS have been estimated to be 800 Mt. The largest magnesite deposits are in the Irkutsk area—the Savinsk deposit and the Onotsk deposit. The Savinsk deposit is unmined, and the Onotsk deposit, which consists of talc-altered magnesite, is currently being mined for talc. The Satkinsk group of deposits, consisting of the Satkinsk, Nikol'sk, and Berezhovsk deposits in the Chelabinsk region, is being mined by the largest magnesite-producing company in Russia—JSC Kombinat Magnazit. This company has the capacity to produce 2.4 Mtpy of dead-burned magnesite, most of which is consumed in-house for refractories production; 100 ktpy of caustic-calcined magnesite; and 24 ktpy of fused magnesite. There are three significant deposits of magnesite in the Krasnoyarsk region—the Talsk, Verkhoturovsk, and Kardakansk deposits. Also in the Krasnoyarsk region, the Severo-Angarsk periclase plant is consuming about 30 ktpy of magnesite from the Kirgiteisk deposit (Troitsky 1997).

In addition to magnesite, the Kul'durskoe brucite deposit in Khabarovsk region contains about 4 Mt of brucite. It has been mined since 1971 and produces about 50 ktpy of ore (Anon. 1996).

Besides Russia, Ukraine and Kazakhstan have magnesite deposits. The Pravdinsk deposit in the Dnepropetrovsk region, Ukraine, contains about 70 Mt of magnesite. This material, however, is talc altered, and preliminary concentration is needed to produce material suitable for the refractory industry. Geological exploration has not been completed at the Mar'yanovsk magnesite deposit in eastern Kazakhstan, so no resource data are available for this deposit.

Serbia and Montenegro

Deposits of magnesite in Serbia and Montenegro extend into Bosnia and Herzegovina. The material is mined in both underground operations and in open-pit quarries; limited production precludes significant exports. These magnesite deposits are hydrothermal sedimentary and hydrothermal vein types. Vein-type deposits are located in Sumadija, Goleš, Dubovac, and Ibar. All the ore requires beneficiation—in this case, heavy media separation—in order to produce commercial quality concentrate (Petrov et al. 1980). Magnesite resources in Kosovo are estimated to be 4.5 Mt, of which 1.7 Mt is calculated reserves.

The principal magnesite mines, operated by Magnohrom Kraljevo, are underground mines at Užice and Čačak in Serbia and Montenegro, respectively. Magnesite is shipped to a magnesite plant in Kraljevo with a capacity of 160 ktpy of dead-burned magnesite and 40 ktpy of caustic-calcined magnesite. Because of the conflict in the 1990s, production at this plant has been significantly below annual capacity.

Slovakia

Slovakia has deposits of magnesite in Košice, Jelšava, and Lovinobaňa. In Jelšava, magnesite is associated with carbonate rocks in an irregularly shaped deposit about 4,000 m long by 1,000 m thick (Grend 1994). Slovenské Magnesitové Závody a.s. Jelšava (SMZ) operates mines in Dúbrava, Jelšava, and Mútnik, Hačava. Material from the semi-ores, a long with imported magnesite, feeds SMZ's 375-ktpy dead-burned magnesite plant in Jelšava. Slovmag a.s. Lubeník operates a mine and a 90-ktpy captive dead-burned magnesite plant in Lubeník.

South Africa

South Africa has been a producer of magnesite for more than 20 years, but the output has been somewhat irregular. The problem is with the mining; the ore occurs in pockets at irregular intervals. South Africa's economically viable deposits of magnesite occur as weathering products of rocks with high magnesium contents. The main magnesite deposits are in Mpumalanga and Limpopo provinces—the Malelane area, in the vicinity of Lydenburg, and an area to the north of the Soutpansberg and in the Burgersfort and Giyani districts. South Africa has two operating magnesite mines, Strathmore (owned by Chamotte Holdings [Pty] Ltd.) at Malelane, Mpumalanga and Syferfontein (owned by Syferfontein Calcite [Pty] Ltd.) in Soutpansberg district, Limpopo. Most of the magnesite is sold as crude material to local farmers for fertilizer applications, but the two operations can produce 12 ktpy of caustic-calcined magnesite (Ratlabala 2003). The reserves of magnesite in South Africa are estimated at 2.5 Mt, and total resources are estimated at 18 Mt (Agnello 2003).

Spain

Spain's magnesite deposits are principally located in Navarra Province, near the French border. The magnesite rocks are composed of lens-shaped crystals arranged in black and white bands (Lugli et al. 2000). There are also smaller deposits in northwest Spain. The total

production capacity is approximately 600 ktpy of crude magnesite (Harris 2001). Magnesita Navarras SA mines magnesite from a deposit at Eugui and has the capacity to produce about 100 ktpy of caustic-calcined magnesite and 70 ktpy of dead-burned magnesite (82%–90% MgO). Magnesitas de Rubian SA produces about 80 ktpy of caustic-calcined magnesite from a magnesite deposit in Lugo. The majority of both producers' caustic-calcined magnesite is destined for the agricultural market.

Turkey

Turkey has both crystalline and cryptocrystalline deposits of magnesite. The principal crystalline deposit is in the Black Sea region. The more important cryptocrystalline deposits, which are in the Eskisehir and Kutaya regions, are of the vein-filling type (Zedef et al. 2000). Another cryptocrystalline magnesite deposit is at Salda Lake in southern Turkey, approximately 150 km northwest of the port of Antalya and near the town of Yesilova. Here, magnesite is mixed with mud and occurs as dunes and as lumps on the lake-shore. The magnesite generally is not compacted and has a specific gravity of 1.60 to 1.80 g/cm³ (Schmid 1989).

Kümaş-Kütahya Magnesite Works Corporation operates a 350-ktpy mine at Kütahya that feeds a 180-ktpy dead-burned magnesite plant. Magnesit AŞ (in the Eskisehir region) can produce about 140 ktpy of dead-burned magnesite from magnesite from its own mines and from imported material. A third company, Konyu Selçuklu Krom Magnezit Tuğla Sanayi AŞ, mines magnesite at Cayirbagi, Helvacibaba, and Konya, and produces dead-burned magnesite for its internal production of refractories.

Other Locations

Two locations in Saudi Arabia containing magnesite deposits have been identified. The first, located in the Zarghat area, about 400 km northeast of Madinah, contains an estimated 1.6 Mt of magnesite. The other major magnesite site is in Jabal Rukman, about 180 km southeast of Madinah (U.S.–Saudi Arabian Business Council 2000). The country is investigating the production of 20 ktpy of fused magnesite from the Zarghat deposit.

Other, apparently minor, magnesite deposits have been reported to occur in Bolivia, Bulgaria, Colombia, Egypt, Guatemala, Kenya, Pakistan, the Philippines, and Zimbabwe.

SYNTHETIC MAGNESIA

Before 1938, the naturally occurring mineral magnesite was essentially the source of all refractory magnesite. Since that time, the manufacture of refractory-grade magnesite and caustic-calcined magnesite from sources other than natural magnesite has steadily increased in importance. Today, approximately two thirds of refractory-grade magnesite used in the western economic countries comes from synthetic magnesite sources. Several basically different methods for production of magnesite from nonmagnesite sources have been studied, and at least four have operated commercially. All involve the calcination of either magnesium hydroxide or magnesium chloride. Magnesium hydroxide may be obtained as a precipitate from magnesium-rich solutions or as a residue remaining after the lime fraction of calcined dolomite is removed as a soluble compound by reaction with solutions of ammonium chloride or hydrogen sulfide. Magnesium chloride may also be obtained as an end liquor after solar concentration of solutions of natural brines for production of salt or potash, or from well brines.

The choice of suitable sites for seawater magnesite plants is limited. Large land masses can cause the seawater to be diluted because of freshwater runoff and tidal action. Other factors, such as coastal topography, a availability of high-purity limestone or dolomite, fuel

source, and market location, are closely studied before a site is selected.

There are more than 20 plants around the world producing refractory magnesite and caustic-calcined magnesite from magnesium hydroxide. In these plants, magnesium hydroxide is obtained by precipitation from solutions such as seawater, seawater bitterns, inland well brines, or end liquors from other chemical processes. The following discussion highlights the larger foreign operations.

Ireland

Premier Periclase Ltd. operates a 90-ktpy plant in Drogheda to produce caustic-calcined and dead-burned magnesite from seawater. The company also produces magnesium hydroxide, and with recent capital investment has begun broadening the markets that it serves, adding the rubber and plastics industries to its traditional chemical and agricultural markets.

Israel

In 1969, Dead Sea Periclase Ltd. began producing dead-burned magnesite from Dead Sea brine, using the Aman process at a plant in Mishor Rotem. The Aman process uses concentrated magnesium chloride from the Dead Sea as a feedstock and does not use lime or dolomite as a reagent. As a result, the magnesite is 99.5% pure and does not include impurities such as SiO₂, Fe₂O₃, and Al₂O₃ that lime or dolomite leaves in the product. The purity of the product has allowed Dead Sea Periclase to enter the specialty magnesite market in addition to traditional applications. The plant has the capacity to produce 70 ktpy of magnesite—60 ktpy of dead-burned and 10 ktpy of caustic-calcined. The plant also produces fused magnesite, magnesium hydroxide, and magnesium chloride.

Italy

Two seawater magnesite operations in Italy have closed in recent years. The most recent closure was Cogema SpA's 85-ktpy operation in Priolo, Iracusa, Sicily, which shut down in March 2003; it is unclear if the plant will reopen.

Japan

Ube Material Industries Ltd. can produce 50 ktpy of caustic-calcined magnesite and 250 ktpy of dead-burned magnesite from seawater at its plant in Ube City. The company also recovers magnesium hydroxide and ships magnesite to Tatehō Dead Sea Fused Magnesite (Mishor Rotem, Israel) for fused magnesite production.

Mexico

Química del Rey SA de CV produces caustic-calcined and dead-burned magnesite from natural subsurface brines, which are pumped from a depth of 10 to 20 m through wells at Laguna del Rey, Coahuila. Total production capacity is 15 ktpy of caustic-calcined magnesite and 95 ktpy of dead-burned magnesite.

Netherlands

Nedmag Industries Mining and Manufacturing BV recovers magnesium chloride brine from a bischofite salt formation at a depth of about 1,500 m in the northern part of the Netherlands. The magnesium chloride is used to produce 150 ktpy of dead-burned magnesite, 8 ktpy of caustic-calcined magnesite, and magnesium hydroxide at the company's Veendam plant.

Other Locations

In addition to the plants described previously, small seawater magnesite plants exist in France, the Republic of Korea, Ukraine, and the United Kingdom.

TECHNOLOGY

Exploration

The search for deposits of any type of magnesite is based on considerations involving the probable origin of different types of magnesite. In the case of crystalline magnesite, possible locations of deposits are areas of limestone or dolomite terrain that have been subjected to folding or igneous activity. In the case of cryptocrystalline magnesite, possible locations are areas of ultrabasic rocks that show extensive alteration to serpentine. Thus, in either case, the search can be confined within the boundaries of areas that show evidence of structural or igneous activity; for instance, an area such as the midwestern United States would not be favorable for the occurrence of magnesite despite its large deposits of limestone and dolomite.

Magnesite formations are generally more resistant to weathering than associated formations; bold outcrops frequently characterize magnesite deposits. This is very evident in the Baja California peninsula where the magnesite stands out as caps on the mountains. Outcrops are sampled by surface chipping and shallow trenching. Sedimentary magnesite is difficult to recognize because it has no clearly distinguishing physical features or characteristic geologic associations.

Following preliminary investigations, a diamond drill program may be carried out to assess the commercial potential of the deposit. The formal final evaluation is based on the size and location of the deposit and the quantity and distribution of undesired minerals containing silica, lime, iron oxide, and alumina. Tests to determine whether the impurities can be removed by ore dressing must be part of the evaluation. To be commercially acceptable, magnesite should contain at least 95% magnesium carbonate, an amount that, depending on the accessory oxides, would result in a dead-burned product containing 90%–94% MgO. Refractory-grade magnesia of that quality would have some demand at the lower end of the price scale. The growing demand is for even higher MgO content, and this places increased emphasis on the need to beneficiate the ore.

Mining

Magnesite mining and processing practices of varying forms and complexity are found in many places around the world. The type of the deposit dictates the method of mining. Large, massive, near-surface deposits are usually worked by open-pit methods. Narrow and deep deposits are worked by underground drifts and stopes. The mined ore is rarely shipped or used in crude form. It is processed near the mine site to yield magnesia products. Invariably some degree of sorting or beneficiation is applied to the ore prior to heat treatment.

Processing

Dead-Burned and Caustic-Calcined Magnesia

In the production of refractory magnesia and caustic-calcined magnesia, magnesite is delivered from the mine to a crushing plant where it is crushed in three stages. Depending on the grade of the ore, the crushed material is conveyed to one of three storage piles. Each storage pile feeds a separate production circuit—the flotation plant, the heavy-medium separation plant, and the rotary kiln plant. Concentrates from the flotation and heavy-medium separation circuits also feed the rotary kiln plant.

The kiln plant feed goes into two separate circuits for calcination. One, for the production of dead-burned magnesite, uses either rotary kilns or shaft furnaces; the other, for caustic-calcined magnesite, uses hearth furnaces or rotary kilns. Some of the raw feed is mixed with flue dust and briquetted before being dead-burned in the rotary kiln. Two classes of refractory magnesia are made: brick grade and maintenance grade.

Table 3. Typical composition of Michigan brine and seawater (grams per liter)

Component	Michigan Brine	Seawater
Magnesium chloride (MgCl ₂)	8.2	4.176
Magnesium sulfate (MgSO ₄)	0	1.668
Magnesium bromide (MgBr ₂)	0	0.076
Calcium chloride (CaCl ₂)	13.64	0
Calcium sulfate (CaSO ₄)	0	1.268
Sodium chloride (NaCl)	5.45	27.319
Potassium chloride (KCl)	0.48	0
Potassium sulfate (K ₂ SO ₄)	0	0.869
Bromine gas (Br ₂)	0.2134	0
Specific gravity	1.264	1.024

Dolomite and brucite are processed in a similar manner. After primary crushing, raw, crushed dolomite is delivered to iron and steel plants, where it is calcined and used as dead-burned dolomite. Brucite is beneficiated in a heavy-medium plant for use as a refractory material.

When seawater or well brine is used as the feed for producing magnesia, dissolved carbonate and sulfate levels are reduced so insoluble calcium compounds do not precipitate with the magnesium hydroxide. To accomplish this reduction, the brine or seawater is either treated with slaked lime or acid to precipitate the carbonates and sulfates as calcium compounds. The filtered, treated solution is then mixed with either dry or slaked lime to precipitate magnesium hydroxide. The resulting magnesium hydroxide slurry is concentrated with thickeners and washed with fresh water in a countercurrent system, then filtered. The filter cake is either directly calcined to produce refractory or caustic-calcined magnesia, or it is calcined and pelletized before dead-burning to give proper size and density characteristics.

Magnesium Hydroxide

Magnesium hydroxide is recovered from seawater or brines by precipitating the dissolved magnesium as magnesium hydroxide with the addition of dolime (CaO•MgO). Because the composition of seawater is slightly different from that of Michigan brine (Table 3), removal of impurities or salable by-products is slightly different.

Michigan brine is pumped from 850 m below the earth's surface. Bromine is removed from the brine by heating followed by chlorination with chlorine gas, which replaces the dissolved bromine with chlorine, producing bromine gas (Br₂). The debrominated solution is mixed with preheated, slaked dolime to precipitate the magnesium hydroxide in settling tanks. The remaining calcium chloride solution is concentrated and can then be sold as a 32% to 45% liquor for a variety of applications.

To recover magnesium hydroxide from seawater, the seawater is first screened to remove any debris before being treated with dolime to remove any dissolved carbonate as calcium carbonate. After calcium carbonate is precipitated, the solution is treated further with sulfuric acid to remove any remaining calcium bicarbonate as calcium sulfate. The solution is then seeded with magnesium hydroxide and pumped to thickeners where the magnesium hydroxide slurry is concentrated. The slurry is filtered to produce a filter cake containing about 50% solids. This material can be sold as a hydroxide or calcined to produce either dead-burned or caustic-calcined magnesia.

Table 4. Magnesium chloride brine chemical composition and characteristics

Magnesium chloride (MgCl ₂)	28.0–35.0 wt %
Chlorine (Cl)	19.8–27.0 wt %
Magnesium (Mg)	6.8–9.2 wt %
Sulfate ion (SO ₄)	1.2–3.5 wt %
Sodium (Na)	0.2–1.0 wt %
Potassium (K)	0.1–0.8 wt %
Lithium (Li)	0.1–0.2 wt %
Bromine (Br)	0.1–0.2 wt %
Iron (Fe)	5–10 ppm
Specific gravity	1.27–1.36 g/L
Bulk density	11 lb/gal

Adapted from Reilly Industries, Inc. 1997.

Magnesium Chloride

To recover magnesium chloride from brines, using the Great Salt Lake brines as an example, the water is pumped to a series of solar evaporation ponds where water evaporates to concentrate the brine. The first salt to precipitate as the water evaporates is sodium chloride. The next group of salts to precipitate is a mix of double salts containing potassium and magnesium. Depending on brine concentration, temperature, and other factors, kainite (MgSO₄•KCl•3H₂O), schoenite (MgSO₄•K₂SO₄•6H₂O), and carnallite (KMgCl₃•6H₂O) may be precipitated. Sodium sulfate is then precipitated from the cooled brine in the winter (even though it is no longer harvested for sale). The final product remaining dissolved in the brine is magnesium chloride. In general, equilibrium is reached at about 35% magnesium chloride (MgCl₂) concentration by weight in the brine. Although most of the sodium and potassium have been removed from the brine at this stage, it still contains some dissolved sulfate. The purity of this brine is sufficient for some applications, but if necessary, it may be purified further. Purified brine then may be further processed to produce the hexahydrate solid formula. The overall production cycle takes about 2 years to complete (Anon. 1984). Table 4 gives a typical analysis of Great Salt Lake brine.

Magnesium Sulfate

Synthetic magnesium sulfate in the United States is normally produced by reacting magnesium oxide, hydroxide, or carbonate with sulfuric acid followed by crystallization. Anhydrous magnesium sulfate can be manufactured only by dehydration of a hydrate; crystallization from an aqueous solution is not possible.

MARKETING

Uses

Dead-Burned Magnesia

Refractory magnesia represents the largest tonnage use of magnesium in compounds. The iron and steel industry is the largest consumer of these products in the United States and most other magnesia-consuming countries. Dead-burned magnesia from magnesite, sea water, or well and lake brines is used as a major constituent in metallurgical furnace refractory products. Steel furnaces, which use 70% of the total, are the largest consumers of refractory products. Furnaces used for cement and lime (7%), ceramics (6%), glass (4%), chemicals (4%), and nonferrous metals production (3%) are other consumers of magnesia-based refractories. Other applications account for the remaining 6% (Kandianis and Kandianis 2002).

Although magnesia refractories can be formed into a variety of shapes, bricks are the most common. Magnesia can be combined with other materials to form bricks with specific characteristics that are used in specific areas of a furnace or as ladle linings. The most common use for magnesia brick is as wear and permanent linings in electric arc furnaces (EAFs) and as a permanent lining in BOFs. Magnesia-carbon brick and MgO-CaO brick are used as wear linings in BOFs, EAFs, and steel casting ladles. Directly bonded magnesia-chrome brick is used in secondary steelmaking furnaces.

Caustic-Calcined Magnesia

Caustic-calcined magnesia has uses in many market segments. In water treatment, magnesia is used to remove silica and heavy metals from industrial wastewater. It is also used as a neutralizing agent for some wastewater streams. Caustic-calcined magnesia is used for removal of sulfur dioxide (SO₂) from industrial flue gases; the magnesium oxide reacts with the SO₂ to form magnesium sulfate. Magnesia competes with calcium compounds in this application. Annually, environmental applications average between 35% and 40% of U.S. shipments of caustic-calcined magnesia.

Magnesia is also used in agricultural applications for animal feed and fertilizer; in the United States, these applications represent about 20%–25% of the total annual caustic-calcined magnesia shipment. Magnesium serves as a structural part of the chlorophyll molecule, a compound necessary for plant photosynthesis. Without sufficient magnesium, either from the soil or from fertilizer application, plants can die. Grazing ruminants, such as cattle and sheep, require magnesium in their diet to guard against hypomagnesia, also known as grass tetany, a potentially fatal disease.

Caustic-calcined magnesia is used as a precursor to other magnesia chemicals, including chlorides, nitrates, and epsom salts. The accounts for about 35% of annual U.S. magnesia shipments.

An important use of caustic-calcined magnesia is in the production of magnesium oxychloride and oxysulfate cements, which are used primarily as flooring in industrial and institutional buildings. Fused and boron-free magnesia or periclase are used for insulation of heating elements in electric furnaces and appliances.

Caustic-calcined magnesia is used in the production of rayon, fuel additives, and rubber. Caustic-calcined magnesia is used to produce magnesium acetate, which is used for neutralization purposes in producing rayon fiber. Caustic-calcined magnesia is a starting material for the production of magnesium-overbased sulfonates, which are used as acid acceptors and sludge dispersants in crankcase lubricating oils and as a fuel additive. Magnesium oxide also may be injected into oil-fired utility boilers where it reacts with vanadium salts to form a magnesium vanadate; this alleviates slagging and corrosion problems encountered when using high-vanadium fuels. In water-based oil-well drilling muds, magnesia is used as a buffer, for viscosity control, and as a corrosion inhibitor. In the rubber industry, caustic-calcined magnesia is used as a vulcanizing agent in the curing of rubbers and elastomers.

In the food industry, caustic-calcined magnesia is used in sugar refining for neutralization of raw cane and beet juices and to reduce scaling in juice heaters, evaporators, juice lines, and other equipment. U.S. Pharmacopoeia (USP)-grade caustic-calcined magnesia can be used in pharmaceutical applications.

Magnesium Hydroxide

After discounting the portion of magnesium hydroxide that is used to produce dead-burned magnesia, the largest use for magnesium hydroxide in the United States is for environmental applications. This portion of the market, which includes industrial water treatment, heavy metals removal, and flue-gas desulfurization, accounts

for about 60% of the total U.S. consumption. For water treatment, magnesium hydroxide is supplied as a suspension containing about 58% solids, and it primarily is used to lower the pH of acidic solutions. In this market, it competes with other acid-neutralizing compounds, the most common being lime and caustic soda (NaOH). Magnesium hydroxide has advantages and disadvantages when compared to the other materials in this use. One of the advantages is that it is a pH buffer, and wastewater treated with it will not exceed a pH of 9.5 even if excess magnesium hydroxide is added. In contrast, excess addition of lime can raise the pH to 12, and excess caustic soda addition can raise the pH to 14. In these cases, back additions of acid are necessary to lower the pH. Magnesium hydroxide also has a higher basicity per unit added than either lime or caustic soda; for equivalent neutralization, 0.72 t of magnesium hydroxide can replace 1 t of lime. Magnesium hydroxide is better than lime or caustic soda at removing some metals such as lead and trivalent chromium. Metal hydroxides that are precipitated with magnesium hydroxide rather than caustic soda or lime tend to form larger crystals, resulting in lower sludge volumes and, hence, lower disposal costs. The solids formed through precipitation by magnesium hydroxide have a cakelike consistency, rather than the gel-like consistency of solids formed by caustic soda precipitation; the cake is easier to handle (Wajer 1994).

One principal disadvantage of magnesium hydroxide is its higher cost compared to that of other water treatment materials. Another disadvantage is its slower reaction rate, particularly when precipitating high concentrations of metals (greater than 2,000 ppm) or neutralizing weak or organic acids. Most treatment systems in use today were originally designed to use lime or caustic soda, and as a result of magnesium hydroxide's slower reaction time, there may not be enough residence time in the system. In some cases, users must reconfigure their systems when switching to magnesium hydroxide.

Magnesium hydroxide slurry also competes with magnesium oxide where there are large neutralization requirements. Magnesium oxide has about 2.5 times as much neutralizing capability as magnesium hydroxide per unit volume, and transportation costs for the oxide are generally lower than those for the hydroxide slurry. In addition, existing lime neutralization systems may be more easily converted to use the magnesium oxide powder rather than the hydroxide slurry.

In flue-gas desulfurization, magnesium hydroxide is used in place of lime in a few applications. Most of the processes designed for industrial gas scrubbing use lime or calcium in some form. Scrubbing with lime produces gypsum products, which need to be landfilled in most cases. The volume of these waste products may be greater than the original waste volume, so lime may not be appropriate for all scrubbing applications. In these instances, magnesium hydroxide may be used. Landfilling, however, may not be as much of a problem in the future for lime scrubber wastes because the by-product gypsum can be used in wallboard.

The second largest use for magnesium hydroxide is as a precursor for other magnesium chemicals, which accounts for about 20% of annual U.S. consumption. About 5% of magnesium hydroxide is used in pharmaceuticals. The pharmaceutical grades of magnesium hydroxide include a 100% $\text{Mg}(\text{OH})_2$ powder used in antacid tablets and a 30% $\text{Mg}(\text{OH})_2$ paste used in liquid antacids such as milk of magnesia.

Flame retardants represent about 3% of the total magnesium hydroxide consumption in the United States. Like magnesium carbonate, magnesium hydroxide can replace alumina trihydrate in some flame retardants. Both alumina trihydrate and magnesium hydroxide function as flame retardants by releasing water vapor in an endothermic reaction that diverts the heat away from the flame,

thereby reducing the formation of combustible gases. Alumina or magnesia remaining after the water is released is believed to have a high surface area available for absorbing smoke. Although the properties of alumina trihydrate and magnesium hydroxide are similar, magnesium hydroxide has higher temperature stability. Magnesium hydroxide begins to decompose at about 330°C, compared with about 200°C for alumina trihydrate. This higher temperature stability makes magnesium hydroxide more attractive for specific flame retardant applications. Some thermoplastics, such as polypropylene or nylon-vinyl, require temperatures in processing that are high enough to begin alumina trihydrate decomposition. In addition, the high processing speed of lines that produce plastic insulation for wire and cable generates enough friction to begin alumina trihydrate decomposition. In these cases, magnesium hydroxide is the flame retardant of choice.

Magnesium Chloride

The largest use for magnesium chloride brine is as a suppressant for dust on dirt roads, construction sites, unpaved parking lots, mines, and quarries. A corrosion inhibitor may be added to the brine to reduce corrosion on structures, such as steel surfaces, that are associated with the sites where the brine is used. The inhibitor forms a protective coating so that the brine will not corrode metal surfaces. Magnesium chloride brine may also be used to melt ice on road surfaces, sometimes in conjunction with an abrasive such as sand. Brines may be used to make oxychloride flooring cements, known as Sorel cements. These are vermin-resistant flooring cements that are used in industrial buildings. Brines also have applications in oil-well completion fluids, as a component of some herbicides, and in regeneration of ion-exchange resins.

Magnesium chloride hexahydrate is almost exclusively used for melting ice. It is used in conjunction with, or in place of, salt for removal of ice and snow from sidewalks and roadways. Magnesium chloride has a lower freezing point than salt and is generally less corrosive to asphalt and cement, but it is significantly more expensive. In most cases, salt is used as the major melting agent for ice and snow, but if the surface that is being treated is expensive to maintain, the additional cost for magnesium chloride can be justified.

Magnesium Sulfate

Natural and synthetic magnesium sulfates have a wide array of end uses. The largest use for magnesium sulfate in all forms is for consumer goods. About 30% of magnesium sulfate is used in food additives and pharmaceuticals. Magnesium sulfate heptahydrate—Epsom salts—is used for mineral baths and in medicine as a cathartic and analgesic soaking agent for bruises, sprains, localized inflammations, and insect bites. Magnesium sulfate is used as a micronutrient in some food products, and it is used in the production of high-fructose corn syrup.

Industrial uses account for about 25% of U.S. magnesium sulfate demand. The primary component of industrial applications is the use of magnesium sulfate as a precursor to other chemicals. It also is used in drying and flocculation applications and in catalyst preparation.

Animal feeds and fertilizers represent about 20% of the U.S. market for magnesium sulfate. Most end uses for magnesium sulfate use synthetically produced material because of its higher purity. Purity requirements for animal feeds and fertilizers are not as stringent, so they mainly contain the natural minerals, which are imported into the United States. The most effective way of preventing grass tetany is to provide magnesium to the pasture through fertilization. Magnesium may also be supplied in the form of Epsom salts or kieserite that is added to the feed or drinking water.

Pulp and paper processing accounts for about 15% of magnesium sulfate use in the United States. Magnesium sulfate is used by kraft pulp mills that use oxygen delignification on soft woods, but it is also used in conjunction with sodium silicate to increase the life of hydrogen peroxide in oxygen-based bleaching processes. Miscellaneous uses, which represent about 10% of magnesium sulfate demand, include adhesives, textiles, matches, metal plating, photographic solutions, rubber coagulation, refractory bonding agents in bricks, and oxysulfate cements.

Grades and Specifications

Specifications for magnesia, including chemical composition, bulk density, particle size, and loss on ignition, are generally set by the consumer for a specific application. Refractory magnesia composition depends on the area of the furnace in which the material is to be used. Magnesia produced from magnesite can contain between 88% and 98% magnesia, with varying quantities of alumina, calcium, iron, and silica impurities. Synthetic magnesia is normally purer than natural magnesia, containing between 92.0% and 99.5% magnesia, with smaller quantities of the same impurities found in natural magnesia. Synthetic magnesia may also contain boron impurities. Most fused magnesia contains greater than 94% magnesia. Some individual specifications are shown in Table 5. As a general rule, dead-burned magnesia containing greater than 97% MgO, with a bulk density of 3.40 g/cm³, and a periclase crystal size that is greater than 120 m, is called high-purity magnesia. Countries that supply this grade include Australia, Ireland, Israel, Japan, Mexico, the Netherlands, and the United States. Dead-burned magnesia from China, Greece, Slovakia, Spain, and Turkey supplies the low- to medium-purity market.

Prices

Magnesia pricing is relatively stable; quoted prices change infrequently. Table 6 shows year-end 2003 prices as quoted in *Chemical Market Reporter*. Prices for Chinese- and European-produced magnesia, as quoted in *Industrial Minerals*, are also shown. These prices are producer list prices, and large customers may receive discounts from these price levels. Because of the variety of grades available, caustic-calcined magnesia prices vary significantly depending on application. Natural caustic-calcined magnesia in bags is quoted at about \$400/t, whereas the high-end rubber and plastic grades of caustic-calcined magnesia were priced at about \$700/t. Recent wide swings in natural gas prices have caused producers to increase pricing for their magnesia products to compensate for higher energy costs. Buying decisions for caustic-calcined magnesia are price-based because of competition from competing mineral products such as caustic soda or dolomite and are significantly influenced by transportation costs.

ECONOMIC OR COMPETITIVE FACTORS

Tariffs and Depletion Provisions

The tariffs on magnesia and magnesium compounds for countries with which the United States has normal trade relations (NTR) are shown in Table 7. In addition, because of trade agreements, some countries have special tariff rates; these are also given in the table. Tariff rates have been established for countries with non-NTR with the United States; in 2003, these countries were Afghanistan, Cuba, Laos, North Korea, and Vietnam. Because there is no appreciable trade between the United States and these countries, the non-NTR tariff rates are not shown.

Depletion allowances have been established for some domestic and foreign ores of magnesium and its compounds. Magnesium

chloride from brines, wells, or saline perennial lakes within the United States has a depletion allowance of 5%. The depletion allowance for both domestic and foreign ores of dolomite and magnesium carbonate is 14%. Depletion allowances for other ores are as follows: brucite, 10% (domestic and foreign); and olivine, 22% (domestic) and 14% (foreign).

By-products and Coproducts

Because a significant percentage of magnesium compounds is extracted from saline solutions and evaporites, salt and bromine are major coproducts recovered during magnesium compound recovery. In addition, potassium compounds and gypsum can be extracted from sediments of seawater evaporite deposits. Sodium, lithium, iodine, and strontium compounds can be obtained from sediments and near-surface brines formed by inland bodies of water. Iodine and calcium compounds are generally extracted from well and lake brines. Bromine is recovered as a by-product of processing Michigan brines.

Costs

Because of the diverse nature of the processes used to produce magnesia and the variety of raw materials that can be used, costs vary widely from operation to operation. Wilburn (1986) provided estimates of costs to produce caustic-calcined and dead-burned magnesia. Although somewhat dated, the report gives some basic information about the relative costs of each raw material source. In general, seawater was the highest cost source for magnesia recovery, which is not surprising considering that it has the lowest magnesium concentration of any of the most commonly used sources. Production costs for caustic-calcined magnesia were generally lower than those for dead-burned magnesia, regardless of the source material, mainly because of lower energy costs associated with the lower calcining temperature. For dead-burned magnesia, energy costs represent 58% to 71% of the total operating cost, compared with 37% to 59% for caustic-calcined magnesia. Sale of by-product materials that can be recovered from a seawater or brine operation helps to offset some of the production costs.

Substitutes

There are few substitutes for dead-burned magnesia in refractory applications. In some cases, alumina, chromite, and kyanite may substitute, but with a loss of performance. Caustic-calcined magnesia competes with a variety of materials, depending on the application. In some cases, caustic-calcined magnesia has entered markets that have been dominated by other materials, so it is considered a substitute. In environmental applications, it competes mainly with lime and caustic soda in wastewater treatment, and with lime and limestone for stack-gas scrubbing. It also competes with magnesium hydroxide in these applications. In fire-retardant applications, magnesium hydroxide is a competitor to alumina trihydrate.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Magnesite and dolomite can normally be mined with minimal interference with other land use. Mine drainage from open-pit or underground operations does not contribute significantly to stream pollution because the drained areas usually contain no significant amounts of soluble materials. Dust collectors and wet scrubbers are used to control stack-gas dust emissions from plants calcining and dead-burning dolomite, magnesite, and magnesium hydroxide.

In magnesia plants based on seawater, the water is returned to the ocean after the magnesia is removed. Recent innovations have decreased the turbidity of the effluent, resulting in minimal changes to the ocean environment. None of the discharges from either natural

Table 5. Grades and specifications for selected caustic-calcined, dead-burned, and fused magnesias

Material and Source Country	Chemical Composition, %						Density, g/cm ³
	Magnesia (MgO)	Silicon Dioxide (SiO ₂)	Calcium Oxide (CaO)	Ferric Oxide (Fe ₂ O ₃)	Aluminum Oxide (Al ₂ O ₃)	Boric Oxide (B ₂ O ₃)	
Caustic-calcined magnesias							
Canada	96.3	0.4	2.7	0.5	0.1	na*	NA†
Slovakia	78.0	1.0	2.5	7.0	0	na	NA
Spain	85.0	3.6	7.0	2.5	0.4	na	NA
United States (brine)	97.0	0.5	1.0	0.3	0.2	na	NA
United States (seawater)	97.2	0.4	0.9	0.24	0.28	NA	NA
Dead-burned magnesias							
Australia	97.0	0.5	2.3	0.1	0.1	na	3.42
Brazil	94.88–98.40	0.25–1.29	0.43–0.77	0.41–2.11	0.05–0.35	0.007	3.07–3.34
China (DBM9010)	91.3	4.0	2.3	1.2	1.2	na	3.2
China (DBM95)	95.4	2.2	1.6	1.0	1.0	na	3.2
China (DBM97)	97.3	0.7	1.4	0.8	0.2	na	3.3
Greece	85–96	1.10–9.0	1.5–3.5	0.15–0.70	NA	na	3.15–3.40
India	>93	4.5	1.2	1.0	0.8	na	3.2
Iran	96.0	1.70	1.1	0.25	0.45	na	3.40
Ireland	97.2	0.25	2.1	0.2	0.07	0.01–0.02	3.43
Israel	99.3	0.03	0.63	0.04–0.07	0.03	0.005	3.43–3.45
Italy	97.3	0.50	2.1	0.1	0.15	0.060	3.46
Japan	98.1	0.36	1.3	0.05	0.06	na	3.48
Mexico	98.7	0.20	0.87	0.12	0.15	0.01	3.43
Netherlands	98.5	0.12	0.74	0.44	0.07	0.01	3.40
North Korea	91.9	4.0	1.8	1.1	0.7	na	3.2
Serbia and Montenegro	85–96	1.0–5.0	2.0–5.5	0.6–3.5	0.3–1.3	na	3.51–3.55
Slovakia	87–90	0.7–3.5	2.0–2.5	4.7–7.5	0.3–0.8	na	3.20–3.35
Turkey	89–97	0.60–6.0	1.70–3.0	0.40–1.20	0.10–0.20	na	3.30–3.45
United States	97.9–98.4	0.25–0.85	0.85–1.05	0.14–0.20	0.12–0.19	0.024–0.064	3.15–3.38
Fused magnesias‡							
UCM§ Electromag 22SR	94.4	3.2	1.4	0.15	na	<0.01	2.36–2.39
UCM Electromag 3L	95.0	2.5	1.4	0.15	na	<0.01	2.35–2.39
UCM Electromag CB	80.6	9.0	1.2	0.15	na	<0.01	2.20–2.30

Adapted from O'Driscoll 1994, 2003a, b, c; Kendall 1996; Martin Marietta Magnesias Specialties 2003.

* na = not applicable.

† NA = not available.

‡ For fused magnesias, source country is immaterial; the manufacturer and trade name is shown instead.

§ UCM = UCM Group plc, Stafford, United Kingdom.

Table 6. Magnesias prices, year-end 2003 (per metric ton)

Country and Material	US\$
China	
Caustic-calcined, 90%–92% MgO	92–98
Dead-burned	
90% MgO	90–92
92% MgO	92–94
94%–95% MgO	122–130
Europe, caustic-calcined*	
Agricultural	138–180
Industrial, natural	241–465
United States	
Caustic-calcined, agricultural grade, 98% MgO	538
Dead-burned	400–406

Adapted from Anon. 2003b; Anon. 2004.

* Converted from British pounds and Euros.

or synthetic magnesias plants has a noxious quality, and their appearance can be made acceptable with modern treatment methods.

Most magnesium compounds are treated as nuisance-causing dusts in the workplace. The American Conference of Governmental Industrial Hygienists has established threshold limit values (TLVs) for magnesium oxide fumes and magnesium carbonate. The TLV for both substances has been established at 10 mg/m³. TLVs for magnesium chloride and magnesium sulfate have not been established. The Occupational Safety and Health Administration has set permissible exposure limits (PELs) for magnesium carbonate and magnesium oxide fumes. The PEL for magnesium oxide fumes was established at 15 mg/m³ (total particulate), with a PEL of 5 mg/m³ for the respirable particulate (International Programme on Chemical Safety 1994b). The PEL for magnesium carbonate (magnesite) has been set at 15 mg/m³ (International Programme on Chemical Safety 1994a). If magnesite contains more than 1% crystalline silica, the TLV and PEL for the material can be much lower because of the potential danger in long-term exposure to crystalline silica.

Table 7. U.S. tariff rate

Harmonized Tariff Schedule No.	Description	Normal Trade Relations	Special ¹	Beginning Effective Date	Ending Effective Date
2519.10.00	Natural magnesium carbonate (magnesite)	Free		1/1/89	12/31/20
2519.90.10	Fused magnesia and dead-burned magnesia			1/1/99	12/31/20
2519.90.20	Caustic-calcined magnesia	Free		1/1/99	12/31/20
2519.90.50	Other magnesia	Free		1/1/89	12/31/20
2530.20.10	Kieserite (natural)	Free		1/1/89	12/31/20
2530.20.20	Epsom salts (natural)	Free		1/1/99	12/31/20
2816.10.00	Magnesium hydroxide or peroxide	3.1% ad valorem	Free (A*, CA, E, IL, J, JO, MX)	1/1/02	12/31/20
2833.21.00	Magnesium sulfate (synthetic)	3.7% ad valorem	Free (A*, CA, E, IL, J, JO, MX)	1/1/02	12/31/20

Source: U.S. International Trade Administration.

¹A*—Generalized System of Preferences; CA and MX—North American Free Trade Agreement; E—Caribbean Basin Economic Recovery Act; IL—United States-Israel Free Trade Area; J—Andean Trade Preference Act; and JO—Jordan Free Trade Agreement.

Because of the chromium content in the material, magnesia-chrome bricks must be disposed of as a hazardous waste if an extract from a representative sample contains total chromium at a concentration greater than or equal to 5.0 mg/L. The waste can be treated by chemical leaching or washing to dilute the concentration, but these options are costly, and if washing is used, the wastewater must also be treated. Another alternative for treatment is high-temperature reprocessing, but few firms have the treatment facilities necessary for this operation (Kendall 1994).

OUTLOOK AND FUTURE TRENDS

Overall, worldwide refractory magnesia consumption is influenced by several trends:

- Consolidation within the refractories industry
- Decreasing consumption because of technologic development in the steelmaking industry
- Production of higher quality refractory materials, leading to longer furnace-lining lives
- A shift from using BOFs to using EAFs in steelmaking, leading to increased use of basic refractories
- A greater demand for high-purity dead-burned magnesia with a bulk density greater than 3.40 g/cm³ and a crystal size greater than 120 µm

China has become the dominant world supplier of dead-burned magnesia in the low- to medium-grade markets. As a result, many producers of these grades have closed because they cannot compete with the lower priced Chinese material (Table 6).

In the United States, the dead-burned magnesia market is likely to continue to be dominated by imports, especially of magnesia from China. Within the past 5 years, the United States has lost three producers of dead-burned magnesia and is left with only one. In addition, the steel production industry has contracted, leaving fewer markets for dead-burned magnesia. For caustic-calcined magnesia, however, the future appears to be a little brighter. Water treatment usage of magnesia and magnesium hydroxide is growing, reflecting increased environmental concerns and increased acceptance of magnesium hydroxide for caustic soda. Animal feed markets are steady, but imports of caustic-calcined magnesia from China are increasingly being barged up the Mississippi River to the major farming states for use in agriculture. This increase in imported material is likely to continue, mainly because of its lower cost compared to U.S.-produced magnesia.

In Europe, the caustic-calcined magnesia market is estimated to be 150 to 200 ktpy, with the majority used for cattle feed. Outbreaks of mad cow disease and hoof and mouth disease in Europe

have had an adverse effect on this market. Animal feed markets are likely to become more difficult to supply with the potential implementation of product certification to prove that there is no contamination of feed ingredients throughout the European Union (EU); this certification is already in place in the Netherlands.

The EU water treatment and flue-gas desulfurization markets have not developed to the extent that they have in North America, and without additional EU legislation that would force a change in practices, these markets are not likely to develop. As with the United States, the EU is facing increased competition from imports of dead-burned magnesia from China. Although the quality is not as high as that of material produced in Europe, the Chinese magnesia can be blended with small quantities of high-purity European material to produce a satisfactory product (Harris 2002).

In Asia, steel production is increasing, and the market for dead-burned magnesia is increasing as well. China's steel production is expanding rapidly, and production in southeast Asia is expected to increase. China supplies its internal needs, and, as with North America and Europe, supplies a significant portion of the Asian market.

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Manganese

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INTRODUCTION

Manganese (Mn), atomic number 25, is a black, brittle, metallic element. Its most widespread uses are in the steel industry and as a component of dry cells. In the metallurgical industry, manganese is used as a deoxidizing and desulfurizing agent, and as an alloying element in certain steel, copper, and aluminum alloys. Nonmetallurgical applications of manganese include battery cathodes (manganese dioxide), soft ferrites (manganese-zinc ferrites) used in electronics, micronutrients found in fertilizers and animal feed (manganese sulfate and manganous oxide), a water treatment chemical (potassium permanganate), a colorant for bricks and ceramics, and others (see also Weiss 1977; Harben, Raleigh, and Harris 1998).

From antiquity until the latter part of the eighteenth century, the mineral pyrolusite (MnO_2 ; from the Greek words meaning “fire” and “to wash”) was considered an iron mineral. Ancient Egyptians and Romans used pyrolusite to control the color of glass. Adding small amounts of pyrolusite removed the greenish yellow discoloration caused by iron impurities in glass, while further additions colored the glass pink, purple, or black (Wellbeloved, Craven, and Waudby 1990). In 1740, J.H. Pott showed that pyrolusite does not contain iron. In 1774, Swedish chemist and apothecary Carl Wilhelm Scheele recognized manganese as an element, and his fellow countryman, Johan Gottlieb Gahn, isolated manganese metal by reducing manganese dioxide with carbon. Until about that time, manganese was used principally as a colorant in glass and pottery. Manganese ore was first mined in the United States in Virginia and Tennessee in the 1830s apparently for this purpose (Jones 1985).

Specific use of manganese in the steel industry dates from 1839, when the element was shown to improve malleability of ferrous articles. In 1856, Robert Forester Mushet demonstrated that steel could be mass-produced by the Bessemer process if manganese was added (Williams 1981). Not many years later, the bulk manganese ferroalloy industry was established, and, by the 1870s, cheap ferromanganese containing 75% or more manganese was available. Since then, manganese has been essential to the commercial production of almost all steels.

The chemical properties of manganese have been utilized for centuries. Umber, a mixture of manganese and iron oxides, was used as a paint drier by the mid-1600s. By the eighteenth century, the oxidizing power of certain manganese chemicals was recognized. Manganese ores were used extensively to produce chlorine until about 1855.

Manganese use as a significant component of batteries dates from 1866, the year that Georges Leclanché filed the master patent for the zinc-carbon dry cell that bears his name. The Leclanché batteries used natural battery-grade manganese ore (gamma MnO_2). Since the early 1960s, however, the Leclanché battery has been replaced by the alkaline battery, which uses electrolytic manganese dioxide (EMD) as the dominant system in the primary (disposable) battery market. Since the 1970s, manganese also has been used in lithium battery technologies. One of the earliest commercially available and now most widely used primary lithium batteries is the lithium-manganese dioxide battery. Today lithium-ion batteries utilizing lithium manganese oxides also are used in the secondary (rechargeable) battery market.

PRODUCTION AND RESOURCES

Although manganese is the 12th most abundant element in the earth's crust (Parker 1967), minable deposits of manganese ore are uncommon. Excluding China, India, Kazakhstan, and Russia, significant production currently is limited to 13 deposits in seven countries (Table 1). Known manganese reserves are limited to those same countries (Table 2).

GEOLOGY

Geochemistry

In nature, manganese occurs in three valence states: divalent (Mn^{2+}), trivalent (Mn^{3+}), and quadrivalent (Mn^{4+}). Common minerals containing Mn^{2+} include rhodochrosite (MnCO_3), rhodonite (MnSiO_3), alabandite (MnS), and spessartite garnet ($\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$). (Mineral formulae are from Kretz, Hunt, and Ramsdell 1951; Hurlbut 1959; and Cairncross, Beukes, and Gutzmer 1997.) Mn^{2+} also is common in the carbonate component of many sedimentary rocks in amounts ranging from trace to a few percent. Minerals containing both Mn^{2+} and Mn^{3+} include braunite ($\text{MnMn}_6\text{SiO}_{12}$) and hausmannite (MnMn_2O_4). Minerals with only Mn^{3+} are uncommon and include bixbyite ($(\text{Mn},\text{Fe})_2\text{O}_3$) and manganite ($\text{MnO}(\text{OH})$). Minerals that contain both Mn^{3+} and Mn^{4+} include the many variations within the cryptomelane ($\text{KMnMn}_7\text{O}_{16}$)-psilomelane ($\text{BaMn}_2\text{Mn}_6\text{O}_{16}$) group. Minerals having only Mn^{4+} include the several polymorphs of pyrolusite (MnO_2). Minerals containing only Mn^{2+} , such as rhodochrosite and rhodonite, are frequently very colorful and, thus, readily identified. Otherwise, manganese oxides are brownish-black (hence, braunite)

Table 1. Manganese ore production, gross weight, Mt

Country	1995*	1999†	2003‡	Deposits
Australia	2.2	1.9	2.6	Groote Eylandt, Woodie Woodie
Brazil	2.4	1.6	2.6	Azul, Morro da Mina, Urucum
China	6.9	3.2	4.0	na†
Gabon	1.9	1.9	2.0	Bangombe
Ghana	0.2	0.6	1.2	N'suta
India	1.8	1.5	1.7	na
Kazakhstan	0.4	1.0	2.4	na
Mexico	0.5	0.5	0.3	Molango
South Africa	3.2	3.1	3.5	Mamatwan, N'chwaning, Wessels
Ukraine	3.2	2.0	2.6	Nikopol', Ordzhonikidze
Other	0.6	0.5	0.5	na
Total§	23.3	17.8	23.2	

* Jones 2000.

† Corathers 2005a.

‡ na = not available (detailed information about all the deposits is not publicly available).

§ Data have been rounded and may not add to totals shown.

Table 2. Known manganese ore resources, Mt contained manganese

Country	Resources
Australia	32
Brazil	23
Burkina Faso	8
China	40
Gabon	20
India	93
Mexico	4
South Africa	32
Ukraine	140
Other countries*	Small

Adapted from Corathers 2005b.

* Including Ghana.

to black; their luster is dependent on grain size and crystallinity. Manganese ores composed primarily of rhodochrosite tend to be a "dirty gray" color and are distinguished from impure limestones by their high density (heft) and tendency to darken (oxidize) rapidly on exposed surfaces.

Some polymorphs of manganese dioxide are electrochemically active, particularly the gamma form (nsutite), and are important constituents of Leclanché dry cells.

Deposits

Geochemically, manganese resembles iron in that the lower valence forms are highly soluble (mobile) and highly reactive, whereas the higher valence forms are highly insoluble (immobile) and both physically and chemically resistant. Thus, in solution, manganese is transportable in reducing environments and is precipitated and thereby fixed in oxidizing environments. Rocks with significant manganese content tend to develop a manganese crust (called *cuirasse*), which is highly resistant to erosion. They generally form bold outcrops and prominent topographic features. Iron and manga-

nese react similarly in oxidizing environments, but iron oxidizes to its insoluble (ferric) state at much lower oxygen concentrations than manganese does to its insoluble (manganic) state. This difference in respective insolubilities is the principal cause for the separation of the two elements in natural systems (Krauskopf 1957).

Most economic manganese deposits originated as sedimentary rocks with high primary manganese content. With two notable exceptions, these deposits can be grouped into three major types (Machamer 1987). The first group (Type I) is lenticular bodies (actually clusters of lenticular bodies) of bedded rhodochrosite with lesser braunite within belts of early Precambrian (Archean) basic volcanic rocks ("greenstone belts"). Type I deposits are clustered around the South Atlantic Ocean and include Morro da Mina and Serra do Navio in Brazil, Matthews Ridge in Guyana, Grande Lahou in Ivory Coast, N'suta in Ghana, Tambao in Burkina Faso, and Kisenge in Congo. These deposits were or are capped by high-grade supergene manganese oxides; the underlying primary manganese carbonate protore associated with these deposits can also be mined. Some younger manganese deposits can also be of this type, including the San Francisco deposit near Autlan, Estado de Jalisco, Mexico; the occurrences in the Franciscan Complex of California; and those of the Olympic Peninsula of Washington.

With the exception of the undeveloped Tambao deposit and the idle Kisenge deposit, the high-grade supergene ores developed on primary Type I deposits are substantially depleted, as may be the primary carbonate ore at Serra do Navio. Primary carbonate ores are being mined at N'suta, Ghana, and Morro da Mina, Brazil.

The second group (Type II) is composed of distinct and laterally extensive beds of braunite, braunite and manganese-bearing carbonate minerals, or cryptomelane with in some particular and unique, highly oxidized, iron- and silica-rich sedimentary rocks of Proterozoic age. The two prominent examples of Type II deposits are the Hotsel Formation in the Kalahari region of South Africa and the Band'Alta Formation near Corumba, Mato Grosso do Sul, Brazil, and Puerto Suarez, Bolivia. These beds, although not everywhere minable, underlie hundreds of square kilometers and probably constitute the most important manganese resources in the world.

The third group (Type III) is composed of laterally extensive beds of shaly manganese oxides, manganiferous shale, shaly manganiferous carbonate, and/or braunite-rich shale, which were deposited in shelf areas of large epicontinental basins. Prominent examples of Type III deposits are those of the Francevillien Series of Gabon (Bangombe and adjoining plateaus of the Moanda Area); the deposits surrounding the Black Sea (Nikopol', Ukraine; Tchiatura, Georgia; and others); and the Azul deposit associated with the Rio Fresco Series in the Amazon Basin of Brazil.

Among the sedimentary manganese deposits that do not fit an established pattern are the young pisolitic deposits of Groote Eylandt in the Gulf of Carpentaria, Australia, and the unique manganese-rich carbonate bed at the base of the Jurassic Taman Formation in the Molango Area, Estado de Hidalgo, Mexico. Deposits that may be similar to the Molango deposit occur along the eastern slope of the northern Ural Mountains in Siberia (Smirnov 1977). Russia mined the oxidized (enriched) portions of these deposits during World War II. The economic potential of the remaining primary carbonate protore is currently being studied.

The famous deposits of the Mansar Schist Belt in the state of Madhya Pradesh, India (Balaghat, Kandri, Mansar, Tirodi, and others) occur in high-grade metamorphic terrane. The deposits are composed mainly of manganese silicate minerals that were capped by high-grade manganese oxides, which by now have been substantially depleted. These may have been Type III deposits that had undergone a phase of supergene weathering and enrichment before

burial and then were subjected to one or more phases of intense metamorphism.

High-value battery-active ores have been produced from the enriched portions of the following: the Bangombe (Moanda) deposit in Gabon; the N'suta deposit in Ghana; the Morro da Mina and Azul deposits in Brazil; and the Morro da Mina deposits in Mexico. The Imini deposit in Morocco is a bed or beds of friable manganese oxides in a dolomite formation from which ore is obtained for chemicals and ceramics (coloring). In the United States and elsewhere, residual deposits of nodular manganese oxides (derived by the weathering of mangiferous dolomites) were mined for ceramics, where color rather than chemistry was the important factor.

The importance of oxidation and weathering effects on manganese deposits, and the importance of recognizing those effects, cannot be overstated. Weathering effects can extend for a vertical range of at least 100 m deep and, in nearly horizontal beds, can extend inward from the outcrop for several tens of meters. The hard manganese oxide crust, which often develops, makes deposits relatively easy to find and protects them from erosion. Weathering and oxidation can change the mineral composition of the ores, concentrate the manganese, and remove impurities, thus rendering the ore more valuable for certain chemical and metallurgical uses. If weathering results in the development of cryptomelane with a corresponding increase in potash content, or it increases the phosphorus content, the metallurgical value of the ore can be significantly diminished.

Large volumes of manganese nodules occur on the floor of portions of the Pacific Ocean and other oceanic basins. These nodules apparently grow by reduction/solution below the sediment-water interface and oxidation/precipitation above it. In the oxidation/precipitation process, the nodules sequester significant amounts of nickel, copper, and other metals, making the nodules a significant resource of these metals. Recovery and processing of manganese nodules was tested by several consortia in the 1970s, but development was discontinued for technical, economic, and legal reasons.

TECHNOLOGY

Exploration

Prospecting and exploration for terrestrial deposits have relied mostly on interpretation of regional geology, followed by physical examination of selected areas. Deposits that crop out are located readily, but there is no reliable guide to "hidden" deposits. Specialized equipment and vessels are used in exploring for and testing possible development of marine deposits.

Mining and Beneficiation

Metallurgical-grade manganese ore is produced mostly by mechanized operations, but small-scale hand mining and sorting is still practiced in India. Virtually all the larger operations around the world are open-pit mines using standard equipment and methods for overburden removal and ore extraction. Bucket-wheel excavators have been used to remove overburden at the Mamatwan mine in South Africa and in the Nikopol' Basin in Ukraine. Haul trucks and/or conveyors transport this material for further processing. South Africa and Ukraine currently account for the largest proportion of ore extracted from underground mines. Most underground mining commonly is done by room-and-pillar methods. Longwall techniques have been used in Bulgaria, and possibly Ukraine, but overburden pressure made these operations impractical.

Battery- or chemical-grade ores have been produced by selective mining of favorable portions of large deposits mined for metallurgical-grade ore or from relatively small mines operated solely for these specialty ores.

Table 3. Manganese alloy specifications

Alloy	% Mn	% C _(max.)	% Si _(max.)	% P _(max.)	% S _(max.)
Ferromanganese					
Standard					
Grade A	78–82	7.5	1.2	0.35	0.05
Grade B	76–78	7.5	1.2	0.35	0.05
Grade C	74–76	7.5	1.2	0.35	0.05
Medium-carbon					
Grade A	80–85	1.5	1.5	0.30	0.02
Grade B	80–85	1.5	1.0	0.30	0.02
Grade C	80–85	1.5	0.70	0.30	0.02
Grade D	80–85	1.5	0.35	0.30	0.02
Nitrided medium-carbon	75–80	1.5	1.5	0.30	0.02
Low-carbon					
Grade A	85–90	0.75	2.0	0.20	0.02
Grade B	80–85	0.75	5.0–7.0	0.30	0.02
Silicomanganese					
Grade A	65–68	1.5	18.5–21.0	0.20	0.04
Grade B	65–68	2.0	16.0–18.5	0.20	0.04
Grade C	65–68	3.0	12.5–16.0	0.20	0.04
Ferromanganese-silicon	65–68	0.8	28.5–32.0	0.05	0.05

Adapted from ASTM 1998.

Virtually all manganese ores are subjected to some form of beneficiation to achieve greater manganese content and/or to remove undesirable impurities. Beneficiation technology as applied to manganese ores is similar to that for iron ores. Most ores are crushed and screened, with the lump product (+6 mm) generally being smelted and the fine product (–6 mm) used as feed for chemical and/or electrolytic processing. Sink-float (heavy liquid media), jigging, tabling, flotation, and high-intensity magnetic separation are among the methods used to upgrade fine manganese ore. In the late 1990s, Humphrey spirals were used to recover manganese fines from tailings at the N'suta mine in Ghana (Brunner 1999). Pneumatic concentration has been used in Morocco and possibly elsewhere. Some manganese ores, particularly in South Africa and, more recently, Gabon, are sintered to raise the manganese content and recover high-grade fines for metallurgical use.

Physical separation technologies, such as flotation and roasting, and chemical separation processes, such as leaching, have been developed for beneficiating lower grade and more refractory resources, such as those of the United States and the lower grade ores of Ukraine. Generally, these processes are relatively costly and give poor recoveries. Bioleaching also has been proposed for recovering manganese from low-grade ores (Rusin and Ehrlich 1995).

Smelting

Manganese ores for use in the steel industry are smelted to produce three basic alloys: ferromanganese, silicomanganese, and ferromanganese-silicon. Specifications for these alloys are given in Table 3. Ferromanganese can be produced in blast furnaces or in electric-arc furnaces, although blast furnace production of ferromanganese is relatively energy inefficient and has been phased out in many countries. Because manganese losses to slag are relatively high, slag from ferromanganese production is often used as feedstock for silicomanganese production. Manganese alloys, particularly those employed in the production of stainless and other specialty steels, are refined

by blowing the liquid alloy with oxygen in a controlled atmosphere to produce medium-carbon or low-carbon alloys.

Chemical and Electrolytic Processes

Manganese chemicals, synthetic manganese dioxide, and manganese metal are produced by a number of chemical processes. Feedstock for these processes is either manganese carbonate, manganese oxide ore in which the manganese oxide has been reduced to the manganous (divalent) state, or manganiferous slag from the smelting process. The feedstock is leached with sulfuric acid, and the resultant manganese sulfate leachate is either electrolyzed or treated chemically to produce manganese metal (EMM and CMM, respectively), manganese dioxide (EMD and CMD, respectively), manganese sulfate, potassium permanganate, and other manganese chemicals (Dean 1952; Deane 1985; Preisler 1991; Grotheer and Clapper 1993).

PRICES

Manganese ore prices are customarily negotiated between buyers and sellers rather than determined through a central exchange. Price is dependent on a number of factors such as chemical analysis (particularly manganese content) and physical character of the ore. The larger year-to-year users of manganese ore have tended to make their purchases by means of annual contract, rather than by spot market purchases. With the decline in smelting of manganese ferroalloys in the United States, the Japanese have been the key factor in setting annual prices since the early 1990s. After the price to Japanese consumers is set (this is known as the international benchmark price), annual settlements usually follow elsewhere. When required, purchases of manganese ore on the spot market are typically higher than those negotiated by contract.

Because manganese ore prices are normally set via annual contracts between purchasers and sellers, very little information about manganese ore prices is publicly available. *Ryan's Notes* or other industry trade publications usually publish the annual negotiated benchmark prices. The U.S. Geological Survey (USGS) estimates annual U.S. manganese ore prices based on fluctuations in the benchmark prices. *Ryan's Notes* started publishing spot market prices for manganese ore traded in North America, on a dollar-per-metric-ton basis, in January 2005.

SPECIFICATIONS

By far, the great bulk of manganese ore used in the metallurgical industry is to make ferroalloys in the iron and steel industry. Lump ores (+6 mm) are preferred for this use. Metallurgical ores are generally expected to meet the following criteria:

- Contain 45% to 48% manganese
- Have a manganese to iron ratio of at least 8:1
- Contain less than 0.15% phosphorus
- Have trace metals content of no more than a few tens of parts per million
- Have low alumina content

These ores are sold in bulk on the basis of an agreed price per dry metric ton unit (one unit is 1% manganese per dry metric ton). Price can be f.o.b. (free on board vessel at port of loading) or CIF (cost, insurance, and freight unloaded at receiving port), depending on whether the buyer or the seller arranges and pays for shipping and delivery. The purchase agreement will specify the maximum allowable content of fines at the point where the buyer takes possession of the ore. A nominal price per dry metric ton unit was published in industry journals, but such publication appears to have been suspended after 2002.

Manganese ore for use as feedstock for chemical or electrolytic processing will have specifications similar to those for metallurgical ore, except that alumina and phosphorus content may not be as critical as in the metallurgical industry. Because buyers can have different specifications for ore chemistry and mineralogy, some plants are designed to process carbonate ores; others can process oxide ores. As discussed in the section on Prices, the price of ore is usually negotiated on individual bases. Because ore is usually ground prior to digestion, fine ore is preferred to coarse ore.

For use in batteries, feed supplements, or other specialty uses, natural manganese dioxide ore has rigid specifications, the most important of which are minimum content of manganese dioxide and maximum content of trace metals and other impurities. These ores are dried, ground, and bagged at the mine. Ores for ceramics must be uniform and consistent within and between shipments, respectively. Prices for these ores are usually negotiated on individual bases, as discussed in the section on Prices.

HEALTH, REGULATORY, AND ENVIRONMENTAL CONSIDERATIONS

Because there are no known deposits in the United States or Canada that are potentially economic sources of manganese, there is nothing in the regulatory or environmental codes of either country that affect manganese mining operations specifically. Manganese mines in Mexico are not known to be subject to any unusual or site-specific regulation. In Ukraine, manganese mines operate with very high waste-to-ore ratios, and mine land reclamation is important. Australia and Brazil are among the countries where particular attention also is paid to restoration of lands mined for manganese.

Manganese is an essential nutrient, and recommended "adequate intake levels" and "tolerable upper intake levels" have been established (Institute of Medicine 2001). Small quantities of manganese may be added to livestock feed and to fertilizers; however, ingestion of too much manganese or inhalation of excessive manganese dust may have adverse health consequences (Agency for Toxic Substances and Disease Registry 2000).

Some manganese ores can contain relatively high base metal concentrations; one overseas smelter has been investigated as a potential source of mercury emissions.

The widespread and growing use of portable electronic and communications devices that operate on dry cells or rechargeable batteries may lead to restrictions on the disposal of batteries containing manganese. Some imported EMM has been reported to contain relatively high levels of selenium (*Ryan's Notes* 2003).

A complex organic manganese compound (methylcyclopentadienyl manganese tricarbonyl or MMT) has been used in the United States and Canada as an antiknock additive in gasolines, but regulatory authorities differ as to its environmental impact (EPA 1994; Environment Canada 2003).

Strategic Concerns

In the early 20th century, the U.S. government and major steel-producing companies in the United States took steps to ensure that adequate supplies of manganese ore would be available in case of emergencies because of

- The critical role of manganese in steel production
- The past importance of natural battery-active manganese dioxide as a component of dry cells
- No known manganese deposits of commercial importance in the United States and Canada

Steel and ferroalloy companies explored for and acquired manganese deposits and maintained significant equity interests in the

companies established to develop those deposits. Following World War II, the U.S. government, through its Defense Logistics Agency, acquired large stockpiles of manganese ore of various grades, manganese alloys, and other downstream manganese products.

With the end of the Cold War and the economic difficulties in the steel industry in the last two decades, the need to maintain stockpiles and strategic reserves of manganese ore is diminished. To maintain domestic ferromanganese production capability and to reduce its inventories, the Defense Logistics Agency has contracted with one company to convert manganese ore in the stockpile into high-carbon ferromanganese. Other manganese materials deemed in excess of stockpile requirements have been sold gradually. Inventories of manganese materials in Defense Logistics Agency stockpiles at the end of 2002 are given in Table 4. Steel and ferroalloy companies have curtailed exploration for new manganese deposits, and several depleted mines have been closed. The remaining equity interests have been sold so no significant U.S. interests are involved in the international manganese ore business.

OUTLOOK

World steel production has been growing at an average rate of 1% per year for many years, and this rate certainly is expected to increase with the explosive growth in steel production in China and India. Although manganese usage in the steel industry has been increasingly efficient, the net demand for manganese in the steel industry has grown because of the increase in steel production itself (Machamer 2002). Also, the demand for manganese in batteries of all sorts will increase, as will the demand for manganese in other chemicals. All sectors of the manganese industry, therefore, can look forward to continued growth. Manganese ore production capacity, however, has decreased because exploration and development of new mines have not kept pace with the depletion of existing mines. The overall outlook for manganese ore demand is strong, with upward pressure on prices in all sectors of the industry already taking place (Trelut 2004).

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Table 4. U.S. government inventories of manganese materials as of year-end 2002^a

Material	Uncommitted Inventory	Sold Pending Shipment	Total
	gross weight, t		
Natural battery ore	75,600	24,700	100,300
Synthetic manganese dioxide	2,730	0	2,730
Chemical ore	84,000	28,300	112,000
Metallurgical ore	689,000	229,000	919,000
High-carbon ferromanganese	731,000	29,300	760,000
Electrolytic metal	1,470	621	2,100

Source: Corathers 2004.

^a Estimated data have been rounded and may not add to totals shown.

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Mica

John W. Schlanz and James T. Tanner Jr.

INTRODUCTION

Mica is a mineral that has a rich history of industrial applications. Dating back to as early as 2000 BC, the ancient Hindus believed mica was a mystical medicinal cure. Over the centuries, mica uses have evolved from decorative ornaments, mirrors, stove windows, and shock-resistant materials in early military applications to its more high-tech applications today in construction materials, paper, plastics, paints, electronics, and others.

The term *mica* is derived from the Latin *micare*, meaning to shine or glitter. Today, it is a generic term that applies to a group of aluminosilicate minerals that possess a sheet-like structure. The most common commercial micas are

- Muscovite, a potassium-based mica, usually colorless to pale green
- Phlogopite, a magnesium-based mica that is yellow to dark brown
- Vermiculite, a hydrated biotite found as bronze-yellow flakes
- Lepidolite, a lithium-based mica with a purplish hue

Other micas with less commercial value include zinnwaldite, a lithium/iron-based mica that is gray to brown; biotite, a magnesium/iron-based black mica; and roscoelite, a vanadium/potassium/magnesium mica that can be green or brown.

Muscovite mica enjoys the most diverse market applications, followed by phlogopite and vermiculite. Muscovite and phlogopite possess unique characteristics and are highly valued because of their physical, chemical, electrical, thermal, and mechanical properties. These properties include high dielectric strength, low coefficients of expansion, cold and heat resistance, and high tensile strength, making these minerals excellent raw materials for electrical insulators, reinforcing materials, and high-temperature applications.

Color plays a key role in identifying markets for these two micas: muscovite is lighter and used in more color-sensitive applications. Phlogopite, however, will typically give superior aspect ratios after grinding, adding to its value as a reinforcement additive.

Commercially, mica is marketed in several forms:

- Sheet mica refers to books of mica mined from pegmatite or loosely consolidated clay deposits. The books can be readily split into thin sheets with specific thicknesses ranging from 0.003 to 0.10 mm. The quality of sheet mica is graded according to 10 quality classifications. Flawed books (excess

Table 1. United States production of scrap, flake, and ground mica, 1999–2003, t

Production	1999	2000	2001	2002	2003
Mine	95,000	101,000	98,000	81,000	98,000
Ground products	111,000	112,000	89,000	98,000	107,000
Imports	21,000	29,000	32,000	38,000	14,000
Exports	11,000	10,000	9,000	10,000	7,000

inclusions, cracks, etc.) are termed scrap mica and may find use in ground products.

- Built-up mica was developed in the late 1800s because of the scarcity and cost of sheet mica, and served as a ready substitute for electrical parts. Formed by layering pieces of mica splittings and binding them with inorganic or organic binders, the constituted sheets are pressed under high temperature.
- Reconstituted mica is mica paper matted from thin delaminated flakes of scrap mica. The mat is usually impregnated with an organic binder and dried at 110°C. Feedstock for reconstituted mica is typically trimmings from sheet mica operations.
- Flake mica is finer mica recovered from scrap or trimmings produced during the processing of sheet mica, or can be beneficiated mica recovered from feldspar, clay, and sand operations.
- Ground mica is produced by wet or dry grinding and sizing of scrap or flake mica. It is by far the largest use of mica, both quantitatively and by application.
- Synthetic mica is produced by crystal growth in slowly cooled melts of various chemical oxides. Cooling periods at controlled viscosities dictate the size of the crystals; extended cooling times result in larger crystals.

PRODUCTION AND TRADE

Scrap and Flake Mica

The data given in this section are from the U.S. Geological Survey's (USGS) *Mineral Commodity Summaries 2004* (Hedrick 2004).

The USGS estimates domestic production of scrap and flake mica at 98,000 t in 2003, as shown in Table 1. North Carolina accounted for approximately 40% of this production from four main

mica producers, three of whom recover mica as a by-product from feldspar operations mining pegmatites known as alaskite. This mica is sold to dry-grind producers for the wall board and joint compound markets. The fourth company recovers mica as a primary product from more weathered deposits and produces feldspar, quartz, and kaolin. The company has in-house capabilities for producing both wet- and dry-ground products.

Remaining U.S. production came from five operations in Arizona, Georgia, New Mexico, South Carolina, and South Dakota, primarily from kaolin, feldspar, and sand operations. The majority of all U.S. production served as feedstock for wet- and dry-ground products, with an estimated value of \$20.2 million on flake production in 2003. Value-added ground product sales contributed another \$29.6 million in the same year.

U.S. production of flake mica for 2003 represents a significant increase of more than 20% from 2002, whereas ground products increased at a lesser rate of 9%. However, both figures indicate a near-static industry using the past 5-year average, because 2002 was a down year due to economic conditions. Imports of flake mica were small at an estimated 7% of total domestic consumption, with Canada, India, China, and Argentina listed as leading exporters of flake and scrap mica into the United States.

World production of flake and scrap mica for 2003 is estimated at 300,000 t, with Russia the leader at one third of production (Table 2). The United States fell slightly behind at 98,000 t. World resources of scrap and flake mica are produced from granite, pegmatites, schist, and clay deposits. Reserves are considered more than adequate to meet anticipated world demand for the foreseeable future.

Sheet mica presents an entirely different domestic picture. U.S. production has been virtually nonexistent for many years, with U.S. consumers dependent on imports or shipments from government stockpile excesses, as indicated by the USGS figures summarized in Table 3. A small amount of sheet mica was produced from a pegmatite in Virginia, but is insignificant to worldwide production. U.S. production is prohibitive because of high costs associated with mining and processing, which is labor intensive.

Although demand for sheet mica decreased in 2003 and has dropped dramatically in the last 5 years, high-quality material remains in short supply. In 2003, an estimated 130 t of unworked mica, split block, and mica splittings valued at \$348,000 was consumed by 5 companies in the United States. Most of this tonnage was fabricated into electrical components. An estimated 1,010 t of imported worked mica valued at \$11.1 million was also consumed.

Imports remained a principal source of sheet mica for domestic supply. Stocks of mica remaining in the National Defense Stockpile (NDS) have declined, and future supplies are expected to be increasingly served by imports, primarily from India, which will certainly lead to increased pricing.

India is the leading exporter of sheet mica into the United States, followed by Belgium, China, and Germany. Table 4 contains estimates of major world production and known reserves. No formal evaluation of world resources of sheet mica has been conducted because of the sporadic occurrence of this material. Large deposits are known to exist in Brazil, India, and Madagascar.

Russia, the United States, and Korea were the world leaders in the production of all types of mica through 2002. Table 5 lists world mica production by country from 1998 through 2002.

GEOLOGY AND MINEROLOGY

All micaceous minerals have similar structures and properties and belong to the phyllosilicate class, referring to leaf-like structures characterized by layers of silicon–oxygen tetrahedrons. The mica

Table 2. World production and reserves of flake and scrap mica in 2002 and 2003*

Country	Mine Production, t	
	2002	2003
Brazil	4,000	4,000
Canada	17,000	17,000
India	2,000	2,000
Korea, Republic of	40,000	40,000
Russia	100,000	100,000
United States	81,000	98,000
Others	35,000	35,000
Total	280,000	300,000

* Reserves and reserve base for all listed are considered large.

Table 3. U.S. sources of sheet mica, t

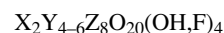
Type	1999	2000	2001	2002	2003
U.S. production	0	0	0	0	0
Imports, plates, sheets, strips, worked mica, split blocks, splittings	4,550	5,430	4,290	1,580	1,140
Exports, plates, sheets, strips, worked mica, crude and rifted into sheet or splittings	1,290	1,150	1,160	723	1,030
U.S. government stockpile excess	708	1,230	1,860	894	1,280
Apparent consumption	3,980	5,500	4,990	1,750	1,390

Table 4. World production and reserves of sheet mica

Country	Mine Production, t		Reserves	Reserve Base
	2002	2003		
India	3,500	3,500	Very large	Very large
Russia	1,500	1,500	Moderate	Moderate
United States	0	0	Very small	Small
Others	200	200	Moderate	Moderate
Total	5,200	5,200	Large	Large

layers are bound by oppositely charged surfaces, with positively charged alkalis linking the negatively charged silicon–oxygen layers. They are easily identified because of their crystal shape, elasticity, and near-perfect basal cleavage; and, because of their molecular structure, they can be readily split into thin films.

Dana (1932), Sinkankas (1964), Bailey (1984), and others classify the various micas into four groups: (1) mica, (2) clintonite (brittle micas), (3) chlorite, and (4) vermiculites. These micas have the following general chemical formula:



where

X = mainly potassium (K), sodium (Na), or calcium (Ca)

Y = mainly aluminum (Al), magnesium (Mg), iron (Fe), or lithium (Li)

Z = mainly silicon (Si) or Al

Given the nature of this writing and its industrial importance, focus is placed on the mica group. Tables 6 and 7 list various properties of selected micas.

Table 5. World mica production by country, t

Country	1998	1999	2000	2001	2002
Argentina (all grades)	3,480	3,097	3,100	2,772	2,357
Brazil	4,000	3,000	5,000	5,000	5,000
Canada	17,500	17,500	17,500	17,500	17,500
France	10,000	10,000	10,000	10,000	10,000
India					
Crude	1,489	1,500	1,500	1,300	1,500
Scrap/waste	966	1,000	950	1,100	2,000
Total	2,455	2,500	2,450	2,400	3,500
Iran	1,084	1,425	2,000	2,000	2,000
Korea, Republic of (all grades)	38,459	24,733	65,249	109,339	100,000
Madagascar (phlogopite)	1,232	54	66	90	45
Malaysia	3,642	3,675	3,835	4,107	4,200
Mexico (all grades)	890	971	1,658	648	700
Morocco	600	210	1,897	na*	na
Norway (flake)	2,500	2,500	2,500	2,500	2,600
Russia	100,000	100,000	100,000	100,000	100,000
Serbia and Montenegro	150	50	100	100	100
South Africa (ground and scrap)	1,558	1,010	676	950	383
Spain	2,500	2,500	2,500	2,500	2,500
Sri Lanka (scrap)	2,800	1,425	1,491	1,161	1,100
Taiwan	7,750	6,966	6,862	9,733	6,595
United States (scrap and flake)	87,000	95,400	101,000	97,800	81,100
Zimbabwe	1,309	1,300	na	na	na
World total	289,000	278,000	328,000	369,000	340,000

* na = not available.

Table 6. Mineralogical properties of selected micas

Property	Muscovite	Biotite	Lepidolite	Phlogopite
Hardness	2–2.25	2.5–3	2.5–4	2–3
Specific gravity	2.7–3	2.7–3.1	2.8–3.3	2.8–2.9
Luster	Vitreous to pearly	Splendent to submetallic	Pearly	Pearly
Optical sign	Negative	Negative	Negative	Negative
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Crystal symmetry	Rhombic/hexagonal	Pseudo-rhombohedral	Hexagonal	Hexagonal
Color	Gray, brown, pale green, violet, yellow, ruby	Green, black, yellow	Rose-red, violet-gray, lilac, yellow, white	Yellow white gray to green, pearly
Streak	Colorless	Colorless	Colorless	Colorless
Others	Transparent to translucent	Transparent to opaque	Twinning common, translucent	

Adapted from Dana 1932; Chesterman 1989.

Mica Group

Elemental substitution takes place within the various micas quite readily. The mica group includes the more common and most widely used mica species such as muscovite, paragonite, and phlogopite. Other micas in this group are biotite and lepidolite. Muscovite and paragonite (both are commonly referred to as muscovite) enjoy the most industrial uses and subsequent exploitation. Muscovite is the most common of all the micas, having a chemical formula $KAl_2(OH)_2(AlSi_3O_{10})$ with a theoretical composition of 11.8% K_2O , 45.2% SiO_2 , 38.5% Al_2O_3 , and 4.5% H_2O . Paragonite is similar in composition, with the potassium replaced by sodium.

Muscovite is commonly found in granites and pegmatites as an original constituent of crystalline rocks high in potash and alumina. Although rare in volcanic rocks, it is commonly associated with mica schists along with biotite. Other host rocks include gneiss, and it is also found in contact zones surrounding igneous

intrusions. The largest and best formed crystals are found in pegmatite dikes associated with granite. Most commercial deposits are derived from pegmatites, both weathered and unweathered, containing 2% to 10% by weight muscovite.

Phlogopite, its name derived from the Greek *phlogopos*, meaning *fire-like*, ranks second in commercial value and is sought for its thermal and reinforcing properties. It has the inherent ability to delaminate easily, resulting in high aspect ratios and low bulk densities. The chemical formula for phlogopite is $KMg_3(OH)_2(AlSi_3O_{10})$, showing substitution of magnesium for aluminum, and having an estimated theoretical composition of 11% K_2O , 43% SiO_2 , 16% Al_2O_3 , and 29% MgO . Phlogopite is associated with ultrabasic rock and metamorphosed limestone and dolomite, and more rarely as a constituent of igneous rocks rich in magnesium. It is a product of both regional and contact metamorphism and is often associated with pyroxene, amphibole, and serpentine.

Table 7. Chemistry and selected properties of three micas

Chemical Constituents	Muscovite	Biotite	Phlogopite
SiO ₂ (silicon dioxide)	46.5	37.0	40.0
Al ₂ O ₃ (aluminum oxide)	34.0	18.0	17.0
K ₂ O (potassium oxide)	10.0	9.0	10.0
Na ₂ O (sodium oxide)	0.8	1.0	0.5
MgO (magnesium oxide)	0.5	8.0	26.0
CaO (calcium oxide)	0.3	na*	na
Fe ₂ O ₃ (iron oxide)	2.5	2.0	0.2
FeO (reduced iron oxide)	1.0	21.0	2.8
Minor elements	na	1.0	0.5
Loss on ignition	4.5	3.0	3.0
Total	100.0	100.0	100.0
Properties	Muscovite	Biotite	Phlogopite
Specific gravity	2.77–2.88	2.70–3.30	2.76–2.90
Mohs hardness	2.8–3.2	2.5–4.0	2.5–3.0
Shore hardness	80–150	na	70–100
Specific heat, at 25°C	0.207	na	0.207
Volume resistivity, ohm/cm ²	2×10^{13} – 1×10^{17}	na	na
Modulus of elasticity, Pa	172×10^9	na	172×10^9
Compressive strength, Pa	221×10^6	na	221×10^6
Volume resistivity, ohm/cm ² at 25°C	5×10^{13}	na	na
Optical axial angle, 2 V	38°–47°	0°–25°	0°–10°
Temperature of decomposition, °C	400–500	na	850–1,000
Dielectric constant	6.5–9.0	na	5.0–6.0
Linear coefficient of expansion $\times 10^{-6}$ cm/°C; range 20° to 600°C	58–79	na	79–97
Coefficient of expansion/°C perpendicular to cleavage; range 20° to 100°C (10^{-6})	15–25	na	$1-1 \times 10^{-3}$
Coefficient of expansion/°C parallel to cleavage; range 0° to 200°C (10^{-6})	8–9	na	13–4.5
Tensile strength (Pa $\times 10^6$)	225–297	na	255–297
Modulus of elasticity (Pa $\times 10^9$)	172	na	172
Dielectric strength (0.025 to 0.030 mm thick) Volts/cm $\times 10^6$	2.4–11.2	na	1.7–0.8
Resistivity, ohm/cm	10^{12} – 10^{15}	na	10^{10} – 10^{13}
Thermal conductivity perpendicular to cleavage at 100°C (K cal/m ² /hr/°C)	0.57	na	0.57

Source: Tanner 1994.

* na = not available.

Biotite constitutes a series with phlogopite, having a similar chemical formula with iron substitution for magnesium. The high iron content, which imparts dark colors, will typically eliminate biotite from any industrial uses. However, because biotite is abundant in granitic rocks, pegmatites, and schists that are also associated with the more desirable muscovites, the mineral is often a factor in exploitation efforts.

Lepidolite is a lithium-based mica with a chemical formula showing substitution of lithium for aluminum— $\text{KLi}_2\text{Al}(\text{OH})_2(\text{AlSi}_3\text{O}_{10})$ —and is not pursued industrially except as a source of lithium. It is confined to granitic pegmatites associated with other lithium-bearing minerals such as tourmaline, beryl, and spodumene. Other lithium-based micas include zinnwaldite, cryophyllite, and manandonite.

Clintonite Group

The clintonite micas are also referred to as the brittle micas, having cleavage similar to the muscovites, but they are distinct in the brittleness of their laminae and chemically by their character. In many respects, they form a transition of the true micas to the chlorites. Examples from the clintonite group include margarite, a calcium-based mica; seyberite, with calcium and magnesium substitution; and chloritoid, which has an iron/calcium base.

Chlorite Group

The chlorite group gets its name from the Greek *chloros* (green) in reference to the common green color associated with these minerals, mainly because of their association with ferrous iron. They are closely related to the true micas in the sense that they exhibit mica-like cleavage, but the laminae are tough and inelastic. Because of the extensive elemental substitution within the series, many names have been applied to a variety of identified species, but for practical purposes, only two are commonly employed. The first, penninite, has thick prismatic crystals and is normally dark green, whereas the second, clinocllore, bears a greater resemblance to true micas, with thin, tubular crystals.

Vermiculites

The vermiculites include numerous micaceous minerals, and in part are closely related to the chlorites, but they vary widely in composition. They are mainly alteration products of the muscovite, biotite, and phlogopite that are highly hydrated. They maintain the micaceous cleavage, but the laminae are generally soft, pliable, and inelastic.

The vermiculites get their commercial value from their high degree of hydration, which gives them the unique quality of exfoliation, or the ability to expand to several times their volume on

exposure to heat and the subsequent evolution of the contained water. Because of this unique quality, the vermiculites service different markets than the micas and are covered in a separate chapter of this book.

THE MICA INDUSTRY

The mica industry can be divided into two distinct but interdependent industries: those that produce sheet mica, and those that produce flake mica. Each industry, although somewhat dependent on the other, produces different end products.

Sheet Mica

The sheet mica industry produces relatively small tonnage as compared to flake—5,200 t versus 300,000 t in 2003 (Hedrick 2004)—which is driven in part by the markets but is also influenced by the high costs of mining and processing sheet mica, the scarcity of these reserves, and the depletion of high-quality material. Because of exacting specifications placed on sheet mica, mining and processing consist of hand cobbing and preparation, resulting in extremely high labor costs. This limits production to countries with cheap labor and, together with low reserves, has greatly influenced U.S. production.

Sheet mica is typically recovered from a large number of small mines that use only basic mechanical equipment, if any. Preparation relies almost exclusively on hand labor to recover the maximum area of usable crystal. Commercial qualities must include flat sheets that are relatively free of defects and flaws, with quality based on complex visual determinations, as indicated in Tables 8 and 9 (a and b). The quality is dictated by size, thickness, visual appearance, electrical and thermal properties, and the degree of preparation.

Commercially, sheet mica is marketed in several forms, depending on the application and quality:

- Block mica, also known as mica block, consists of sorted blocks of mica with an area of 6.5 to 91 cm² (1 in.² to 14 in.²) or greater. The minimum thickness is typically 7 mils; it is available in natural form or split and cut into sizes and shapes specified by the customer. Mica blocks are classified into different categories depending on the extent of staining and other flaws. The average sheet thickness can vary from 7 to 16 mils or greater. Sections having holes, cracks, and cross grains are removed by hand.
- Mica thins consist of block mica dressed to a thickness of 2 to 7 mils. Fabricated mica is made from mica thins for the electrical and other industries.
- Mica films consist of block mica dressed to a thickness of 0.8 to 4 mils and are generally made from high-quality block.
- Mica splittings are layers split from mica blocks and are specified as 10 layers being less than 12 mils thick. Splittings are typically processed by hand with sharp knives to the required thickness. The splittings are classified into three forms: loose-form splittings, book-form splittings, and wrapper splittings. Book-form mica splittings consist of individual books of mica from the same block or mica thins, with each book containing 4 to 10 sheets. Loose mica splittings consist of irregular shapes and sizes that are supplied in a loose form.
- Mica scrap is the irregular pieces of mica from run-of-mine ore that is smaller than the mica blocks with surface areas of 3.25 to 9.75 cm² (½ in.² to 1½ in.²).

Figure 1 depicts a typical process flowsheet for sheet mica. Care must be exercised in the mining process to not damage the sheets while maintaining large surface areas. Therefore, much is

Table 8. Quality of mica based on size (ASTM D351)

ASTM Grade	ASTM Size, Area of Rectangle, cm ²	Minimum Dimension of One Side, cm
A-1 special	232–310	8.89
1	155–232	7.62
2	97–155	5.08
3	65–97	5.08
4	39–65	3.81
5	19–39	2.54
5½	14–19	2.22
6	6–15	1.91

Adapted from Mica Manufacturing Co. Pvt. Ltd.

done via hand cobbing after initial blasting (if used). The hand-cobbed books of mica are trimmed and cut manually to remove rough edges and any large flaws or impurities, and sorted by size.

The smaller books report as mica scrap; the larger books are subjected to additional cutting and trimming and classified as mica block. This product may undergo additional hand cutting and trimming before being sorted by size and quality. Quality is determined visually by the workers according to the criteria listed in Table 8, and is therefore highly subjective and dependent on the experience level of the labor force. After classifying the mica block, the workers split the layers by hand and sort them according to thickness into mica thins, mica films, and mica splittings.

Mica scrap is produced from the small books sorted from the run-of-mine ore and may contain the cuttings and trimmings from the mica blocks. The mica scrap is used to manufacture mica paper, or can undergo primary crushing in hammer mills or similar type impact crushers to produce sized mica flake. The mica flake may be used for micanite products or sold to grinding facilities to produce mica powders.

Micanite/Mica Paper

Micanite, or built-up mica, is a sheet product made from thin laminates of mica splittings and, in some cases, mica flake. The pieces of splittings are bonded with various agents such as shellac, epoxies, silicone, or other binders. Variations in the quality of mica and type of bonding agent can impart specific properties to the micanite, producing thick or thin, or stiff or flexible products, which can be manufactured into sheets, ribbons, or other forms.

Mica paper, or reconstituted mica, is similar but is generally produced from flake mica or scrap, and is typically of lower quality. The actual process is similar to making paper: the scrap or flake is pulped with various binders and pressed into paper-like sheets.

Because of sheet mica's unique electrical and thermal properties, most sheet mica products are used in the electronics industries. Its mechanical properties allow cutting, punching, stamping, and machining to exacting tolerances.

Micanite and mica paper, which serve similar markets, are used primarily as electrical insulators. Mica paper is a conventional insulating material and finds many applications for general purposes, but particularly as insulation for bus bars. Both products are used to produce mica tape, an essential insulator for large rotating machines, although the higher grade micanite is desired when greater flexibility is required, such as for end windings of turbine generators and high-voltage cable. Both products may have cloth, glass, plastic, or other backings applied to enhance flexibility.

Other major micanite products are essentially bonding materials, including flexible sheet, heat-resistant sheet, molding mica, and

Table 9a. Quality classification of mica, visual properties (0.018 cm minimum thickness)

ASTM Classification	Crystalline Discoloration	Air Inclusions				Appearance						Waviness				
		Very Slight*	Slight†	Medium	Heavy	Cloudy Stains	Light Black‡ and Red Stains (Mineral)	Black Stains (Mineral)§	Red Stains (Mineral)	Black and Red* Stains (Mineral)††	Green Stains (Vegetation Type)	Clay Stains	Nearly Flat	Slight	Medium	Heavy
V-1, clear	X	X	X	X	X	X	X	X	X	X	X	X	#	X	X	X
V-2, clear, slightly stained	#††	#	X	X	X	X	X	X	X	X	X	X	#	X	X	X
V-3, fair stained	#††	#	#	X	X	X	X	X	X	X	X	X	#	X	X	X
V-4, good stained	#††	#	#	#§§	X	X	X	X	X	X	X	X	#	#	#	X
V-5, stained A quality	#	#	#	#†	X	X	X	X	X	X	#††	X	#	#	#	X
V-6, stained B quality	#	#	#	#	X	#	X††	X	X	X	#***	#	#	#	#	#
V-7, heavily stained	#	#	#	#	#	#†	#††	X	X	X***	#	#††	#	#	#	#
V-7A, densely stained	#	#	#	#	#§	#§	#§	X***	#***	X	#	#***	#	#	#	X
V-8, lack dotted b	#	#	#	#	#	#	#	X	X	X	#	X	#	#	#	X
V-9, black spotted	#	#	#	#	#	#	#	#††	X	X	#	X	#	#	#	X
V-10, black stained	#	#	#	#	#	#	#	#***	#††	X	#	#††	#	#	#	X
V-10A, densely black and red stained	#	#	#	#	#	#	#	#§	#††	#	#	#††	#	#	#	#

Table 9b. Quality classification of mica, visual properties (0.018 cm minimum thickness)

ASTM Classification	Hard	Soft	Stones/Holes†††	Buckles	Reeves†††	Ridges	Tears	Cracks	Hairline Cracks	Wedge	Tangle Sheet	Herringbone§§§	Sand Blast
V-1, clear	#	X	X	X	X	X	X	X	X	X	X	X	X
V-2, clear, lightly stained s	#	X	X	X	X	X	X	X	X	X	X	X	X
V-3, air stained f s	#	X	X	X	X	X	X	X	X	X	X	X	X
V-4, good stained g s	#	X	X	X	X	X	X	X	X	X	X	X	X
V-5, stained quality A q	#	X	X	X	X	X	X	X	X	X	X	X	X
V-6, stained quality B	#	X	X	X	X	X	X	X	X	X	X	X	X
V-7, evenly stained h s	#	S	X	S	X	X	X	X	X	X	X	X	S
V-7A, densely stained	#	#	X	#***	X	#***	X	X	X	X	X	#	#
V-8, lack dotted b	#	X	X	X	X	X	X	X	X	X	X	X	X
V-9, lack spotted b	#	X	X	X	X	X	X	X	X	X	X	X	#
V-10, lack stained b s	#	X	X	X	X	X	X	X	X	X	X	X	#
V-10A, densely black and red stained	#	S	X	X	X	X	X	X	X	X	X	X	#

Adapted from Mica Manufacturing Co. Pvt. Ltd.

Symbols: # = Permissible; X = Not permissible; S = Permissible only if specified.

* Few and tiny in one fourth of usable area.

† In one half of usable area.

‡ Uniformly distributed.

§ Heavy.

** Black and red.

†† Very dense.

†† Slight amount of black mineral stain.

§§ In two thirds of usable area.

*** Medium.

††† Perforation through the laminae.

†††† North Carolina term for cross grain.

§§§ Numerous rulings that intersect to form vees.

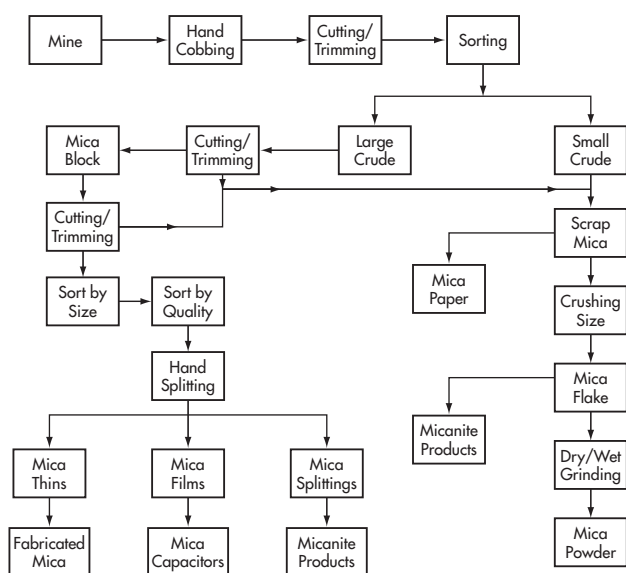


Figure 1. Typical flowsheet for sheet mica

segment plates. Molding mica has found the highest use over the past several years for V-rings, end caps, tubes, and bushings for use as insulators in transformers, armatures, commutators, and motor starters. Washers can be cut or die-stamped from molding sheets for use in electromagnets and control gears.

Flexible sheet, which will typically contain special backings, is used in electrical motor and generator armatures, coil insulation, electric furnaces, and magnet and commutator core insulation. The flexible sheets can be cut to specific sizes and shapes to permit winding or wrapping without heating.

Heat-resistant sheets are used where high-temperature insulation is required and are produced from both muscovite and phlogopite splittings. The phlogopite is used when working temperatures are maximized at 900°C, and muscovite splittings are used below 600°C. Examples of use include electric iron elements, wound heater elements, resistance heaters, and other industrial applications.

Segment plates are prepared by pasting together splittings with a varnish and pressing at high temperature and pressure. These plates, cut or ground to specific shapes, are used as insulators in the copper commutator segments of direct current motors and generators. Phlogopite is the desired raw material because it tends to wear more evenly with the copper elements. Although muscovite is more wear resistant, it may create uneven wear that could affect the operation of the motors.

Table 10 lists estimates of micanite/built-up mica sold or used in the United States by product in 2001 and 2002 (Hedrick 2004).

Fabricated Mica

Owing to excellent natural structural stability and dielectric properties, sheet mica can be fabricated into a wide variety of specific shapes and sizes by hand cutting, stamping, or die-punching. Fabricated mica finds uses in thermionic valve bridges, condenser plates, cathode tube assemblies, optical filters, retardation plates in lasers, and stove and kerosene heater windows. Specialized applications are found in missile systems, medical electronics, and radar systems, and more common applications can be found in domestic uses such as heating elements for irons, toasters, and hair dryers.

Fabricated mica products are typically available in standard shapes and sizes, or can be custom made according to specifications

Table 10. Built-up mica (by product) used or sold in the United States

Product	2001		2002	
	Tons	Value, \$	Tons	Value, \$
Flexible plate (cold)	77	693,000	73	363,000
Heater plate	W*	W	W	W
Molding plate	195	1,700,000	194	1,510,000
Segment plate	48	1,780,000	7	1,000,000
Tape	W	W	W	W
Other	71	1,150,000	66	398,000
Total	411	5,678,000	354	3,420,000

* Withheld as proprietary data, but included in totals.

tions by the manufacturer. Die-punched washers are used in transistors and diodes as insulators to protect against excessive heat. Small discs can be used as spacers in thermionic vacuum tubes, holding the tube elements in position while insulating the elements from each other. Condenser plates are die cut and coated with silver ink for electrodes in mica capacitors.

Lathe-cut discs are used in liquid level indicators, breathing apparatus, communication devices, and fuses. Because of temperature and pressure resistance, thin-cut sheets provide excellent optical mediums for measuring liquid levels and steam pressure in boilers.

Mica Capacitors

Mica capacitors are produced from mica films. The highest quality films are used in the manufacture of capacitors for calibration standards. Lower quality films are used in transmitting capacitors, and the lowest grades go into the production of receiving transmitters.

The films are cut, cleaned, and silvered on each side by a screen-printing process. The thickness of the mica film dictates the capacitance of the plates, and variations in the thickness of the silver coatings control dissipation. The capacitors can consist of single or multiple layers of mica film for stacked units. The stacked units may be interlaced with silver foil, and capacitance is predetermined so the proper number of plates can be used. The plates are generally stamped with multiple patterns and tested for electrical properties. Finished products can be dipped in varnish and treated under heat and pressure to achieve compactness.

Flake Mica

World production of flake mica far out-distances the production of sheet mica (Tables 2 and 4; Hedrick 2004). Although scrap and cuttings from sheet mica production are a source of mica flake, the majority is produced by more conventional means, either from mines operated solely for mica recovery or as a by-product from clay, quartz, and feldspar operations. Some of the mica flake is sold as-is for manufacture of micanite, mica paper, and others, but the majority of flake production is used to produce mica powder via wet and dry grinding.

Flake mica from scrap typically does not need any type of beneficiation, being the result of cautious mining techniques and hand cobbing. Mica flake from scrap can go directly into a product or to grinding mills.

Mica flake recovered from more conventional mining (i.e., by-product from feldspar, mined from pegmatites, etc.) will require some method of extraction from run-of-mine ore. Common methods of extraction, after crushing and grinding, include gravity separation and flotation.

Exploration—Sheet Mica

The spotty occurrence of sheet mica in pegmatites and the unpredictable nature of the size, shape, and attitudes of pegmatites preclude the development of a systematic exploratory drilling program. Drilling can only delineate the pegmatite and will not yield much information about the size, quality, or amount of mica present because sheet mica occurs in and only scattered pockets within the pegmatite, making it difficult to detect its presence and establish any pattern of occurrence. The common method of sheet mica exploration is to sink a test pit in an effort to locate the mica, but this is costly and results are problematic at best. The quality of mica present, however, can be determined with enough certainty to give the miner reason to continue or abort the exploration program. The size, shape, and attitude of the pegmatite are often determined by stripping and trenching. Test pits can be selected in this fashion or information can be obtained to supplement the data from test pits. Another common method of exploring for sheet mica is to sink a shaft along the dip of the vein or sink a vertical shaft to cut the vein at the desired depth. Experienced workers examine any large mica crystals found for quality (Chapman 1983).

Exploration—Flake Mica

Mica ranging from thumbnail to subsize size is found in weathered pegmatites, alaskites, schist (weathered and hard rock), gneiss, and clay deposits. The amount and quality of this mica are evaluated by conventional techniques, usually involving core drilling at 61-m intervals to establish the extent of the deposit. Once the possibility of a viable deposit is determined, a closer drilling pattern is used. In pegmatites, it is necessary to drill on 7.6-m centers to determine the presence of xenoliths or roof pendants, more accurately defining the actual size of the ore body. Drill cores are usually 3.8 to 7.6 cm in diameter and 15 to 31 m long. The cores or drill cuttings are normally removed in 1.5-m segments. Auger drilling is sometimes used in soft material. However, it is very difficult to obtain a representative sample of a particular section when using this procedure because of the probability of intermixing foreign material with the vein material.

Evaluating the cores is difficult and time consuming. Determining the mica content by chemical analysis is of little help because the accessory minerals have the same elements. X-ray diffraction (XRD) can be used but is time consuming and expensive. Petrographic analysis is also time consuming and its accuracy is questionable. A combination of flotation, magnetic separation, and dewatering has been found to be the most effective and least time-consuming method for determining mica content.

Mining—Sheet Mica

Sheet mica is recovered by either sinking a shaft along the strike and dip of a pegmatite or by open-pit surface mining of semihard pegmatite ore. In either case, it is a very economically risky mining procedure because of the cost involved in locating the vein and the unpredictability of the quality and quantity of the mica that might be recovered once the vein is located and worked (Chapman 1983).

In underground mining, the main shaft is driven through the pegmatite at suitable angles to the dip and strike using air drills, hoists, and explosives. Crosscuts and raises are developed to follow promising exposures of mica. When a pocket of mica is found, extreme care is exercised in the removal to minimize damage to the crystals. Small explosive charges of 40% to 60% strength are carefully placed around the pocket and care is exercised with the drilling procedure so the mica will not be penetrated. The charge is just sufficient to shake the mica free from the host rock. After blasting,

the mica is hand-picked and placed in boxes or bags for transporting to the trimming shed where it is graded, split, and cut to various specified sizes for sale.

Sheet mica is no longer mined in the United States because of the high cost of mining, the small market, and the high capital risk. Most sheet mica is mined in India, where labor costs are comparatively low and where there are relatively few environmental regulations.

Mining—Flake Mica

At the present time, flake mica is recovered in the United States from weathered pegmatites, weathered alaskites, weathered mica schist, and unweathered alaskite and pegmatites. Flake mica is also recovered from sedimentary sources associated with kaolin deposits in Georgia (Avant and Pickering 2000). It is mined by conventional open-pit methods. In soft residual material, dozers, shovels, scrapers, and front-end loaders are used in the mining process. Trucks transport the ore to the processing plant. Often kaolin, quartz, and feldspar are recovered along with the mica.

Hard-rock mining of mica-bearing ore requires drilling and blasting. After blasting, the ore is reduced in size with drop balls and loaded on the trucks with shovels for transport to the processing plant, where mica, quartz, and feldspar are extracted.

In earlier times, hydraulic mining was common. Numerous mica washing plants or jigs dotted the sides of the mountains in western North Carolina, Georgia, and Alabama. The soft, weathered mica ore was pushed into a pile with a dozer and washed with hydraulic hoses into the processing plant.

Evaluation and Product Development

As with all industrial minerals, several factors determine the test program implemented in any evaluation project. The material to be tested could be from a new, unexplored deposit or from an existing operation seeking to develop a new market or create a value-added product.

In developing a new or value-added product, much is already known about the material, and the evaluation may be as simple as characterizing the product to determine if it can meet imposed specifications for the targeted market. Some process development may be necessary if the material requires modifications to conform to the specifications.

For an unexplored deposit, the evaluation becomes more complex. Often, not much, if anything, is known about the deposit, and the development could require a multistage project, including several stages of bench testing, followed by pilot-plant testing, and eventually flowsheet design and plant construction.

Bench testing of a previously unexploited ore body begins with a preliminary program in which the feed is characterized and initial beneficiation tests are conducted. Caution must be exercised in obtaining a representative sample for any development program. Mica content and quality should be determined early in the development phase so the process can be designed accordingly (i.e., whether the mica is suitable for wet- or dry-ground products, which will influence the beneficiation approach).

It is never too early to begin investigating markets for any potential products, shipping options, and associated pricing. Good efforts in this area early in the development program can pay tremendous dividends later, particularly in establishing good relationships with possible consumers.

Feed characterization includes chemical analysis, mineralogical examination, and particle-size distribution of either the feed as received or crushed ore, depending on the nature of the deposit. Chemical analysis and mineralogical data allow identification of

the minerals present, leading to identifying potential markets. The size distribution gives an idea to grindability and examining the size fractions will indicate liberation size. The latter is critical; as in most industrial mineral applications, mesh of grind is defined by product specifications and not ore properties, although this is less critical with mica, especially those targeted for wet or dry grinding.

Preliminary beneficiation tests identify the primary product, determine how the material will respond to various processing techniques, give some insight to possible markets, allow the process engineer to become familiar with the material, and manufacture products on a small scale at relatively low cost. In most cases, the focus is to produce the highest grade product possible, and yields are secondary. Obviously, a working knowledge of the markets and pricing, product specifications, and process costs is essential to properly assess resultant data, draw accurate conclusions, and make appropriate recommendations.

Assuming the preliminary testing has been successful (i.e., suitable product can be made, processing is reasonable from a cost standpoint, product yields are acceptable or can be improved, etc.), follow-up bench testing is recommended. The objective of this phase should be optimizing product grades, recoveries, and costs. A small amount of concentrate may be produced and submitted to potential customers for feedback. The possibility of producing secondary products, or by-products, is studied in detail, although an experienced engineer will have a good feel for by-products from the initial testing.

Although the preliminary and follow-up testing can be performed in a single stage, the resultant data should be accurate and complete enough to begin a reasonable economic feasibility study. This should include both operating and capital costs, current product pricing, and other incidentals such as environmental permitting, tailings disposal, and air and water treatment when applicable.

Pilot-plant testing is the next step in the development process. This stage proves the bench process on a continuous basis and provides important scale-up data such as more exact equipment and water requirements (percent solids, retention times, etc.). Process variables can be investigated, allowing the optimization of operating parameters and product grades and recoveries. Tailings and water treatment, becoming ever more important in new operations, can be thoroughly investigated, allowing these treatment circuits to be properly designed.

The pilot plant can produce tonnage of product for the more stringent market evaluations of ten required by the eventual consumers of the product. It is not uncommon for a new raw material to go through a qualification process performed by the consumer. This evaluation can range from the consumer determining key product characteristics in their own laboratory to actually using the product on a trial basis in their manufacturing facility. For the latter, several tons of product may be requested.

Sufficient tonnage for market evaluations is especially critical for industrial minerals and, in particular, mica products. Although market specifications may be defined, performance can often be the determining factor. Producing concentrate for thorough market testing will allow a full evaluation of performance before costly plant design and construction.

The pilot plant can provide an excellent training ground for future operators. In industrial mineral plants, particularly if flotation is involved, variations in the operating parameters can significantly affect product quality. Because product consistency is critical, operators should be aware of the key parameters, how to maintain them, and how to recognize cause-and-effect disruptions so they can be corrected without major loss of production.

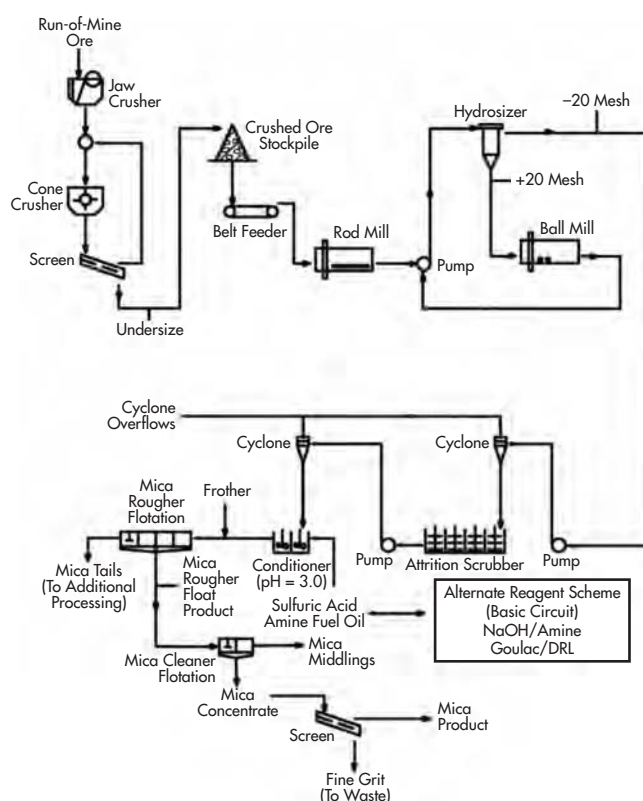


Figure 2. Typical flowsheet for mica flotation

Because finances will be the final justification for proceeding with any development, all bench, pilot-plant, and economic data must be reliable, and a lack of experience or proper information can be fatal to the investors. This again stresses the importance of matching the raw material to proper markets and processes based on product specifications, ore characteristics, and all associated costs.

Figure 2 depicts a common flowsheet for recovering mica from hard alaskite ores and weathered pegmatites via flotation. The run-of-mine ore is subjected to primary crushing using jaw crushers, followed by secondary cone crushing. The cone is typically operated in closed circuit with a screen at 14 mm (½ in.) to ensure a constant feed size to the stockpile. Stockpiling of the crushed ore allows the mine and crushing circuit to operate on an 8-hour day, 5 days per week schedule while maintaining the plant's capability of operating 24 hours per day, 7 days per week.

The 14-mm ore is fed at controlled rates into rod mills for primary grinding. Rod mill discharge reports to screens, or more commonly hydrosizers, to classify the ground slurry at 20 mesh. The oversize, or +20 mesh, reports to secondary grinding in ball mills and returns to the hydrosizer to close down the circuit. The under-size, or -20 mesh, serves as process feed.

Sizer overflow is pumped through cyclones to wash out fines (-200 mesh), which is essential to maintain product specifications on downstream products. The cyclone underflow is thickened and subjected to attrition scrubbing at 65% to 75% solids, preparing the feed for flotation.

Scrubbing serves multiple purposes, including removing surface staining and dispersing any clays or slimes that may be present, and creates fresh particle surfaces for the flotation reagents. Flotation of mica, like most nonmetallic minerals, relies

on the creation of specific surface charges, making surface preparation of the particles via attrition scrubbing essential for efficient performance.

The scrubbed pulp goes through a second cyclone step to remove additional fines and clays freed by scrubbing and to rethicken the pulp for conditioning. Figure 2 shows acid circuit flotation using sulfuric acid to decrease pH to 3.0 or less. An amine-type reagent is used as the primary collector, and #2 fuel oil may be used as an additive. These primary reagents are added to a mixing tank, or conditioner, to ensure complete exposure of the minerals to the reagents.

An alternative reagent scheme allows flotation in basic circuit ($\text{pH} = 7.5$ to 8.0), although it is not as selective as the acid circuit flotation. This reagent schedule requires a second conditioning step and uses caustic soda in the first conditioner as the pH regulator. A highly refined tall oil (DRL) is also added in the first conditioner along with an amine collector. Calcium lignin sulfate (Goulac) is added as a depressant in the second conditioner.

A frother is added to the conditioned pulp on entering the flotation cells. The frother is typically an alcohol-based surfactant that reduces the surface tension between the particles and air bubbles, aiding the attachment efficiency.

Flotation of mica is typically a rougher and cleaner step, with the rougher flotation product (froth product) reporting to a second set of cleaner cells to remove additional gangue minerals. The final cleaner froth product, or mica concentrate, will pass across a fine screen (80 to 100 mesh) to remove any sands that may have been entrapped in the froth. Rougher tailings can be further processed to recover other mineral values.

The screened mica product can be filtered and dried, or simply pumped to drain bins to lower the moisture content. Flake mica recovered via flotation, either acid or basic circuit, is used primarily as feedstock for dry grinding. Although consumers of wet-ground mica prefer products void of any chemical additions, floated flake has been used as feed for wet-ground mica in the absence of sufficient scrap supplies.

Figure 3 shows a typical flowsheet for recovery of mica flake via gravity separation. Spiral separators are the equipment of choice; they take advantage of shape factor and density differences between the mica and sand.

Feed preparation is similar to the flotation process, involving primary and secondary crushing and grinding followed by classifying to a predetermined size (8 to 20 mesh). The ground pulp is pumped to a bank of rougher spirals to produce a preliminary mica concentrate. The rougher product is pumped or gravity fed to a second bank of cleaner spirals to remove additional sands, producing the final mica product. This final product is dewatered in drain bins and used as feed for wet ground or high-quality dry-ground mica powder. The spiral tails may report to flotation processing for the recovery of additional mica and other mineral values.

Spiral concentration offers several advantages to the mica flake producer. No chemicals are used in the process, thus producing a concentrate suitable for wet grinding if the mica properties are compatible. The spirals, using shape and density, also produce a coarser, more delaminated product, leaving the "booky" mica flakes in the tailings for flotation recovery. Recovery of the coarser, highly delaminated flake produces an excellent feed for the grinding process.

A third and less used process for flake recovery is pneumatic concentration. The U.S. Bureau of Mines developed the Zig Zag concentrator using air flow to separate the mica from sands. It contains both a rougher and cleaner zone, each with separate air flows, and the final concentrate is collected from cyclones. Figure 4 presents a conceptual schematic of a Zig Zag installation.

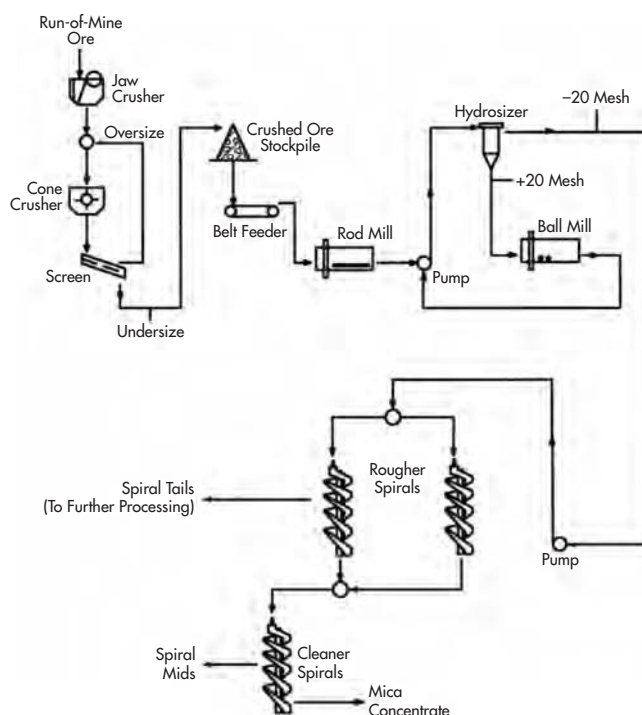


Figure 3. Typical flowsheet for gravity concentration

The Zig Zag separator is essentially an air classifier for coarse particles. The shape and density of the mica as compared to sands allow the mica to act as a smaller particle than equivalently sized sand when introduced into an elutriation type of environment. Therefore, in closely sized fractions of mica-bearing ore, the mica particles will react as a finer particle, thus allowing it to report as an overflow product and the heavier sands drop out as an underflow product.

The Zig Zag concentrator has the advantage of operating dry, thus no water or chemicals are required, and can produce flake suitable for wet grinding if the mica properties are applicable. Because it performs on an elutriation principle, it concentrates mica that already possesses a high degree of delamination at a coarse size, which is advantageous to producing high-grade ground products.

To be effective, the Zig Zag separator requires a feedstock that is relatively high grade, containing coarse mica that is already somewhat delaminated. Any "booky" flake will react as a larger particle and report with the sands, thus limiting recovery. The feedstock must also be classified into narrow size fractions before separation for the elutriation principle to be effective. This requires not only multiple screens but also multiple Zig Zag units to treat the various size fractions.

The United States is one of the world's leading producers of flake mica, using all three beneficiation processes previously described in some capacity. Table 11 shows estimates for U.S. production and value by state for 2001 and 2002 (Hedrick 2002).

Whatever beneficiation process is used to recover the flake mica, it is vital that the mica properties be defined early in the design phase. If the mica is suitable only for dry grinding, then any of the processes can be used. However, if the mica is targeted for wet-grinding applications, using surface-altering chemicals should be avoided and process options should be defined accordingly (i.e., gravity or pneumatic separation). Many operating plants use spiral separation on coarser ore and flotation to recover

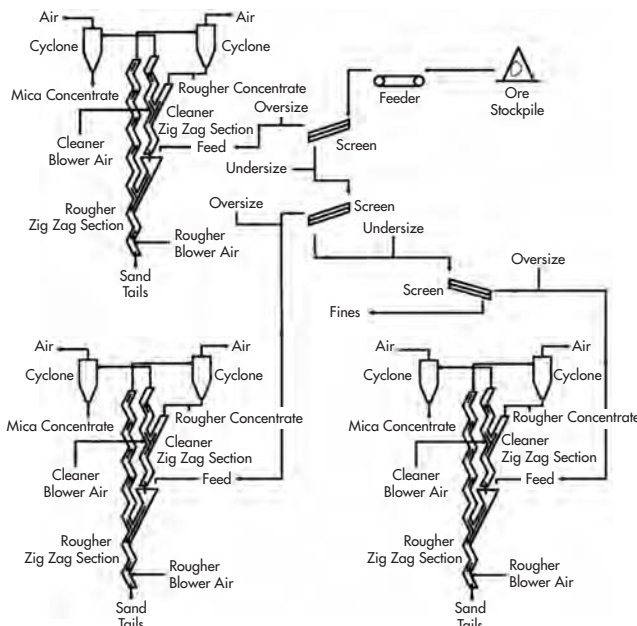


Figure 4. Conceptual schematic of a Zig Zag installation

Table 11. Flake mica production in the United States

State	2001		2002	
	Quantity, t	Value, \$	Quantity, t	Value, \$
North Carolina	51,000	3,890,000	40,000	3,130,000
Others*	47,000	4,100,000	41,000	4,240,000
Total	98,000	7,990,000	81,000	7,370,000

* Includes production for Arizona, Georgia, New Mexico, South Carolina, and South Dakota.

finer mica, producing flake for both wet and dry grinding. Table 12 shows a general classification of ground mica by size and use.

Dry-Ground Mica

Dry-ground mica is produced from flake and scrap mica by size reduction in hammer mills and fluid-energy mills. Each produces a size-specific product for different markets. A micronized product, produced in specialized fluid-energy mills, is an extremely fine-sized powder.

Hammer mills produce a relatively coarse product. Mica flake or scrap is fed to the hammer mill, followed by classification. The mill can be run in closed circuit with an air classifier, but screens are used more often because of the coarse product sizes.

A first scalping screen returns coarse mica back to the mill for additional grinding. It is not uncommon for the hammer mill to contain graded sieves to replace the scalping screen, which allows the mica to remain in the mill until it reaches a specific size. The undersize reports to a series of screens to produce sized products for various applications. Figure 5 shows a typical hammer mill setup.

Hammer-milled mica has typical top sizes of 2 to 30 mesh and is suitable for coarser applications such as drilling muds, welding rods, roofing shingles, construction fillers, auto components, and some pearlescent pigment applications. Beneficiated flake mica

Table 12. General classification of ground mica products

Grade	Mesh Size	Typical Use
Coarse flake	6	Oil-well drilling, artificial snow
Medium coarse flake	10	Decorative, Christmas decorations, display materials
Fine to coarse flake	16	Concrete block fillers, refractory brick, gypsum board, asphalt roofing, shingles
Coarse to fine powder	30	Metal annealing, absorbent in explosives, disinfectants
Medium fine powder	60	Welding electrodes, cables and wire, foundry works, pipeline enamel, lubricants, adhesives
Fine powder	100	Textured paints, acoustical plasters, ceiling tiles
Superfine powder	325	Paints, plastics, rubber, paper

Source: Skillen 1992.

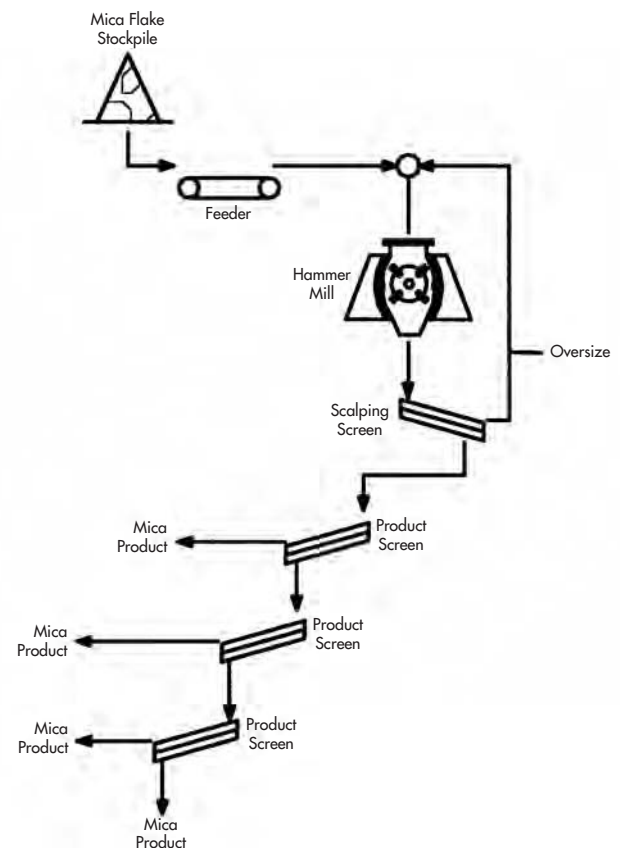


Figure 5. Typical hammer mill setup

(flotation concentrates, gravity separated) can also serve some of these markets without requiring additional grinding.

Fine-powdered dry-ground mica and "superfine" micronized mica are produced in fluid-energy mills. These mills use a stream of high-velocity gas to force collision of the mica flakes, resulting in breakage and grinding through particle-to-particle impact and attrition to sizes finer than 100 mesh. Commercial units are equipped with air classifiers to return coarse mica back to the grinding chamber.

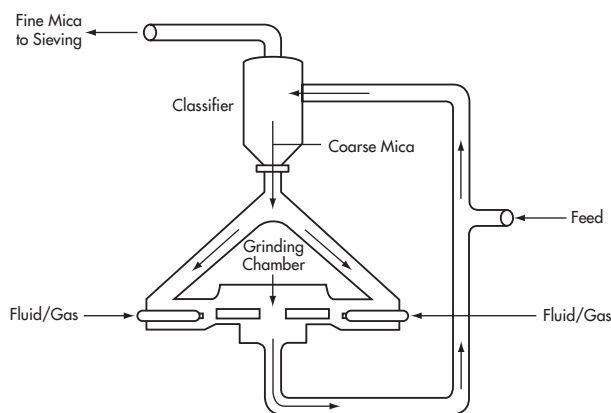


Figure 6. Cross-section view of a typical fluid-energy mill

Controlling temperature, composition, and humidity of the gas stream allows other functions to be incorporated into the size-reduction process, including drying. Many dry-ground producers prefer to feed the mica flake at moisture contents of 10% to 15%. Using superheated steam allows for very fine particle size reduction and is used to produce micronized mica. Figure 6 shows a cross-section view of a typical fluid-energy mill for grinding mica flake.

Dry-Ground Products

The largest consumption of dry-ground mica (–100 mesh) is in joint compounds for wallboard. This industry consumed about 59% of U.S. dry-ground products in 2002 (Hedrick 2002). The mica is a cost-effective filler and surface agent in the cement, which fills the joints between panels and is used as a finish coat on ceilings. It acts as a reinforcing pigment that reduces penetration into porous surfaces and enhances the mixing and troweling properties of the compounds. Mica's natural heat resistance, mechanical and thermal strength, and low moisture absorption make it an ideal filler for joint compound applications.

Dry-ground mica's low bulk density and nonabrasive, noncombustible properties make it an excellent filler in gypsum wallboard panels, and an effective replacement for asbestos. It provides good thermal insulation and sound absorption as well as fire resistance—all desirable properties in wallboard panels.

Coarse, hammer-milled mica and beneficiated flake is an additive in drilling muds that prevents loss of circulation and seepage in loose-rock formations. It serves as an effective sealant because of its plate structure, facilitating the overlapping of particles to bridge openings. It also aids in keeping solids in suspension, critical to maintaining or regaining circulation. Various particle-size distributions are used to prevent specific types of circulation loss associated with different rock formations.

About 15% of dry-ground mica is consumed in the paint industry, which is the second largest market (Hedrick 2002). The mica is a pigment extender that enhances suspension, reduces chalking, prevents shrinkage and shearing of the paint film, brightens color tones, and increases resistance to water penetration and weathering. It also increases the paint's adherence to all types of surfaces. Dry-ground products are used extensively in texture and traffic paints where slip and sheen are not as important as in high-quality paints.

High-quality flake (low iron content) is used in pearlescent pigments, providing luster in paints and other decorative products.

It imparts excellent reflective and refractive effects because of its high index of refraction, creating a “mother-of-pearl” appearance that can range from white to silver to a multitude of colors, varying in texture from a silky luster to a glittering sparkle.

In 2002, the plastics industry consumed more than 5% of dry-ground mica production (Hedrick 2002). Mica in plastics serves as an inert filler and extender, especially in automobile parts such as fenders. It acts as a reinforcing material, providing improved mechanical properties and increased strength, stiffness, and dimensional stability while suppressing sound and vibration. Mica-reinforced plastics exhibit reduced warpage and superior surface properties when compared to other fillers and have proved to be effective replacements for more expensive fiberglass in many plastics.

Both hammer-milled powder and ground powder are used in the manufacture of rutile-based welding rods. The mica is added as a flux to prevent slag formation and increase arc stabilization. The mica helps form a fusible slag and produces a good seal at the fusion zone of the arc. It also provides resistance to the harmful effects of oxidation from heat and other gases. The properties contributed by the mica to the flux coating will influence the quality of the welding rod.

Mica is used as an asbestos-free substitute to enhance sound-proofing of acoustical tiles and automobile floors and fire-wall mats. The mica offers multiple advantages in these applications by not only reducing noise but also serving as a vibration absorbent and flame retardant.

The natural properties of mica make it an ideal substitute for asbestos-free friction materials used in applications such as brake shoes and clutch plates. Because mica is not brittle like other inert materials and is stronger than iron, it will reinforce, stiffen, and harden the products, imparting strength to prevent ruptures and reduce warping. Its plate structure allows the mica to lock together under compression in all types of conditions.

Dry-ground mica is used in asphalt roofing shingles and rolled roofing, as a surface coating to prevent sticking of adjacent layers. Dusting the products with mica powder during fabrication improves venting of gases during vulcanization. In a related market, mica is used as a mold lubricant in the manufacture of auto tires. It retains sulfur while permitting air and moisture to escape during curing, creating a uniform pore structure that improves resiliency and reduces shrinkage.

Other uses of dry-ground mica include decorative coatings on wallpaper and UV protection in concrete, stucco, and tile surfaces. It is used in fire extinguishers to keep the powder free-flowing and prevent packing inside the container. When added to certain gaskets, mica powder can reduce shrinkage and increase resistance to swelling from organic liquids and oils.

Wet-Ground Mica

Almost all industrial applications of mica benefit from the grinding process, which enhances its physical properties. These properties improve proportionally to the degree of delamination that occurs. Because wet grinding produces superior delamination as opposed to dry grinding (more breakage), wet-ground products possess significantly better properties and thus higher pricing than dry-ground products. Although economics of wet versus dry grinding can dictate the use of the lower priced dry-ground products, as requirements in composite reinforcement, cosmetics, and paints become more stringent, wet-ground products will become more essential.

The majority of wet-ground mica is produced in chaser-type, or Muller, mills. Although some producers claim proprietary grinding methods that produce good wet-ground products, the Muller mill has proven itself over time to create superb delamination, and

remains a popular choice for wet-ground mica. Figure 7 shows a typical wet-grinding flowsheet using the Muller mill.

Muller milling of mica is a batch process in which the mill is charged with a predetermined tonnage of mica flake. Water is added to the mill to form a paste consistency of 25% to 30% moisture. Grinding periods, which are determined through extensive laboratory tests, can range from 6 to 10 hours. Additional water may be required throughout the grinding period because heat from friction and grinding energy will evaporate the moisture from the batch.

Following the grinding, the mica is flushed from the mill into a sluice box that removes coarse grit or sand. Depending on the mica feed grade, this step may not be required.

The sluice box discharge is pumped to a series of settling tanks to recover the ground mica. Initial settling may last only a few hours, with the overflow reporting to a second settling tank that could have a retention time of up to 24 hours. Underflows are combined and treated for additional dewatering with filter presses or centrifuges. The final overflow is typically lost as waste.

The filter cake, or centrifuged product, is conveyed to a dryer. Indirect heat dryers, such as steam tube dryers, are usually used to minimize losses of fine mica and prevent discoloration. Direct heat dryers, or air-swept dryers, result in excessive losses of the finest product.

The dried mica normally passes through a hammer mill, sand mill, or other type of attritioner to break up any clumps that form during drying. It is then screened to remove coarse mica, which can be returned to the mill for the next grinding period. The screen undersize is packaged for market, or reports to further classification or chemical treatment to produce specific products.

A major challenge in producing wet-ground mica is the dewatering and recovery of the finest mica, which more often than not is the best product. It is not unusual for fine losses to range between 15% and 20% by weight of the final product. Because the use of surfactants and flocculants is avoided to prevent altering the mica's surface properties, much of this fine mica is lost in the settling tank overflows. This has resulted in the use of long settling times.

Wet-Ground Products

Uses of wet-ground mica overlap some dry-ground markets, and include paint, rubber, coatings, plastics, sealants, and so forth. Some exclusive uses of wet-ground mica are in cosmetics, pigments, powder coatings, and wallpaper.

The largest use of wet-ground mica is the paint industry, particularly automotive paints. As a filler in coating formulations, the plate structure of mica adds beneficial rheological properties, reinforcing the paint film during drying and reducing oxidation effects, as well as thermal expansion and contraction. Adding mica to paints also increases flexibility, reduces cracking, and improves adhesion. The mica is compatible with all pigments and is easily wetted with oils, thinners, water, or emulsions, becoming evenly dispersed throughout the paint film. In exterior paints and roof coatings, mica provides UV protection by reducing light penetration, and improves weathering by controlling moisture and gas permeability.

In paints and coatings, wet-ground mica can be used as-is for filler and extender, or can be coated to be a substrate for pigments, creating a variety of special effects from high lusters to pearlescence to two-tone metallic finishes. The high aspect ratios created via the wet-grinding process enhances these special effects.

The ability to highly delaminate produces near-transparent plates that are ideal for the adherence of coatings and light refraction. The mica brightens the tone of colored pigments while transmitting and reflecting light, imparting decorative effects and increasing gloss more effectively than irregularly shaped particles.

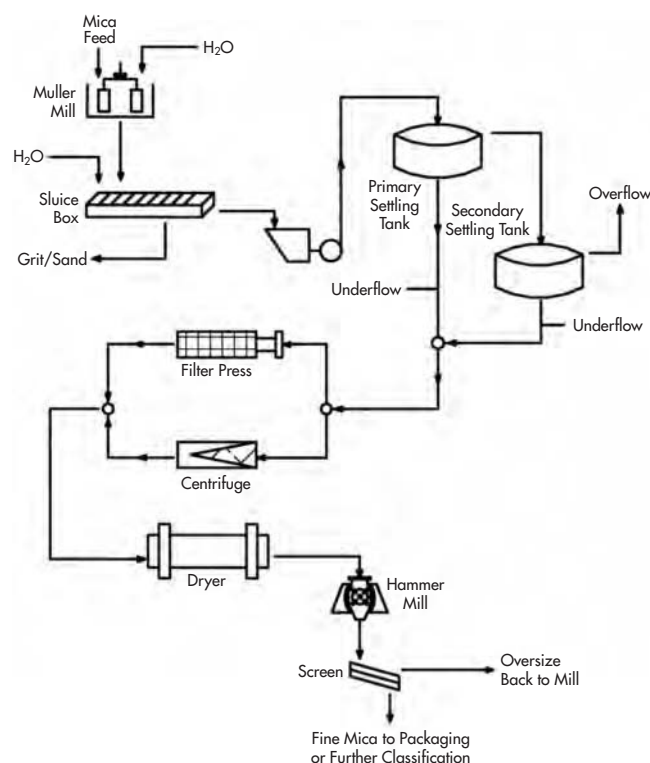


Figure 7. Typical wet-grinding flowsheet using the Muller mill

shaped particles. Controlling the plate thickness can impart different effects. Thin mica plates enhance the pearlescent effects, whereas thicker particles add to luster finishes by creating interference colors and adding depth to the finish.

Coating mica with metal oxides creates nacreous pigments, imparting a high index of refraction that enhances pearlescent or metallic effects. Coating the mica with TiO_2 produces white nacreous pigments. The color effects can be supplemented by overcoating the titanium-coated mica with other colorants such as iron oxide (yellow), ferrocyanide (blue), chromium oxide (green), and carmine (red). Specialty coatings combined with the natural enhancement properties of the wet-ground mica allow for the spectacular colors seen on many of today's automobiles, and also find uses in leather coatings, powder coatings for appliances and outdoor furniture, printing inks, and marine paints.

Mica that is surface modified with silane can improve its performance in paints and plastics. The silane acts as a coupling agent to form a molecular bridge across the organic binders and inorganic fillers of composites to create stronger and more stable bonds. These bonds, which are water and chemical resistant, improve the adhesion properties, prevent moisture penetration for improved durability, and transfer strength from the mica to the resins for better strength and stiffness. Altering the surface from a hydrophilic to hydrophobic state improves dispersion properties, making the mica more compatible with a wider variety of binders and resins.

Wet-ground mica is widely used in the cosmetics industry to produce lipsticks, eyeshadows, nail polish, foundation make-up, soaps, and other bath and body products. Cosmetic grades require Food and Drug Administration (FDA) approval under the *Code of Federal Regulations* (CFR 2002). Because it is inert, nontoxic, and

noncarcinogenic while imparting spectacular decorative effects, it is an ideal additive to skin-care products.

Mica can be added as-is or surface coated, much the same as in paints and plastics. Mica coated with titanium dioxide, iron and zinc oxides, bismuth oxychloride, and other colorants serves as brilliant pigments in cosmetic formulas. Coatings with iron oxide to absorb light, and a further coating of interference color to reflect light creates two-tone effects that appear to change color as the angle of light changes.

Particle size of the mica plays a role in the appearance of cosmetics. Smaller sizes create a smooth sheen, medium-sized particles impart a satin finish, and larger particles give a sparkling effect. The mica's relatively low coefficient of friction improves the spreadability and hiding power, and will disperse readily in most dry formulations.

Mica Powder Quality

Whether ground wet or dry, the quality of mica powders are determined by the following criteria and test procedures:

- Percentage retained on 200 and 325 mesh is measured as follows: with a combination of wet and dry screening, a weighed amount of mica powder is wet screened through a 325-mesh sieve and the +325 mesh is dried and weighed. The residue is placed on a rack of 200- and 325-mesh sieves and ro-tapped for 20 min. The amount of mica retained is weighed and recorded. Results are presented in weight percent retained and cumulative percent passing. The total -325 mesh includes both the wet- and dry-screened fines.
- Bulk density of mica powder is measured using a Scott-White volumeter with a 2.54-cc cube. For coarser micas such as oil-well grades, a 7.6-cc cube, 12.7 cm on a side, is employed.
- True specific gravity is measured with an air comparison pycnometer. Accepted values can also be measured with conventional glass pycnometers using distilled water as the displacement liquid.
- Chemical analysis can be determined by any reliable method, including atomic absorption, x-ray fluorescence, or wet chemistry.
- Free crystalline silica is determined down to 1% using XRD.
- Moisture is determined on a weighed 50-g sample dried at 110°C. After drying, the sample is reweighed and moisture content—reported as weight percent—is calculated from the difference.

$$\% \text{ moisture} = [(\text{wet wt.} - \text{dry wt.}) / \text{wet wt.}] \times 100$$

- The index of refraction is determined using petrographic microscopy and immersion oils of known refractive indices.
- Oil absorption is determined according to ASTM Test D-28 (Gardner rub-out method). A 5-g sample of mica is placed on a smooth glass plate and linseed oil is added drop-wise from a burette with constant mixing with a spatula. When the mica becomes saturated with oil to a point where the mixture begins to curl when the spatula is scraped across the mica, the end point has been reached. The amount of oil is recorded, and results are reported as grams of oil per 100 lb of mica.

$$\text{oil absorption} = (20 \times \text{mm of oil} \times \text{oil specific gravity}) / 45.45$$

- The brightness of the mica is determined by a photovolt reflectance meter (manufactured by the Photovolt Company, a division of Soragen) or other suitable reflectance meters using a green filter (550 μm). The mica powder is prepared by pressing it into a smooth layer, avoiding any cracks or voids.

- The surface area can be measured with any of several surface area analyzers on the market.
- The grit content is an indicator of the amount of “sands” contained in a flake or powder mica product. Although used to evaluate the grade of ground products, it is also used to determine the mica content of beneficiated concentrates.

Grit content of fine mica powder is determined by settling and decantation. A weighed amount of mica (50 g) is mixed in 1 L of water and allowed to settle for 15 sec, followed by decantation of one half of the suspended solids. The mixture is diluted again to a volume of 1 L and is decanted after 15 sec. The procedure is repeated until the decanted slurry begins to become transparent. The procedure proceeds using 10-sec settling times until clear water is decanted. The settled residue, or grit, is collected, dried, weighed, and reported as percent grit. The collected grit may be screened on 70 mesh to report the size of the grit.

Another method uses a Franz Isodynamic separator, which is a high-intensity electromagnet capable of multiple settings. Used primarily on beneficiated concentrates between 16 and 140 mesh, it has proven effective in separating mica, biotite, and sand, allowing an accurate measurement of concentrates grades.

Grit content of coarse micas can be determined by vanning methods. A 25-g sample of mica is placed on a vanning plaque or a 21.6 \times 28 cm piece of rough cardboard. The mica is vanned, allowing the sand to roll away from the mica via shape factors, and the separation is judged visually. Both products are collected and weighed to determine the weight percent of grit.

- The aspect ratio, or the width-to-thickness ratio, can be measured with electron microscope image analysis, although this method is often not reproducible. Laser diffraction techniques are providing more reliable and repeatable measurements.

Table 13 presents estimates on U.S. production of wet- and dry-ground mica powder by use for 2001 and 2002 (Hedrick 2002). Approximate values are included.

The information in Table 13 shows that wet-ground mica enjoys significantly higher pricing in the marketplace compared to dry-ground powders. The 2002 pricing shows wet-ground products selling at an average price of \$960/t, whereas dry-ground averaged \$180/t. Average pricing for 2003 (not shown in Table 13) increased slightly to \$1,000/t for wet-ground mica and \$200/t for dry-ground products. It is also noteworthy that other uses, which accounted for 21% of sales, contributed 44% of the total value. These smaller markets averaged significantly higher unit pricing than all others at \$627/t. Table 14 reports 2002 pricing.

Comparatively, *Industrial Minerals* magazine reports October 2004 pricing as follows (Anon. 2004a; in U.S. dollars):

- Indian micronized—300 to 545/t
- Indian wet ground—500 to 1,000/t
- India dry ground—200 to 430/t
- U.S. dry ground—210 to 400/t
- U.S. wet ground—535 to 1,300/t
- U.S. micronized—535 to 930/t
- U.S. flake—250 to 480/t

Transportation

Mica is shipped by truck or railroad. Maximum truckload shipments are considered to be 20.4 t; maximum rail shipments are 27.2 t. Bulk

Table 13. Amount and value of ground mica produced in the United States in 2001 and 2002

End Use	2001			2002		
	Tons	Value, \$	Unit, \$*	Tons	Value, \$	Unit, \$
Joint compound	46,000	8,100,000	178	58,000	10,600,000	183
Paint	20,000	8,030,000	407	15,000	3,880,000	266
Plastics	3,000	947,000	290	5,000	2,270,000	465
Drilling muds	4,000	422,000	102	W†	W	209
Other‡	17,000	10,600,000	629	21,000	12,900,000	627
Total	89,000	28,100,000	314	98,000	29,400,000	302
Grinding Method						
Dry	W	W	147	W	W	180
Wet	W	W	771	W	W	960

* Represents average price per ton.

† Data withheld to avoid disclosure of proprietary data.

‡ Other uses include electrical insulation, roofing, rubber, textile and decorative coatings, welding rods, and miscellaneous uses.

Table 14. Mica pricing in 2002 by type

Type	Price, US\$
North Carolina dry ground	230–400/t*
North Carolina wet ground	535–1,300/t*
North Carolina micronized	535–930/t*
North Carolina flake	250–480/t*
U.K. dry ground	350–465/t
U.K. wet ground	900–1,050/t
U.K. micronized	450–610/t
Indian dry ground	230–432/t
Indian wet ground	400–1,000/t
Indian micronized	362–545/t
India mine scrap for mica paper	245–365/t†
South Africa dry ground	325–355/t, 20–60 mesh‡
South Africa muscovite sheet	9–80/kg§
Phlogopite block	14.95/kg
Phlogopite splittings	4.89/kg

Adapted from Harben 2002.

* free on board (f.o.b.) plant

† f.o.b. Chennai

‡ f.o.b. Durban

§ f.o.b. port

truckloads and bulk rail shipments are also made to avoid extra costs for palletizing, bagging, and shrink wrapping. Mica is usually palletized and shrink wrapped for shipment.

Future Trends

Many mica markets are driven by construction, housing starts (wallboard, joint compounds, paints), and consumer durable goods and thus depend on overall economic conditions and a healthy gross national product (GNP). U.S. Census statistics (available at <http://www.census.gov>) indicate an overall increase in housing starts in the United States for 2002, 2003, and 2004, but an increase in U.S. mica production has not been reflected because of foreign imports. Recent natural disasters in the United States in 2004 and 2005 may provide a boost in rebuilding and damage repair.

An informal survey of mica producers and consumers shows an optimism for wet-ground mica because inroads have been made into the plastics and pigments markets, providing a good profit mar-

gin, and a solid market is anticipated for the near future. Less enthusiasm is shown for dry-ground mica because pricing has become stagnant.

An aggressive campaign for U.S. energy independence could result in increased demand for drilling mica related to oil and gas exploration, but this would largely be tied to pending decisions of current political administrations, both domestically and internationally. Off-shore exploration and access to protected wildlife and environmental preserves could increase demand.

Alternative Products

Substitutions for flake and mica powder are not possible in applications that take advantage of the unique properties that the mica imparts to the end product. In certain applications where the mica acts primarily as a filler, some lightweight aggregates such as diatomite, vermiculite, or perlite might be used. Sand and talc have been used as a substitute in roofing shingles because of lower pricing, but the shingle quality suffers. Talc can also be used in place of mica in some lower quality paints as well as mold releases. Boron nitrate, a relatively new cosmetic additive, can replace mica and provide many of the same qualities.

Sheet mica substitutes are numerous, particularly in electrical and insulation uses. These substitute materials include acrylics, cellulose acetate, fiberglass, nylon, phenolics, polyester, styrene, and vulcanized fiber. Trade name products that might be used in place of the sheet mica include Benelex, Delrin, Duranel, Kapton, Kydex, Lexan, Lucite, Mylar, Plexiglass, and Teflon.

GOVERNMENT AND LEGISLATION

Allowance of Deduction for Depletion

The *U.S. Internal Revenue Code* (1997) allows a deduction based on the depletion of natural resources for most mining operations. According to the code, the depletion allowance for mica is quoted at 22% for operations within the United States. The allowance for depletion under Section 611 is applied to the gross income from the property, excluding an amount equal to any royalties paid or incurred by the taxpayer, although such allowances must not exceed 50% of the taxable income from the property computed before the allowance for depletion.

Mining, as defined in Section 613 of the same code, includes not only the extraction of the ores from the ground but also deposits of waste and residue that are reclaimed for mineral values. Also included are the treatment processes and transportation of

the minerals from the point of extraction from the ground to the plants and mills that is not greater than 80.5 km (50 miles). Exceptions for transports greater than 80.5 km can be granted under special circumstances.

Environmental Regulations

Mica mining, like any mining operation, is subject to local, state, and federal regulations. The Mine Safety and Health Administration (MSHA) monitors mica mining operations for conformance to safety standards. Most states have labor departments that mirror the function of MSHA. Both state air and water environmental agencies together with the U.S. Environmental Protection Agency (EPA) oversee air and water quality issues associated with mica mining.

Most states have land management departments that regulate dam safety, erosion, sedimentation, and reclamation. All mines must control erosion and sedimentation and are responsible for restoring mined-out areas. Most reclamation is accomplished through backfilling, contouring, and seeding operations. In cases where this is impractical or undesirable, lakes for water recreation may be built. The U.S. Army Corps of Engineers has jurisdiction over any lands that are designated as wetlands.

Code of Federal Regulations

Mica powders as color additives have been included in the CFR. Section 73.1496 (2002) lists specifications for mica powder as a color additive in drugs. Although exempt from certification, the statute lists limits on particle size at 100% passing 10–60 mesh; loss on ignition (at 600° to 650°C) at less than 2%; lead at less than 20 ppm; arsenic at less than 3 ppm; and mercury at less than 1 ppm.

Section 73.2496 (2002) of the same code addresses cosmetic-grade mica. Although no specifications are listed, cosmetic-grade mica powder as a color additive is approved and exempt from certification. Effective November 26, 2002, Subpart D of the same code (Medical Devices), the FDA amended color additive regulations to provide for the safe use of mica-based pearlescent pigments in contact lenses.

Government Stockpiles

The U.S. government maintains a National Defense Stockpile (NDS) of strategic minerals that includes muscovite block, film, and splittings. The National Defense Act for fiscal year 2003 (Public Law 107-314), enacted into law in December 2002, reauthorized the transfer of funds from the NDS Transaction Fund for operation and maintenance of the NDS.

The bill authorized the disposal of 22,880 kg of all mica types classified as excess to goal. Stocks of mica classified as excess to goal at the end of fiscal year 2002 were not subjected to disposal limits. Excess fiscal year 2002 NDS mica stocks were 10,144 kg of muscovite block, 506 kg of mica film, and 12,230 kg of phlogopite splittings.

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Nepheline Syenite

Virginia T. McLemore

INTRODUCTION

Nepheline syenite is a light-colored, medium- to coarse-grained holocrystalline, silica-deficient, feldspathic, plutonic igneous rock largely made up of nepheline, sodium feldspar (albite), and alkali feldspar (orthoclase, microcline), but no quartz. Nepheline syenites are essentially syenites that are undersaturated in silica. Crystallizing from magma undersaturated in silica results in the formation of nepheline instead of albite feldspar (Harben 2002). Trace minerals include sodalite, augite, aegirine, biotite, hornblende, sphene, zircon, iron oxides (magnetite), apatite, garnet, muscovite, corundum, and other minerals rich in alkalis or in rare earth elements (REEs). Commercial nepheline syenites typically are high in alumina (>23%), low in silica (<60%), low in iron (<2% Fe₂O₃), and high in alkalis (Na₂O + K₂O >15%).

As a raw material, nepheline syenite is used in manufacturing glass, ceramics, and flatware (Allen and Charsley 1968; O'Driscoll

1990; Potter 1990; Bourne 1994; Guillet 1994). The major commercial deposits for glass and ceramics use are in Ontario, Canada, and North Cape, Norway (Tables 1 and 2; Figure 1). The largest production of nepheline syenite, however, is from four operations in Russia for manufacture of alumina with by-products of sodium, potassium, and portland cement (Table 3). Russian deposits are generally too high in iron for use in glass and ceramics. Deposits elsewhere in the world have been mined for predominantly local use (Tables 1 and 2; Figure 1), but little information is available about these operations.

Phonolite, the fine-grained equivalent of nepheline syenite, has been exploited in France, Germany, and the Czech Republic (Bolger 1995). Because of its fine grain size, however, phonolite is difficult to upgrade to a high commercial standard. Material containing 2% to 5% Fe₂O₃ can be used in the manufacture of colored glass and some ceramics.

Table 1. Major worldwide nepheline syenite mines and deposits

Mine	Company	Mining Method	Startup Date	Capacity, tpy	Comments
Khibiny, Kola, Russia	Apatit Production Association	3 open pit, 2 underground	1929	1,500,000	Apatite with by-product nepheline syenite produced
Lovozero massif, Kola, Russia	na*	na	na	na	By-product of REEs production from syenite, urtite
Kiya-Shaltyr and Goryachegorsk, Siberia	na	na	na	na	Aluminum production from urtite and ijolite
Blue Mountain, Havelock, Ontario	Unimin Corporation	Open pit	1955	700,000	Crush, magnetic separation, sizing, fine grinding
Blue Mountain, Nephton, Ontario	Unimin Corporation	Open pit	1936	Included with Havelock Mine	Crush, magnetic separation, sizing, fine grinding
North Cape, Stjernoya, Norway	North Cape Minerals AS (owned by Unimin)	Underground	1961	330,000	Nepheline syenite
Fourche Mountain, Arkansas, United States	3M Company	Open pit	1947		Roofing granules, construction aggregates
Canaan, Rio de Janeiro, Brazil	Unimin Corporation		1980	134,000	Litchfieldite
Sichuan, Shuiye, Anyang, Henan Province, China	Fineton Industrial Minerals Ltd.	Under development	1994	35,000	100,000 t of ore
Bursa Orhaneli, Turkey	Matel Hamade San ve Tic AS	Open pit	na	na	40 Mt of nepheline syenite
South Africa		Quarries	na	na	Crushed stone, nepheline syenite

Adapted from Woolley 1987; *Industrial Minerals* 2003.

* na = not available.

Table 2. Potential nepheline syenite deposits worldwide

Deposit	Predominant Lithology	Comments
French River, Ontario, Canada	Nepheline syenite gneiss	Examined in 1980–1984
York River, Ontario	Nepheline pegmatites	Small quarries
East Road, Ontario	Nepheline syenite gneiss	No development
Coldwell, Ontario	Nepheline syenite	Examined for nepheline syenite
Ice River, British Columbia, Canada	Nepheline syenite	43 Mt delineated
Trident Mountain, British Columbia	Nepheline syenite gneiss	None
Mount Copeland, British Columbia	Nepheline syenite	None
Obedjiwan, Gouin Reservation, Quebec, Canada	Nepheline syenite	Preliminary tests
Wind Mountain, New Mexico, United States	Nepheline syenite	Underground mine proposed; property is for sale
Table Mountain, Oregon, United States	Nepheline syenite	None
Gardar (Ilimaussaq, Gronnedal-Ika, Igaliko), southern Greenland	Nepheline syenite	Exploration for REEs
Loch Borolan, Scotland	Nepheline syenite	None
Iivaara Complex, Finland	Ijolite, melteigite	No development
Koga, Pakistan	Nepheline syenite	Planned capacity of 28,571 t
Pouzac, Pyrenees, France	Pyroxene foyaite	None
Norra Karr, Sweden	Nepheline syenite	Exploration
Brenk, Eifel, Germany	Phonolite	Mined for colored glass
Foya, Sierra de Monchique, Portugal	Foyaite	Development
Zelenice, Mas, Czech Republic	Phonolite	Minor production
Kaleiber, Azerbaijan, and northern Iran	Nepheline syenite	Ceramics and glass production
Jabal Sawda, Saudi Arabia	Nepheline syenite	Exploration
Jabal Abu Khuruq, Egypt	Nepheline syenite	26 Mt
Arroya Grande, San Carlos Mountains, Mexico	Nepheline syenite	Exploration
Meponda, Mozambique	Nepheline syenite	4.3 billion t
Australia	Nepheline syenite	None
Cameroon	Nepheline syenite	None
Congo	Nepheline syenite	None
Angola	Nepheline syenite	None

Adapted from Woolley 1987; *Industrial Minerals* 2003.

Nepheline syenite is used in products other than glass and ceramics. Its high-strength and weather-resistant properties allow for uses as roofing granules, road materials, rip rap, as well as asphalt and concrete aggregate (Allen and Charsley 1968; McLemore and Guilinger 1993, 1996; Guillet 1994; McLemore, Guilinger, and Oumiette 1994; McLemore et al. 1996a). Because nepheline syenite has high brightness, inertness, and easy wetting and dispersion in parent formulations, it is desired in pigments and fillers. Its UV attenuation characteristics and resistance to weathering make it suitable for use as roofing granules by blocking sunlight and preventing degradation of an asphalt roof. Fines are used as a coloring and fluxing agent in the manufacture of brick and as compaction fill. For local needs, nepheline syenite is used as dimension and crushed stone. Its lack of quartz, or free silica, and relative hardness enables nepheline syenite to be used as a silica-free abrasive. Other potential uses include as fertilizer, ingredients in refractory cement, and paper (Allen and Charsley 1968).

PRODUCTION AND TRADE, RESOURCES, AND RESERVES

Nepheline syenites are found throughout the world (Figure 1, Tables 1, 2, and 3; Allen and Charsley 1968; Woolley 1987; Platt 1996), but only a few deposits are sufficiently low in iron, or have iron in a form that could be inexpensively removed, for use in glass or ceramic manufacture. Magnetic separation, however, after drying and crushing can reduce the dark iron-mineral content. Production of nepheline syenite for glass and ceramic use is mostly from mines

at Blue Mountain, Havelock, and Nepton, Ontario; and North Cape, Norway, where resources are adequate to meet future needs (Table 1). The world's largest nepheline syenite deposit is on the Kola Peninsula in Russia and is mined for alumina. Other deposits in the world, some of which have had test shipments or minor local production, have been explored (Tables 1 and 2), but no known significant production has occurred, except for uses other than glass and ceramics. Other uses are typically included in aggregate production, and separate figures are not readily available. Because commercial nepheline syenite is a high-bulk, low-cost material, it typically needs to be located near appropriate transportation and within reasonable distance of potential markets.

GEOLOGY Mineralogy

In North America, typical nepheline syenite consists of approximately 25% nepheline, 55% sodium feldspar (albite), and 20% potassium feldspar (microcline). In Norway, typical nepheline syenite consists of 34% nepheline, 56% potassium feldspar, and 10% biotite and pyroxenes. The most common of the feldspathoid minerals, nepheline is nominally a sodium aluminosilicate with the formula $\text{NaAlSi}_3\text{O}_8$, but potassium invariably substitutes for a portion of the sodium. The amount of potassium (K_2O) in natural nepheline ranges from 2.5% to 10% (3% to 12% K_2O) by weight. In an alkali-rich magma deficient in silica, nepheline will crystallize, instead of albite and quartz. Accessory or trace iron minerals



Figure 1. Nepheline syenite mines and deposits worldwide

such as corundum, zircon, or other refractory minerals are undesirable. Other feldspathoid minerals in nepheline syenite include leucite, sodalite, and crancrinite.

Chemical Properties

Like feldspar, nepheline syenite provides alkalis that act as a flux to lower the melting temperature of a glass or ceramic mixture, which prompts faster melting and saves fuel (Allen and Charsley 1968; O'Driscoll 1990; Potter 1990; Bourne 1994; Guillet 1994). It also improves the workability of the glass batch by lowering the viscosity, and it imparts a unique quality of toughness to the glass, which makes it more resistant to breakage. The alumina in nepheline syenite increases resistance to scratching and breaking, improves thermal endurance, and increases chemical durability. The low iron content provides the necessary whiteness of the powdered material utilized for clear glass and other end uses, such as fiberglass, extender pigments, and fillers.

Nepheline syenite has a higher alumina/alkali ratio (37%, compared to 30% in sodium feldspar and 32% in potassium feldspar), which means less material is required to achieve the same fluxing action (Saller 1999). With rising temperature, the alkalis become more active and first dissolve the clay particles and then the free silica (Saller 1999).

Minor amounts of iron are observed in the alkali feldspars within nepheline syenite (Platt 1996). Iron concentrations are frequently higher in sanadine than in orthoclase and microcline, which typically contain <0.2% Fe. The iron content is related to magma temperature.

Structure

Nepheline belongs to the hexagonal crystal system, and the structure is based on six-member rings of silica tetrahedra, with apices alternating in direction, forming hexagonal and polygonal voids. Al^{3+} replaces Si^{4+} in some of the tetrahedra and therefore compensates

Table 3. Production of nepheline syenite, by country, t

Year	Russia	Canada	Norway	Turkey	South Africa*
1980	na†	599,699	217,000	na	na
1981	na	587,565	223,000	na	na
1982	na	552,838	224,000	na	na
1983	na	523,249	219,565	na	na
1984	na	520,640	225,731	na	na
1985	na	467,186	227,465	na	na
1986	na	467,491	218,421	na	na
1987	na	506,415	240,000	na	na
1988	na	539,835	287,000	na	na
1989	na	555,728	na	6,000	na
1990	na	na	306,000	6,000	na
1991	na	486,000	292,000	6,000	20,966
1992	1,500,000	566,000	340,000	6,000	na
1993	1,390,000	549,000	315,000	6,000	na
1994	1,500,000	602,000	279,000	18,000	98,667
1995	1,500,000	616,000	294,000	35,000	145,459
1996	1,300,000	606,000	300,000	na	137,706
1997	940,000	647,000	310,000	114,201	114,201
1998	889,000	636,000	319,835	11,500	104,000
1999	772,000	676,000	304,592	na	82,000
2000	814,000	717,000	330,000	na	na
2001	na	734,000	330,362	na	na
2002	na	724,000	330,461	na	na

Adapted from Guillet 1994; Bolger 1995; Levine 1995, 1996; Minister of Industry 1999, 2001; Levine and Wallace 2000; British Geological Survey 2002; Gurmendi 2002; Kuo 2002; Natural Resources of Canada 2003; Taylor et al. 2003; Chapman et al. 2004.

* Production from South Africa was for crushed and broken stone.

† na = not available.

Table 5. Comparison of chemical compositions of nepheline syenite, %

Oxide	Khibiny, Russia	York River (Nepheline Gneiss), Ontario	Obedjiwan, Quebec	Mount Copeland, British Columbia	Iivaara (Ijolite), Finland	Loch Borolan, Scotland	Norra Karr, Sweden	Jabal Sawda, Saudi Arabia	Jabal Abu Khuruq, Egypt
SiO ₂	54.01	41.73	54.65	56.9	46.15	48.19	56.37	50.3	63.49
TiO ₂	1.20	0.29	1.07	0.55	0.38	1.75	0.01	0.07	0.03
Al ₂ O ₃	21.05	27.48	20.91	21.0	15.7	18.52	24.95	25.8	20.56
Fe ₂ O ₃	2.60	1.84	2.38	2.6	6.59	4.51	0.31	1.39	1.2
FeO	1.80	4.52	3.79	2.6	na*	1.68	0.20	0.46	na
MgO	0.77	1.24	1.11	0.7	5.52	1.12	0.07	0.18	0.18
CaO	1.80	6.78	0.56	1.6	14.16	10.29	0.25	1.46	0.64
K ₂ O	5.30	3.16	7.21	6.1	2.61	8.05	5.20	4.48	5.99
Na ₂ O	9.50	11.05	6.25	7.5	7.24	3.44	11.73	9.38	7.48
MnO	0.17	trace	0.06	0.24	0.18	na	0.05	0.06	0.24
P ₂ O ₅	0.09	0.14	0.05	0.02	0.77	na	0.01	0.03	0.04
CO ₂	na	0.93	0.64	0.2	na	na	na	na	na
Loss on ignition (LOI)	1.14	0.52	1.14	0.5	0.93	3.45	0.1	5.93	na
Total	99.43	99.68	99.82	100.51	100.23	101.00	99.25	99.54	99.85

Adapted from Shand 1939; Baragar 1953; Tilley 1953; Lehigh 1960; Currie 1976; Liddicoat, Ramsay, and Hedge 1985; Hosterman, Patterson, and Good 1990; Landoll, Foland, and Henderson 1994; *Industrial Minerals* 2003.

* na = not available.

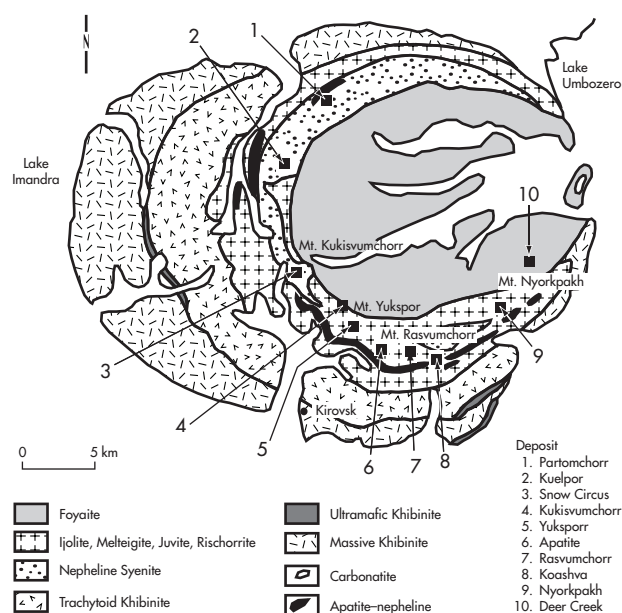
types of economic deposits. Economic nepheline syenite deposits for glass and ceramic use, however, are rare because few are low enough in iron content and refractories. In addition, these deposits are not typically found in the vicinity of other types of economic deposits. Nepheline syenite from the Khibiny Complex on the Kola Peninsula in Russia is recovered for the manufacture of aluminum, a by-product of apatite production. Some nepheline syenite deposits that are potentially suitable for glass and ceramic use are not currently economic because they are too far from potential markets or the available transportation facilities are inadequate. The major deposits that have produced or are producing nepheline syenite are listed in Table 1; other deposits are listed in Table 2, many of which have had minor production. Many additional deposits are found in the world (Allen and Charsley 1968; Woolley 1987), but they are remote from markets or little information is available at the current time.

Major Deposits

Russia

In Russia, Apatit Production Association produces apatite and nepheline syenite from the Khibiny Complex, the world's largest phosphate deposit and the largest agpaite nepheline syenite complex. Annual capacity is 1,500,000 t of nepheline syenite (Levine and Wallace 2000). The unique apatite–nepheline deposits of the Khibiny Complex, discovered in 1924 and mined since 1929, are a major source of very high-grade phosphate, aluminum, and Portland cement using nepheline concentrates from the apatite tailings.

The 362- to 377-Ma domed complex is approximately 40 km in diameter (Figure 3; Kramm et al. 1993) and composed of several intrusive phases emplaced in the following succession: (1) alkaline-ultrabasic rocks, represented by relics of ultrabasic rocks and early ijolite; (2) large intrusions of agpaite nepheline syenite (also known as khibinites) in the outer arc and the core; (3) late ijolite and urtite; and (4) carbonate stock. Apatite–nepheline deposits are associated with the ijolite–urtite that forms an arc approximately 100 m thick and 11 km long within the agpaite nepheline syenite (Guillet 1994; Dudkin and Tyapina 1997). The deposits consist of 10% to 80% nepheline; 15% to 75% apatite; 1% to 25% aegirine;

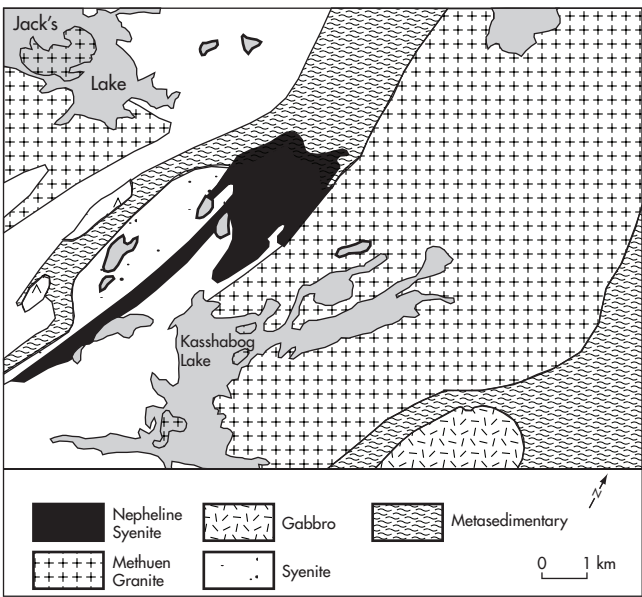


Adapted from Atzamastsev 1994.

Figure 3. Geology of Khibiny Complex, Russia

and 5% to 12% sphene, titanomagnetite, and feldspar (Notholt 1979; see Table 5 for a chemical analysis of nepheline syenite from various areas of the world).

Mining operations consist of four facilities, an apatite–nepheline beneficiation complex consisting of two plants, and auxiliary facilities. The Apatit Production Association has explored deposits of apatite–nepheline ore, with total ore reserves of more than 3.6 billion t. The deposits are developed by two open-pit and three underground mines at Yukspor, Kirovsk Saami, Rudnik Rasvumchorr, and Tsentralny (Figure 3). Production from two additional



Adapted from Hewitt 1961.

Figure 4. Geologic map of the Blue Mountain nepheline syenite deposit, Ontario

open pits, Koashva and Nyorkpakh, has occurred in the past. Pilot tests to produce titanium–silicon pigment from sphene concentrate have been successful (Dudkin and Tyapina 1997).

Nepheline syenite is a by-product of REEs production from the Lovozero massif on the Kola Peninsula. The massif, 351 to 371 Ma, is a layered suite consisting of eudialytic syenite and alternating layers of foyaitite, urtite, luja vrite, and associated rocks (Vlasov, Kuz'menko, and Yes'kova 1966; Kramm et al. 1993). Loparite is the predominant REE mineral mined.

At Kiya-Shaltyr and Goryachegorsk mines in Siberia, nepheline is recovered from urtites and ijolites and used for produc-

ing alumina (Levine and Wallace 2000; Kuzbass Chamber of Commerce and Industry 2002).

Ontario

Blue Mountain, Havelock, and Nephton in Ontario are the largest nepheline syenite deposits for glass and ceramics industries in the western hemisphere. Approximately 58 km northeast of Peterborough in Methuen Township, they are reachable by both highway and railroad and are probably the first operations mined for nepheline syenite in North America, with production beginning in 1935. When Unimin Corporation purchased the deposit from Indusmin Division of Falconbridge Ltd. in 1990, it became the world's largest supplier of nepheline syenite and feldspar. Reserves are estimated at 19 Mt with large resources available for future exploration (Dawson 1961; Turek and MacGregor 1984).

The Blue Mountain and Nephton nepheline syenites are part of an 1,280-km belt of nepheline syenite gneisses in the Grenville Province of southern Ontario. The origins of this belt are controversial, with theories ranging from primary alkaline igneous origin to metamorphic to metasomatism (Payne 1968; Currie 1976).

The Blue Mountain nepheline syenite gneiss, 1,285 Ma, is a very homogeneous body forming a teardrop-shaped mass approximately 2,130 m long and 1,000 m wide (Figure 4) (Krough and Hurley 1968). Epidote-amphibolite-grade metasedimentary rocks surround the deposit. The nepheline syenite is zoned with a core of hornblende nepheline syenite surrounded by biotite nepheline syenite and marginal outer zones of nepheline-poor muscovite syenite. Typically, the nepheline syenite is foliated to massive, coarse- to medium-grained white rock with a granitic texture that consists of albite (50% to 54%), microcline (20%), nepheline (22% to 30%), 4% mafic minerals, and other accessory minerals, including aegirine-augite, andradite, biotite, calcite, cancrinite, corundum, hastingsite, hornblende, magnetite, muscovite, riebeckite, and zircon. Because of its homogeneity, medium- to coarse-grain size, and low iron content, the deposit is economic (Table 6).

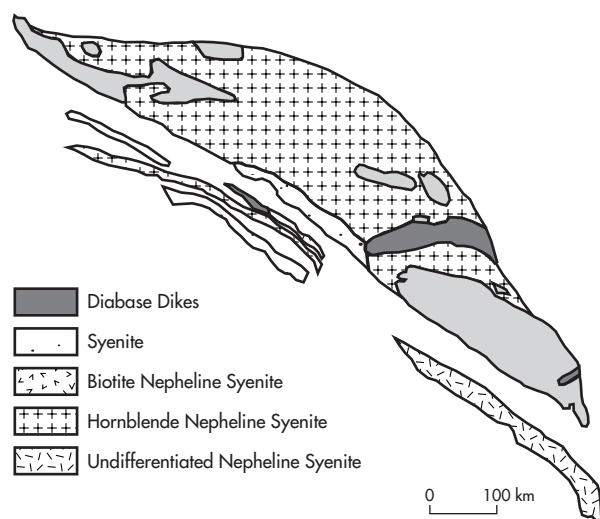
Norway

At North Cape, Stjernoya, Norway, 10 Mt of nepheline syenite have been produced on Stjernoya Island since 1961 when Norsk Nefelin,

Table 6. Chemical composition of unprocessed, raw nepheline syenite from Blue Mountain, Ontario, %

Oxide	Muscovite Nepheline Syenite Gneiss (Quarry)	Hastingsite-Biotite Nepheline Syenite Gneiss	Biotite Nepheline Syenite	Andradite-Nepheline Syenite Gneiss	Muscovite-Biotite Nepheline Syenite Gneiss	Nepheline-Biotite-Muscovite Gneiss, Stony Lake	Nepheline Syenite Gneiss (Quarry)
SiO ₂	58.4	58.72	58.57	58.69	59.68	58.79	58.84
TiO ₂	0	0.01	0.05	0.01	0	0.03	0
Al ₂ O ₃	24.8	23.07	23.68	22.70	23.48	23.77	23.26
Fe ₂ O ₃	0.75	0.93	0.66	1.31	0.59	1.06	1.43
FeO	0.46	0.91	0.90	0.67	0.37	0.81	0.53
MnO	0.01	0.04	0.02	0.04	0	0.04	0.05
MgO	0.14	0.03	0	0.07	0.21	0.04	0.03
CaO	0.59	0.53	0.35	0.56	0.26	0.41	0.66
K ₂ O	4.34	5.23	5.82	4.61	4.68	4.42	4.75
Na ₂ O	10.48	10.20	9.57	10.51	9.52	10.69	10.09
H ₂ O	0.42	0.42	0.31	0.19	0.66	0.28	0.19
P ₂ O ₅	0.01	0.01	0.07	0.01	0	0.02	0.01
CO ₂	0.10	0.14	0	0	0.04	0.05	0.13
Total	100.50	100.24	100.00	99.37	99.49	100.41	99.97

Adapted from Hewitt 1961; Currie 1976.



Adapted from Guillet 1994.

Figure 5. Geologic map of the North Cape nepheline syenite, Stjernoya, Norway

a division of Elk em-Spigerveket AS, began mining underground (Geis 1979) on Stjernoya Island. A series of mergers and acquisitions resulted in Unimin Corporation acquiring the property in 1993 from North Cape Minerals Co. (which had bought it from Norsk Nefelin). Even though Stjernoya is 400 km above the Arctic Circle, the warm waters of the Atlantic Gulf Stream keeps the ports free of ice all year. The nepheline syenite is used in glass and ceramics.

The deposit is lens shaped, 1,700 m by 300 m in size (Figure 5), and consists of weakly foliated biotite- and hornblende-pyroxene-nepheline syenites, which contain feldspar (56%); nepheline and minor plagioclase (34%); hornblende (0.3% to 2.5%); biotite (2.5% to 6%); aegirine (1.3% to 3.8%); calcite, clinopyroxene, titanite (trace to 1.2%); and magnetite (Geis 1979). Associated rocks include alkaline pyroxenites, carbonatites, and fenites. Chemical analyses are given in Table 7. Reserves exceed 300 Mt (Geis 1979).

Other Deposits in North America

French River, Ontario. Also known as Bigwood-Rutter or Bigwood, this deposit lies near the northeast corner of Georgian Bay straddling the French River and consists of nepheline syenite gneiss within an alkaline syenite complex that is 975 Ma (Hewitt 1961). The more northerly Rutter nepheline syenite is coarse to medium grained, granoblastic, moderately foliated to massive and consists of salmon pink nepheline (12% to 49%); white albite (16% to 40%); pink microcline (6% to 22%); perthite (3% to 56%); and hastingsite (1% to 24%); with aegirine-augite, apatite, biotite, titanite, zircon, magnetite, and opaque minerals. Approximately 5,000 m by 500 m in size, it contains numerous small pegmatitic segregations.

The southern French River nepheline syenite is similar but contains only 12% to 25% nepheline; 40% white albite; 30% white microcline; 10% biotite; and less hastingsite, with minor graphite, zircon, pyrite, and magnetite (Hewitt 1961). It is approximately 4,000 m by 700 m in size and strongly foliated. Syenite completely surrounds both nepheline syenites. Chemical analyses are given in Table 8. The nepheline syenite is intruded by pegmatites containing sodalite, cancrinite, and molybdenite.

When Steep Rock Resources Inc. examined the deposits during 1980 to 1984, it found flotation methods to be most effective in

Table 7. Chemical composition of raw and processed nepheline syenite from North Cape, Stjernoya, %

Oxide	Stjernoya, Norway (Pyroxene)	Stjernoya, Norway (Biotite)	Glass Grade after Processing	Ceramic Grade after Processing
SiO ₂	52.73	52.37	57.0	57.0
TiO ₂	0.51	1.14	na*	na
Al ₂ O ₃	23.71	na	23.8	23.8
Fe ₂ O ₃	1.90	na	0.10	0.12
FeO	1.89	1.10	na	na
MgO	0.24	3.11	na	na
CaO	2.54	8.30	1.3	1.1
K ₂ O	8.08	6.87	na	na
Na ₂ O	7.78	0.61	7.9	7.8
MnO	0.06	0.25	9.0	9.1
P ₂ O ₅	0.01	0.05	na	na
CO ₂	0.77	1.88	na	na
LOI	0.26	0.26	na	na
Total	100.48	75.74	99.10	98.92

Adapted from Guillet 1994.

* na = not available.

Table 8. Chemical composition of nepheline syenite deposits from French River, Ontario, %

Oxide	French River Raw	French River Product	Rutter Raw	Rutter Product
SiO ₂	56.35	62.2	59.03	61.7
TiO ₂	0.16	0.01	0.03	0.01
Al ₂ O ₃	20.31	22.0	21.81	22.2
Fe ₂ O ₃	2.66	0.08	2.34	0.18
FeO	4.09	na*	1.34	na
MnO	0.18	0.00	0.03	0.00
MgO	0.11	0.08	0.06	0.07
CaO	1.69	0.33	0.53	0.44
K ₂ O	4.86	4.45	4.36	4.42
Na ₂ O	8.31	10.2	10.78	10.5
H ₂ O	0.69	na	0.15	na
P ₂ O ₅	0.04	na	0.02	na
CO ₂	0.67	na	0	na
Total	100.02	99.35	100.48	99.52

Adapted from Hewitt 1961; Guillet 1994.

* na = not available.

removing the iron minerals. Since 1991, SGS Lakefield Research has tested some of the material.

York River, Ontario. Nepheline gneiss was quarried in several areas for ceramic or aluminum use, but the high calcium probably makes it undesirable for ceramic manufacture (Currie 1976). The 903-Ma gneisses form thin east-dipping sheets in between granitic and gabbroic rocks. The upper portion of the layered bodies is leucocratic. Table 5 gives chemical analyses.

East Road, Ontario. East of Bancroft, this deposit consists of two broad bands of nepheline gneiss within hybrid syenite. The 900-Ma nepheline gneiss contains nepheline, plagioclase, biotite, and corundum, and a scapolite nepheline gneiss is present (Currie 1976). Nepheline-bearing pegmatites with minor biotite,

Table 9. Chemical composition of unprocessed, raw nepheline syenite from the Ice River Complex, British Columbia, %

Oxide	Ijolite	Urtite	Nepheline Syenite	Sodalite Syenite
SiO ₂	43.7	43.5	53.9	54.4
TiO ₂	1.2	0.19	0.11	0.20
Al ₂ O ₃	25.8	26.2	23.1	21.9
Fe ₂ O ₃	1.6	1.1	0.8	2.0
FeO	3.7	2.1	0.8	0.9
MnO	0.15	0.5	0.05	0.11
MgO	2.7	0.4	0.1	0.8
CaO	5.4	9.7	1.6	1.3
K ₂ O	4.5	4.9	8.8	6.3
Na ₂ O	9.9	10.4	7.8	10.7
P ₂ O ₅	0.09	0.05	0.00	0.01
CO ₂	0.8	0.3	0.1	0.2
Total	99.54	99.34	97.16	98.82

Adapted from Pell 1987.

Table 10. Chemical composition of raw and processed nepheline syenite from Fourche Mountain, Arkansas, %

Oxide	Blue Syenite, Hornblende	Gray Syenite, Biotite	Blue Syenite after Processing	Gray Syenite after Processing
SiO ₂	60.3	60.8	61.2	61.9
TiO ₂	1.1	1.2	0.3	0.2
Al ₂ O ₃	19.9	19.6	21.5	21.1
Fe ₂ O ₃	4.7	4.3	0.9	0.2
MgO	1.2	0.9	na*	na
CaO	1.3	0.8	na	na
K ₂ O	5.3	5.9	na	na
Na ₂ O	6.3	6.7	na	na
LOI	0.1	1.3	na	na
Total	100.2	101.5	83.9	83.4

Adapted from Guillet 1994.

* na = not available.

hornblende, calcite, garnet, zircon, galena, apatite, and molybdenite were prospected for nepheline and corundum. No economic development has occurred.

Coldwell Complex, Ontario. About 375 km northeast of Sault Ste. Marie near Lake Superior, this deposit is 25 km in diameter and was examined for nepheline (Woolley 1987). The rock types that make up this complex are 1,108 Ma and consist of gabbro, ferroaugite syenite, syenite to syenodiorite, biotite gabbro, nepheline syenite, granite and quartz syenite, as well as hybrid syenites (Shaw 1997). The complex consists of three overlapping ring complexes that become progressively younger to the southwest. The nepheline-bearing rocks, including nepheline syenite, form a ring in the western part of the complex and vary in texture from allotropic granular to porphyroclastic to mosaic granoblastic (Mitchell and Platt 1982).

Ice River, British Columbia. An alkaline ultramafic complex approximately 23 km south of Field, this deposit is located near and in the Yoho and Kootenay national parks. This deposit was originally closed to mineral prospecting because of its location, but recent "right to access" legislation introduced in British Columbia

has redefined the area as "Special Management," and, with careful planning, economic development within property boundaries is allowed (Currie 1976; Termuende and Geo 1998).

In the 18-km-long U-shaped Ice River complex, two distinct suites are present: (1) an early, rhythmically layered, jacupirangite (feldspar free), ijolite, and urtite, cored by a carbonatite plug and crosscut by carbonatite dikes rich in mafic silicates and oxides; and (2) a later zoned and crosscutting syenitic series, associated with a zeolite and feldspar-bearing carbonatite. Graded layers are 10 to 200 m thick and nepheline increases toward the top of each layer and with differentiation, except for the last carbonatite intrusion (Currie 1976; Termuende and Geo 1998). Ijolites predominate and consist of clinopyroxene, nepheline, phlogopite, magnetite, and sphene. Urtites are coarse grained, foliated, and consist of nepheline with lesser aegirine and minor amounts of wollastonite, kaersutite, melanite, albite, sphene, calcite, and apatite.

A thin rim of saturated fine-grained leucosyenite in contact with the country rocks surrounds the complex. The syenites are unlayered, forming an elliptical pipe-like mass, zoned from a greenish sodalite syenite core through pale gray nepheline syenite to darker-colored mafic-rich rocks at the margin. Chemical compositions are in Table 9. Approximately 43 Mt of nepheline syenite have been delineated (Termuende and Geo 1998). The area has potential for magnetite, lead-zinc, and sodalite.

Trident Mountain, British Columbia. About 83 km north of Revelstoke in the Big Bend of the Columbia River, a lenticular nepheline syenite gneiss forms the core of the mountain range and contains nepheline (10% to 40%); white to pink microcline (25% to 50%); white albite (10% to 30%); biotite (trace to 30%); and aegirine (Currie 1976).

Mount Copeland, British Columbia. On the southeast flank of Frenchman's Cap Dome, 25 km north west of Revelstoke, three main alkaline rocks are exposed: a basal nepheline syenite gneiss overlain by alkaline amphibolites and syenites. The nepheline syenite is zoned and consists of nepheline, K-feldspar, and albite with minor aegirine and sphene. A chemical analysis is in Table 5.

Obedjiwan, Quebec. On the north shore of the Gou in Reservation, approximately 150 km north of Chibougamau, this deposit is 8 km in diameter and is zoned from a core of nepheline syenite to aegirine syenite to a rim of gabbro (Currie 1976). The central nepheline syenite is 1,050 Ma, lineated to foliated, coarse-grained, and consists of albite, microcline, perthite, nepheline, and biotite. An ijolite plug, 199 m in diameter, lies within the nepheline syenite. Although the area is remote, preliminary tests were made to recover nepheline and nepheline syenite, but the results of the tests are unknown. A chemical analysis is given in Table 5.

Fourche Mountain, Arkansas. Since 1947, Fourche Mountain nepheline syenite, in Pulaski County, has been quarried and crushed for use as roofing granules, road material, riprap, and asphalt and concrete aggregate by 3M Co. Fines are used as a coloring and fluxing agent in the manufacture of bricks and as compaction fill. Impurities within feldspars are too fine to remove for use in glass and ceramics. Bauxite derived from weathering of the nepheline syenite was first mined in 1895 for alumina. Two types of syenite, a blue nepheline syenite with hornblende and a gray biotite nepheline syenite, are found. Chemical analyses are in Table 10. Other nepheline syenites are found in Hot Spring and Saline counties, Arkansas.

Wind Mountain, New Mexico. This is one of several plutons that form the Cornudas Mountains in the northern Cenozoic Trans-Pecos alkaline magmatic province. With an approximate diameter of 2.5 km, Wind Mountain is one of the largest exposed intrusions in this belt (McLemore et al. 1996a, 1996b). There has been no production

Table 11. Chemical composition of nepheline syenite from Cornudas Mountains, New Mexico, %

Oxide	Average Wind Mountain TNSP ₂ [*]	Range of Wind Mountain TNSP ₂ Samples [*]	Deer Mountain [†]	Processed Wind Mountain TNSP ₂ (Pit 1)	Processed Wind Mountain TNSP ₂ (Pit 2)
SiO ₂	59.84	56.3–63.3	57.3	64.70	63.80
TiO ₂	0.12	0.03–0.14	0.48	<0.01	<0.01
Al ₂ O ₃	18.84	17.6–20.8	19.6	20.50	20.90
Fe ₂ O ₃ [‡]	4.90	1.54–6.48	6.85	0.52	0.40
MgO	0.73	0.07–1.80	0.44	<0.05	<0.05
CaO	1.23	0.68–1.40	1.52	0.23	0.20
K ₂ O	5.35	4.80–6.32	5.46	6.74	6.73
Na ₂ O	7.82	7.20–8.80	7.03	7.62	8.23
MnO	0.27	0.14–0.35	0.38	Not available	Not available
P ₂ O ₅	0.11	<0.05–0.11	0.13	<0.05	<0.05
LOI	2.24	1.02–2.91	2.62	Not available	Not available
Total	101.45	Not available	101.81	100.31	100.26

Adapted from Barker et al. 1977; McLemore and Guilinger 1993; Schreiner 1994; McLemore et al. 1996a, 1996b.

^{*} Adapted from McLemore and Guilinger (1993) and McLemore et al. (1996a, 1996b); unaltered surface and drill core samples ($n = 5$).

[†] Average from Barker et al. 1977 ($n = 4$) and Schreiner 1994 ($n = 2$).

[‡] Total iron as Fe₂O₃.

except for test shipments in 1995 of nepheline syenite for use as sand-blasting material.

From 1991 to 1995, Addwest Minerals, Inc., began exploration and development of the Wind Mountain nepheline syenite for use in manufacturing amber-colored beverage containers, flatware, and ceramics for use as an abrasive and as roofing granules (McLemore et al. 1996a). The company is presently for sale, and the future of mining at Wind Mountain is unknown.

The Wind Mountain laccolith consists of six mineralogical and textural zones (Table 11; Figure 6; McLemore and Guilinger 1996; McLemore et al. 1996a, 1996b). The laccolith is typically gray to cream colored and weathers to darker colors. Accessory minerals form dark-colored aggregates dispersed throughout the rock. Chemical variations among the individual map units within the laccolith cannot be readily discerned by utilizing major element analyses (McLemore et al. 1996a, 1996b). The syenites, however, contain more barium and strontium than do the nepheline syenites (McLemore et al. 1996a, 1996b). These chemical analyses of the Wind Mountain laccolith suggest that the zonation appears to be controlled by crystal fractionation, volatile separation, and cooling history, not different pulses of magma (McLemore et al. 1996b). Differential cooling of the magma resulted in the textural variations at Wind Mountain.

The outer zone of the Wind Mountain nepheline syenite (TNSP₂) was developed as a constituent in glass, ceramics, and flatware, and for use as an abrasive. Compared to other commercial sources of nepheline syenite, the Wind Mountain nepheline syenite contains high iron (Table 11). When the Wind Mountain nepheline syenite is crushed and passed through a specialized rare-earth magnet, however, the resulting product is similar in composition to a Grade B product specified by Unimin Canada Ltd. and has been certified by Coors Inc. as being suitable for amber-colored glass and ceramics. Physical and chemical test results of Wind Mountain nepheline syenite meet or exceed standards for use as roofing granules, dimension stone, aggregate, and abrasives (McLemore and Guilinger 1996).

Mining is projected to be by underground, room-and-pillar methods, and planned processing methods are crushing, grinding, magnetic separation, and screening. At full production, Wind

Mountain is expected to process 3,000 tpd or 700,000 tpy. Current proven, probable, and inferred reserves total 200 Mt for a mine life of more than 100 years (*Industrial Minerals* 1995).

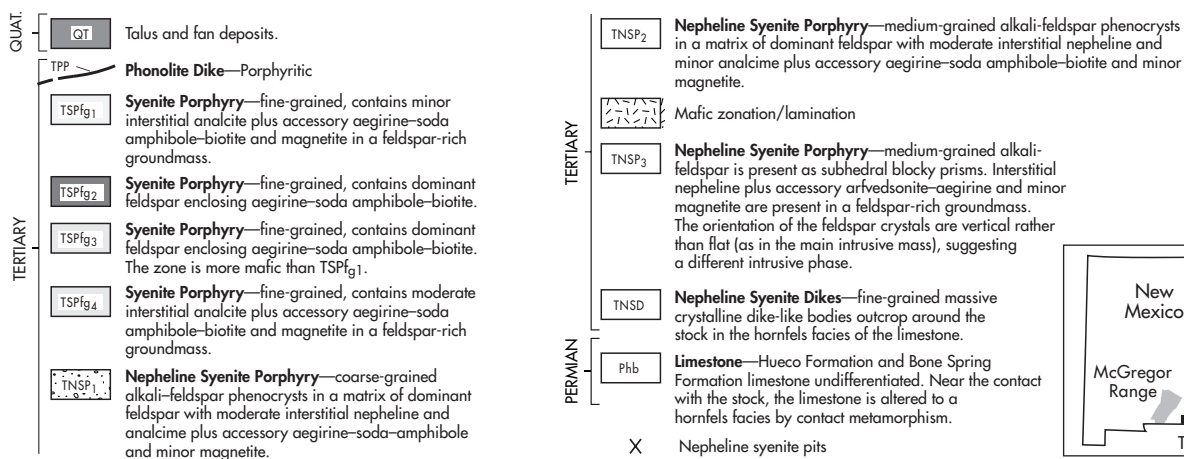
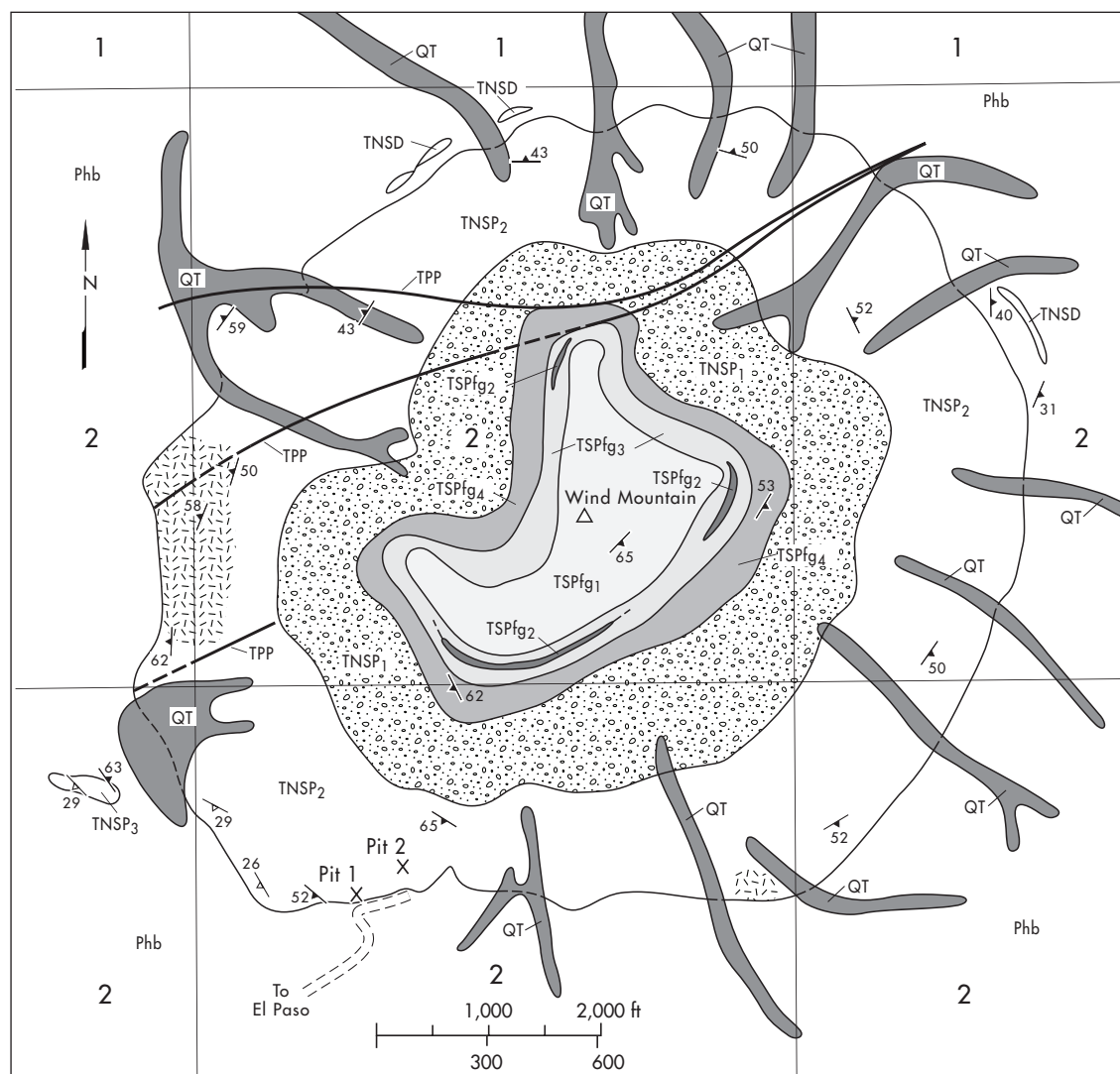
Additional mineral resource potential in the Cornudas Mountains is limited. Although the nepheline syenite of nearby Deer and San Antonio mountains may have potential for glass or ceramic use, the other laccoliths, dikes, plugs, and sills are not suitable for glass or ceramic use because of high iron contents and heterogeneous composition (Table 11).

Table Mountain, Oregon. Located in Lincoln County, this deposit is approximately 1 km² and 100 m thick and contains an estimated 700 Mt of nepheline syenite of 33.6 Ma. Light to medium gray (with a blue tint), it takes a good polish and contains nepheline, albite, analcime, aegirine-augite, olivine, riebeckite, and opaque minerals (Tatsumoto and Snavely 1969).

Other Deposits in the Rest of the World

Canaán, Brazil. About 40 km from the city of Rio de Janeiro is a 20-km² circular litchfieldite stock that intruded Precambrian quartzofeldspathic gneisses and migmatites and is surrounded by alkali syenite. The litchfieldite contains 55% microcline and perthite, 20% nepheline, 15% albite, and 10% biotite, and minor amounts of cancrinite, sodalite, corundum, zircon, pyrite, magnetite, and accessory minerals (Woolley 1987; Guillet 1994). Chemical analyses are in Table 12. In 1978, Austral Mineracao and Servicos Ltd. tested nepheline syenite in a pilot plant, but it did not go into production even though nearby markets were identified. Companhia Baiana de Pesquisa Mineral (CBPM) developed the deposit, which consists of 8.4 Mt of reserves that have to be magnetically separated, and then sold it to Unimin Corporation for production.

Gardar Alkaline Province, Greenland. This contains three nepheline syenite complexes: Ilimaussaq, 1,130 Ma (Paslick et al. 1993), Gronnedal-Ika, 1,300 Ma (Blaxland et al. 1978), and Igaliq bodies. Currently, mining companies are examining the potential for REEs, U, Zr, Y, and Nb (Steenfelt 1991). Ilimaussaq is an oval complex that shows an extensive fractionation trend from alkaline augite syenite to peralkaline agpaitic nepheline syenites (Markl 2001). Gronnedal-Ika consists of foyaites, which are overlain by a variety of alkaline rocks, including nepheline syenite. Igaliq consists of



Adapted from McLemore et al. 1996a, 1996b.

Figure 6. Geologic map of Wind Mountain, New Mexico

Table 12. Chemical composition of raw and processed nepheline syenite from Canaan, Brazil, %

Oxide	Raw	After Processing
SiO ₂	55.6	58.8
Al ₂ O ₃	22.9	23.0
Fe ₂ O ₃	3.5	0.1
CaO	0.8	0.6
K ₂ O	6.7	6.3
Na ₂ O	9.1	10.3
LOI	1.0	0.9
Total	99.2	100.0

Adapted from Guillet 1994.

four intrusions, each containing nepheline syenite: North Qoroq, 1,270 Ma (Blaxland et al. 1978), South Qoroq, 1,160 Ma (Blaxland et al. 1978), Motzfeldt, 1,350 Ma (Paslick et al. 1993), and Igdlertfigssalik, 1,170 Ma (Blaxland et al. 1978).

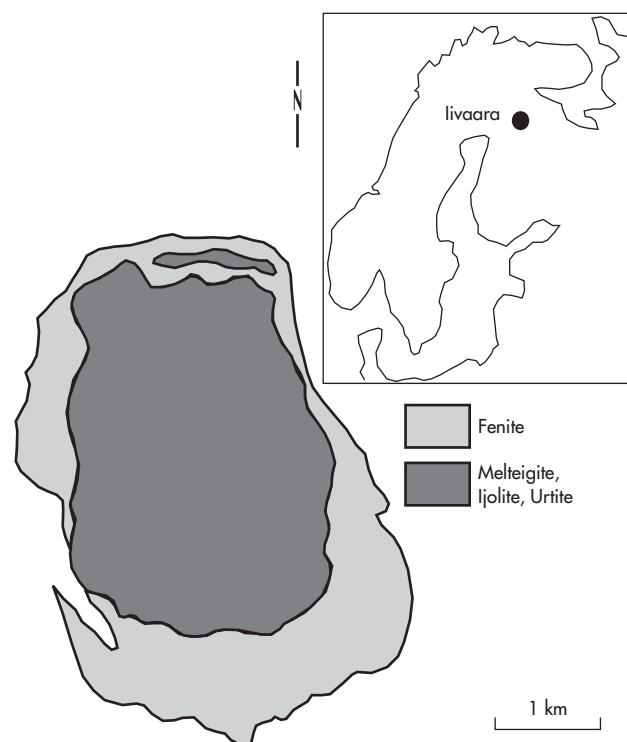
Loch Borolan (Borralan), Scotland. Near Ledmur, Sutherland County, a 26-km², 300-m thick laccolith consists of quartz syenite, nepheline syenite (also called borolanite), and ultrabasic rocks (Shand 1939; Notholt 1979; Waters 2003). Typical borolanite in the southeastern end of the laccolith, which is about 430 Ma, is dark gray. A chemical analysis is given in Table 5.

Iivaara Complex, Finland. An intrusive core, 8.8 km², of melteigites, urtites, and ijolites, is surrounded by 100 to 300 m of fenite (Figure 7). The complex, 367 to 373 Ma in age (Kramm et al. 1993), can be divided into three zones: (1) outer fenite; (2) transitional rocks; and (3) the main alkaline intrusion, which consists of mixed and interlayered nepheline-clinopyroxene rocks: urtite (>70% nepheline); ijolite (50% to 70% nepheline); and melteigite (<50% nepheline). Economic development is hampered by the remoteness of the deposit and high iron content.

Koga Complex, Pakistan. Local glass and ceramic companies in Pakistan are expected to replace feldspar with nepheline syenite from the Koga, Buner District, Swat Himalayas, North West Frontier Province (NWFP) (Bolger 1995). The Koga Complex, 300 Ma old, consists of a carbonatite plug within a nepheline syenite (including ijolite) intrusion that is surrounded by fenite (Tilton, Bryce, and Mateen 1998). Sarhad Development Authority began pilot mining about 1993 and plans a capacity of 28,571 tpy of enriched nepheline syenite. Approximately 8,571 tpy of high-iron nepheline syenite could be produced for use by the steel, foundries, and refractory industries in Pakistan.

Sichuan, China. The Sichuan nepheline syenite in Shuiyue town, Anyang, Henan Province, contains more than 100 Mt of homogeneous material developed by Fintan Industrial Minerals Ltd. of Hong Kong. Sichuan Nanjiang Nonmetal Industry Co., currently the only company mining nepheline syenite in China (Bolger 1995), has built a 35,000-tpy modular plant and is able to make products suitable for the glass and ceramic industries (Industrial Minerals 2003). Twenty-two other nepheline syenite deposits have been found in China; the more important ones are at Nanjiang, Guangdong Fogang, and Yunnan Gejiu (Bolger 1995).

Uludag Deposit, Turkey. Matel Hammed Sanve Tic AS produces nepheline syenite from the Uludag deposit near Bursa Orhanli for making floor tile (Crossley 2003). A mine opened in 1989 that continued production into 1995 (Bolger 1995). Reserves are estimated at more than 40 Mt. The Hamit nepheline syenite pluton, central Anatolia, Turkey, is dark gray-green, medium-grained, and occasionally porphyritic with alkali feldspar.



Adapted from Kramm 1994.

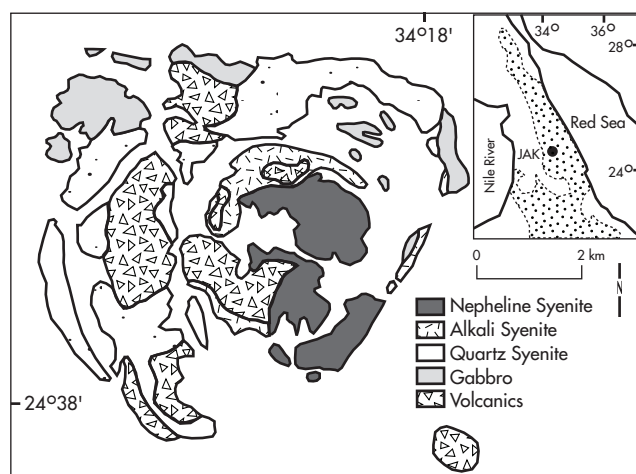
Figure 7. Geology of Iivaara, Finland

Norra Karr, Sweden. Examined for development of nepheline syenite, this complex consists of a variety of lithologies, including grennaite (fine grained, alkali feldspar, nepheline, aegirine, eudialyte, catapleite), lakarpite (arfvedsonite-albite-nepheline syenite), pulaskite, and kaxtorp (pectolite-eckermannite-aegirine-nepheline syenite) (Blaxland 1977). A chemical analysis is given in Table 5.

Elsewhere in Europe. Several deposits are scattered throughout Europe, but little information is known about them. Pyroxene foyaite is found at Pouzac, Pyrenees, France. Phonolite at Brenk, Eifel, in Germany has been mined for colored glass by Solvay Alkali GmbH (Bolger 1995). The Monchique nepheline syenite deposit in southwest Portugal was examined by Empresa de Desenvolvimento Mineiro SA in 1993. Because the deposit is high in iron, it would have to be magnetically separated (Bolger 1995). Keramos AS produces phonolite as a feldspar substitute from the Zelenice deposit in Mast, Czech Republic (Crossley 2003).

Iran. Kaleiber and Sarab nepheline syenite in the Alps and Himalayas in northern Iran is used for ceramics and glass and alumina (National Geoscience Database of Iran 2004).

Jabal Sawda, Saudi Arabia. Deposits range in composition from alkali-feldspar syenite to nepheline syenite and consist of perthitic alkali feldspar (60% to 90%) and nepheline (0% to 40%), with sodalite, very minor plagioclase, ferro-hastingsite, aegirine, augite, biotite, and opaque minerals. The K₂O content of the pluton ranges from 4% to 6%; the Na₂O content from 6% to 8%; and the FeO + Fe₂O₃ + MnO + MgO + TiO₂ content from 2% to 13% (Table 5; Liddicoat, Ramsay, and Hedge 1985). The deposits have undergone some bulk testing by Saudi ceramics companies and are currently under an exploration license granted to Maaden, the state mining company.



Adapted from Landoll, Foland, and Henderson 1994.

Figure 8. Geology of Jabal Abu Khuruq (JAK), Egypt

Jabal Abu Khuruq (Khuruq), Egypt. This nepheline syenite, approximately 130 km northeast of Aswan, was first studied from 1966 to 1969. It consists of an oval complex of ring dikes of alkalic syenite surrounding stocklike intrusions of nepheline syenite that were emplaced about 89 to 90 Ma (Figure 8; Hosterman, Patterson, and Good 1990; Landoll, Foland, and Henderson 1994). The nepheline syenites are divided into various types, including nepheline-bearing alkaline syenite, foyaite, and diorite (fine-grained, granular textured rock similar in composition to foyaite) (Landoll, Foland, and Henderson 1994).

The main deposit contains 26 Mt of nepheline syenite with an additional 40 to 50 Mt in other parts of the massif. The Russian National Aluminum-Magnesium Institute (VAMI) determined that the nepheline syenite, with an annual production of 100,000 t of alumina, would also yield 1.5 to 1.6 Mt of soda and 30,000 to 35,000 t of potash (Hosterman, Patterson, and Good 1990). A chemical analysis is given in Table 5.

Arroya Grande, Mexico. The Industria Penoles SA examined the Arroya Grande nepheline syenite near San Jose in the San Carlos Mountains for alumina. The nepheline syenite contains 60% orthoclase; 25% nepheline; 5% plagioclase; 1% augite; 8% magnetite; and 0.7% sphene (Hosterman, Patterson, and Good 1990). Associated rocks include diorite, pulaskite, phonolite dikes, and lamprophyres. The age is 27 to 29 Ma (Bloomfield and Cepeda-Davila 1973). Industria Penoles SA also investigated nepheline syenite for alumina at Ciudad Victoria, Tamaulipas (Minnes, Lefond, and Blair 1983).

Africa and Elsewhere. Several deposits are found in Africa, but little is known about them. Approximately 4.3 billion t of nepheline syenite, 538 Ma, have been estimated to occur in Meponda, Mozambique (Lulin et al. 1985). Several small, iron-rich nepheline syenite deposits have been mined for road material in South Africa. Deposits are also known to occur in Australia, Cameroon, Kirumba, Congo, Angola, and Lulwe Hill, Malawi.

TECHNOLOGY

Exploration Techniques

Because most nepheline syenite deposits are found in relatively shallow complexes of subvolcanic origin in well-defined rift-related continental provinces, and are associated with alkaline or carbonate complexes, these areas are favorable exploration targets. Many

nepheline syenite complexes form circular, zoned plutons, locally surrounded by fenite. Like many industrial mineral deposits, however, other factors must be considered in locating a commercial deposit, especially the proximity to potential markets and available inexpensive transportation.

Mineral exploration typically is expensive and can require 10 years or more of study before a decision is made to develop the deposit. Satellite images, remote sensing, geologic maps, geophysical studies, such as airborne gamma-ray spectrometry (Steenfelt 1991), magnetics, and gravity are useful in identifying regional alkaline provinces. Once the mineralized areas are identified, the explorationist conducts field examinations of the area. Detailed geologic maps are prepared to help characterize the rocks at the surface and to predict the types of rocks in the subsurface. Surface sampling, stripping, drilling and trenching, bulk sampling, and even panning are still used in the beginning phases of exploration. Samples are examined for favorable lithology and mineralogy and submitted to laboratories for chemical analyses. Petrographic studies are important in locating commercial nepheline syenite deposits. For instance, the use of cathodoluminescence can be used to identify the Fe^{+3} in feldspar, which typically characterizes an uneconomic deposit.

Despite the numerous exploration techniques available, ultimately the deposit must be drilled. Several drilling techniques are available that provide samples from depth of the potential deposit. In some cases, test or exploration pits or adits are dug in order to provide enough material for metallurgical testing or other purposes.

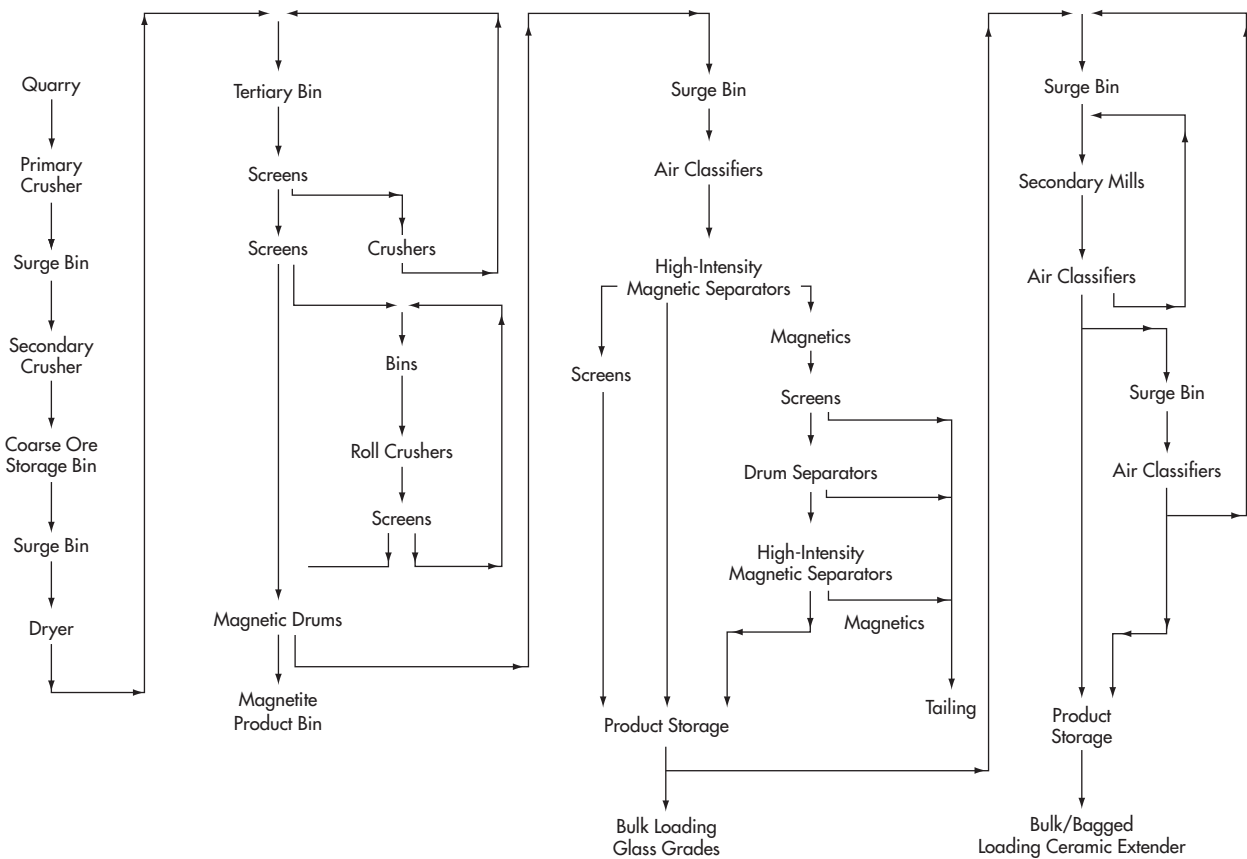
Mining

Nepheline syenite is normally extracted through standard open-pit or quarrying methods. The deposits are drilled and blasted and loaded on trucks with front-end loaders (Harben 2002). Mines in Norway and Russia also use underground methods. In Norway, underground room-and-pillar mining is employed, while, in Russia, block caving is used at a depth of 600 to 700 m. Rock mechanics research has shown that the optimum room size in Norway is 50 m long and 25 m wide. The underground deposits are drilled, blasted, crushed, and trucked via a spiral ramp (Harben 2002).

Processing

After the nepheline syenite is quarried, it is crushed, dried in rotary kilns, passed through flotation circuits and magnetic separators, and bagged or shipped in bulk (Moll 1996). Any iron must be removed from the finished product, especially for glass and ceramics use, by high-intensity magnetic separation. Fine-particle-size grades are separated by air classification. The raw material must have low moisture content for glass and ceramics use. A flow sheet is shown in Figure 9. Other uses of nepheline syenite can tolerate more iron in the finished product and typically require only crushing, screening, and sizing. In addition to the mines and processing facilities at Blue Mountain and Nephon, Unimin Canada has two plants near Toronto, which produce 15 to 20 grades of nepheline syenite. Chemical compositions of selected grades are shown in Tables 13 and 14. Of the 15 grades that North Cape Minerals (Unimin Corporation) produces in Norway, the three more popular products are glass-grade Altafloat, ceramics-grade Altaflux, and amber- and filler-grade Minex 10, 20, and 30 (Karlsen 1998). Glass grades are usually crushed to 600 μm , whereas ceramic and filler grades are finer than 75 μm (Moll 1996).

In Russia, nepheline syenite is used to produce aluminum (Figure 10). Where Al_2O_3 in nepheline syenite is more than 20%, $\text{Na}_2\text{O} + \text{K}_2\text{O}$ are less than 10%, and SiO_2 does not exceed 55%, nepheline syenite can be processed by sintering to produce alumina,



Adapted from Minnes, Lefond, and Blair 1983.

Figure 9. Production flow sheets for two milling plants at Blue Mountain, Ontario

Table 13. Typical glass-grade compositions of nepheline syenite, wt %

Chemical Composition	Unimin Canada A Grade	Unimin Canada B Grade	North Cape	
SiO ₂	60.2	60.1	55.9	
Al ₂ O ₃	23.5	23.4	24.2	
Fe ₂ O ₃	0.08	0.35	0.1	
MgO	trace	trace	trace	
CaO	0.3	0.3	1.3	
K ₂ O	5.1	4.9	9.0	
Na ₂ O	10.6	10.5	7.9	
P ₂ O ₅			0.1	
LOI	0.4	0.3	1.0	
Sieve Analyses, %	U.S. Sieve No.	U.S. Sieve No.	Tyler Sieve No., %	
On 25 mesh	0.0	0.0	On 28 mesh	0.0
30	0.1	0.1	32	0.1
40	14.5	14.0	53	4.9
50	48.0	46.0	48 30.0	
100	86.0	84.0	65	52.0
200	98.0	97.2	200	89.0
Pan	2.0	2.8	Pan	11.0

Adapted from Minnes, Lefond, and Blair 1983; Guillet 1994.

Table 14. Chemical analyses and physical properties of products from Nepton, Ontario

Properties	MATRIX Glassy Phase Promoters (Fiberglass) 131	MATRIX Glassy Phase Promoters (Fiberglass) 134	SPECTRUM Ceramic Fluxes
SiO ₂ , wt %	60.00	59.70	60.20
Al ₂ O ₃ , wt %	23.40	23.40	23.60
Fe ₂ O ₃ , wt %	0.1	0.34	0.08
CaO, wt %	0.44	0.56	0.35
MgO, wt %	0.02	0.03	0.02
Na ₂ O, wt %	10.30	10.30	10.50
K ₂ O, wt %	5.20	5.10	4.80
LOI, %	0.51	0.61	0.42
Free-silica content	<0.1%	<0.1%	<0.1%
pH	10.1	10.1	10.1
Melting point	1,868°F/1,020°C	1,868°F/1,020°C	1,868°F/1,020°C
Bulk density, loose	83–87 lb/ft ³	83–87 lb/ft ³	38–55 lb/ft ³
Specific gravity	2.61 g/cm ³	2.61 g/cm ³	2.61 g/cm ³

Adapted from Unimin Corp.

materials, riprap, and asphalt (Allen and Charsley 1968). Fines are used as a colorizing and fluxing agent in the manufacture of brick and as compaction fill.

Dimension Stone, Abrasive, Aggregate, and Other Uses

Nepheline syenites that have a pleasing appearance, can take a polish, and are relatively homogeneous without fractures can be used as a dimension stone. Many places use crushed nepheline syenite for aggregates. Other uses are as a mild abrasive for sand blasting, as welding fluxes in welding electrodes, and for extrusion and binding of coating fluxes.

Alumina

A significant amount of nepheline syenite is used in the manufacture of alumina and aluminum metal. Russia produces most of its aluminum needs from nepheline syenite because of the high alumina content in nepheline syenites. Several other countries also have examined nepheline syenite deposits for the purpose of manufacturing alumina and aluminum metal, but none have obtained the success of the Russians.

MARKETING

Consumption

Glassmaking is the major use for Canadian and Norwegian nepheline syenite, consuming approximately 70% of both countries' production. In addition, 28% of Norwegian output went to ceramics and 2% to filler. The Canadian mines supply approximately 15% of their additional output for ceramics and the balance for filler applications (Ciullo 1996). Most of the Russian production is for local manufacture of aluminum.

Exports

Canada and Norway are major exporters of nepheline syenite (Table 16), while the United States is one of the predominant importers (Table 17). Most of the remaining nepheline syenite production in the world is for local use. There are no reported exports of nepheline syenite from Russia.

Prices

Comparative price information is not readily available in today's competitive market for raw materials. Canadian nepheline syenite production was valued at C\$86.56/t in 2000 and has remained essentially flat over the last 5 years but is now more than double the 1992 price (Rogers 2002). Harben (2002) quoted prices as low-iron, 30-mesh, glass grade at C\$22/t; a higher-iron, colored-glass grade at C\$20 to C\$21/t; ceramic grade, 200 mesh, at C\$58 to C\$62/t; and bagged filler at C\$67 to C\$135/t.

Transportation and Distribution

As with many industrial minerals, transportation is critical to the competitiveness of a nepheline syenite deposit, and changes in transportation costs can make or break an operation. Most glass-grade nepheline syenite is sold in bulk and shipped by rail, with some truck haulage. For its product, Unimin Canada Ltd. leases hopper cars exclusively to a void contamination (Guillet 1994). Ceramic-grade nepheline syenite is bagged and shipped by rail or truck. Although all of the nepheline syenite from Norway is shipped by barge, transportation in other countries can be truck, rail, or barge.

Alternative Materials

For glass and ceramic uses, feldspar is the predominant competitor for nepheline syenite, although aplite and quartz-feldspar sands can

Table 15. Summary of feldspar and nepheline syenite performance in coatings

Dispersibility	Very good
Oil absorption/resin demand	Low
Chemical resistance	High
Weatherability	Very good
Tint strength	Low
Color development	Very good
Tint retention	Very good
Sandability (primers)	Poor
Chalking	Very good
Frosting	Very good
Abrasion resistance	Very good
Scrub resistance	Very good
Stain resistance	Very good
Mildew resistance	Very good

Adapted from Cuillo and Robinson 2003.

Table 16. Exports of nepheline syenite from Canada

Region	Value of Exports, 1995, C\$	Value of Exports, 2001, C\$
United States	37,292,000	43,903,000
Europe	943,000	1,916,000
Japan	483,000	1,109,000
Mexico	71,000	79,000
Other	3,520,000	4,371,000
Total	42,309,000	51,378,000

Adapted from Mining Association of Canada 2002.

be used in some cases. The choice between feldspar and nepheline syenite in glass and ceramics is tied to price, which is dependent on location and transportation costs. In U.S. markets, feldspar sources in Georgia and North Carolina and aplite in Virginia compete successfully with nepheline syenite. Increasing use of plastic containers will affect the use of glass and result in less demand for raw materials. A variety of alternative materials can be substituted for nepheline syenite in pigment and filler uses: calcium carbonate, kaolin, feldspar, silica, and talc. Most of the aluminum production in the world is from bauxite and recycling.

ECONOMIC OR COMPETITIVE FACTORS

Strong growth in the production of ceramics, particularly in Italy, Spain, and China, has been the main driver of the steady rise in nepheline syenite and feldspar demand over the past 20 years. Sales of flat glass and insulation-grade fiberglass are dependent on the health of the construction industry. When the construction industry is booming, demand for flat glass and fiberglass rises; when the industry is in recession, demand drops. A positive factor for nepheline syenite, processed or raw, is that it enters the United States and most countries free of tariffs, except for some countries that may levy value-added taxes (Minnes, Lefond, and Blair 1983; Guillet 1994). On the down side, energy costs have increased since 1999 and added as much as 20% to the cost of production (Rogers 2002). Starting in 2000, energy surcharges were instituted to recover the added costs due to increased energy costs.

Table 17. Imports of nepheline syenite for consumption in the United States

	1998	1999	2000	2001	2002
Imports, t	320,000	311,000	356,000	336,000	333,000
Value, US\$	24,100,000	23,200,000	24,800,000	24,100,000	26,100,000

Adapted from Potter 2001, 2002.

Also, recycling is reducing the need for raw materials. Approximately 34% of all glass containers produced are recycled; most bottles and jars contain 25% recycled glass (Rogers 2002). Ceramic recycling, however, is not significant in the North American market.

Regulatory and Environmental Concerns

Increasing pressure is being applied to the glass industry to reduce the use of glass products in order to reduce litter and municipal waste. In some areas, glass recycling, the reuse of glass containers, and use of alternative materials such as plastic are increasing.

Because its tailings are typically small and nontoxic, nepheline syenite operations pose no threat to the environment. Locally, dust can be a problem, which is easily controlled.

Classified as a Class 2A probable carcinogen in 1997 and as a Class 1 carcinogen in 1999, crystalline silica is becoming a serious health concern for feldspar and aplite producers. Since nepheline syenite is devoid of free silica, many nepheline syenite deposits that are not necessarily suitable for glass or ceramic production are being examined for potential abrasives uses.

OUTLOOK AND FUTURE TRENDS

For the near future, known resources of nepheline syenite are adequate to meet projected world demand. Competition between the major companies will remain high as a result of relatively low growth and low demand, and the price will probably remain flat, continuing a 5-year trend. It is possible, however, that increased ceramics production in Italy, Spain, Brazil, China, and Mexico could result in more demand for nepheline syenite. Clayworld now offers an iron-bearing nepheline syenite that has an established record of performance in the gres tile industry. Another factor is the housing market, which remained relatively robust throughout 2002 but is expected to slow in the near future. This trend could reduce demand for nepheline syenite and other raw materials for applications such as sanitary ware and ceramic tile. Increased use of plastics also could lower the demand for glass and ceramics.

Although increased glass recycling will result in a lower demand for nepheline syenite, glass manufacturers that use recycled materials are still confronted with incompatibility, inconsistency, and contamination issues. By mid-2002, many glass companies were predicting higher sales for the near future, boosted by increased beer and wine sales, as well as the introduction of new ready-to-drink low-alcohol "refreshers."

Container glass, which uses more feldspathic materials than other sectors of the glass industry, is facing strong competition from other forms of packaging. The positive environmental image of glass over other forms of packaging, particularly polyethylene terephthalate (PET) bottles, however, has helped glass to recover some of its lost market share.

Sales of flat glass and insulation-grade fiberglass are dependent on the health of the construction industry—in both the commercial construction and new housing sectors—and on the automobile industry. In Asia, flat- and fiberglass industries were severely affected by the fall in demand resulting from the Asian financial crisis of 1997–1998. In Europe and the United States, flat-

glass production continued to rise in the 1990s but stagnated in 2000. The strong competition between producers for the major ceramics markets of Italy and Spain is likely to keep European feldspar prices low, and the development of a potential new project in Egypt will probably have a negative effect on European prices. In the Far East, the development of the very large Chinese feldspar industry to support domestic demand and exports will exert a downward pressure on markets.

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Nitrogen and Nitrates

Peter W. Harben and Carlos Theune

INTRODUCTION

Historically, deposits of guano or the waste from slaughterhouses and fish-processing plants have been used as crude fertilizers worldwide, and in northern Chile, natural nitrates have been used as fertilizer since the pre-Hispanic times of the Incas and the Atacama people. Chile remains the world's sole producer of natural nitrates. Modern exploitation of caliche deposits of natural sodium nitrate (*salitre*, saltpeter, nitratine, or simply natural nitrate [NaNO_3]) in the Atacama Desert began around 1830, although minor artisan exploitation is reported as early as 1810. The main use at that time was in the manufacture of gunpowder, with minor application as a fertilizer. Early in the eighteenth century, the territories containing nitrates belonged to Bolivia and Peru, but mainly Chilean, British, and German enterprises exploited the nitrates. After almost 40 years of disputes, a war between Chile and the alliance of Bolivia and Peru (Pacific or Saltpeter War), from 1879 to 1883, ended with Chile retaining all territories of the Tarapacá and Atacama regions (18°30' to 25° latitude south) and the establishment of definitive borders between Peru, Bolivia, and Chile.

Saltpeter became by far Chile's most important commercial enterprise for more than 100 years, peaking in 1912, when some 170 nitrate operations employed as many as 46,500 workers. Total saltpeter production from 1830 to 1929 was 90 Mt (95% NaNO_3) based on the mining of 1.13 billion t of caliche ore over a total surface of 5,000 km². Despite this prodigious production rate, the supply from Chile soon fell short of the growing demand for nitrogen products to be used in explosives, nylon, plastics, resins, and intensive agriculture, forcing the search for a large-scale replacement. Given that the earth's atmosphere consists of about 79.1% nitrogen by volume, 20.9% oxygen, 0.036% carbon dioxide, and trace amounts of other gases, extraction from the air was an obvious potential nitrogen source. What evolved was the fractional distillation of liquid air or natural gas to produce synthetic ammonia (NH_3) through the Haber-Bosch process (described later in this chapter). Cheaper synthetic ammonia production hit the saltpeter industry hard, and the world recession of 1929 was the final blow to the Chilean saltpeter industry. Although the María Elena and Pedro de Valdivia operations were built in 1925 and 1931, production of *salitre* remained at 1,000 ktpy until the late 1970s. The saltpeter industry revived in 1988, however, when the former state-owned Sociedad Química y Minera de Chile was privatized and evolved into SQM, the world's main producer of natural nitrates.

PRODUCTION AND TRADE

Ammonia

At approximately 150 Mtpy of contained N (as anhydrous ammonia), the modern production of nitrogen is dominated by the synthetic variety; just 1 Mtpy comes from natural nitrate production. Since the 1970s, new synthetic nitrogen fertilizer production has centered on natural-gas-rich countries of the Caribbean and Middle East plus several large consumers such as China, India, Indonesia, and Pakistan. The main producing regions are China with 22% of world production, North America with 18%, the former U.S.S.R. with 10%, Western Europe with 11%, Central Europe with 5%, South Asia with 15%, and the Near East with 5%. More than 80 countries produce 100+ Mtpy of contained N as anhydrous ammonia. More than half of the 11.5 Mtpy exported comes from Russia (22%), Trinidad and Tobago (14%), Ukraine (11%), and Canada (7%), and the major importers are the United States (31%), Western Europe (30%), and Asia (20%). Of the 43 Mtpy of contained N produced as urea, China and India account for 43%, and the United States and Canada a further 11%; about one quarter of 10 Mtpy exported comes from Russia/Ukraine and the Middle East, and almost 50% of imports go into Asia. A feature of international trade in fertilizer materials is the increased popularity of urea and the ammonium phosphates because of their high nutrient concentration.

Natural Nitrates

The primary product obtained from caliche is NaNO_3 , which in turn is processed to potassium nitrate (KNO_3) and specialty blends containing phosphates, sulfates, borates, and other nutrients. This makes it difficult to trace trade figures back to processed ore and obtained *salitre*, so in the tables in this chapter, total f.o.b. (free on board) value is much more relevant than tonnage.

As of 2004, three companies produce saltpeter and mixed fertilizer in Chile: SQM Holding, which includes SQM, SOQUIMICH Comercial (produces mixed fertilizers), and PCS Yumbes (formerly Miñera Yolanda); Compañía de Salitre y Yodo de Chile (COSAYACH); and ACF Minera. Exact figures are unavailable, but almost a fourth of total Chilean saltpeter production is for internal consumption.

Table 1 shows how Chilean exports of natural nitrates and specialty fertilizers have been steadily growing.

Table 1. Chilean nitrate exports, 2000–2003

Exporter	HTS Code	Product	2000		2001		2002		2003	
			Quantity, t	f.o.b., million US\$	Quantity, t	f.o.b., million US\$	Quantity, t	f.o.b., million US\$	Quantity, t	f.o.b., million US\$
SQM Holding	31025000	NaNO ₃	197,936	32.8	193,867	35.1	148,388	25.9	189,122	33.7
	28342100	KNO ₃	342,077	85.4	391,484	92.9	322,922	76.0	476,795	116.1
	31059010	Na+KNO ₃	160,929	30.3	191,945	31.1	226,403	42.3	218,518	39.5
	31059090	NKS type	55,328	11.1	54,690	12.5	45,749	15.3	42,470	10.2
	31054000	NPK type	5,563	2.3	4,295	1.8	10,568	3.2	7,460	3.6
PCS Yumbes (formerly Minera Yolanda)	31025000	NaNO ₃	0	0.0	0	0.0	1,521	0.2	0	0.0
	28342100	KNO ₃	5,093	1.3	50,717	12.9	70,689	15.7	40,340	8.9
	31059010	Na+KNO ₃	0	0.0	0	0.0	0	0.0	0	0.0
	31059090	NKS type	0	0.0	0	0.0	0	0.0	0	0.0
	31054000	NPK type	0	0.0	0	0.0	0	0.0	0	0.0
COSAYACH	31025000	NaNO ₃	0	0.0	0	0.0	1,456	0.2	2,621	0.4
	28342100	KNO ₃	0	0.0	311	0.1	15,995	3.4	19,829	4.8
	31059010	Na+KNO ₃	0	0.0	0	0.0	0	0.0	42	0.0
	31059090	NKS type	0	0.0	0	0.0	4,856	1.2	16,266	4.0
	31054000	NPK type	0	0.0	0	0.0	0	0.0	0	0.0
Total Chile				163.3		186.2		183.6		221.2

Table 2. Destination of Chilean nitrate exports 2000–2003

Destination	2000, %	2001, %	2002, %	2003, %
Latin America	36.0	20.4	36.4	32.1
Europe	29.6	30.2	24.7	27.0
United States and Canada	18.0	25.2	23.3	21.6
Australia and Asia	15.9	20.3	11.5	15.0
South Africa	0.5	3.9	4.1	4.4

Table 2 shows that the world distribution of Chilean nitrate exports during 2000–2003 remained well balanced, in terms of f.o.b. value.

GEOLOGY

Natural nitrate ore in Chilean caliche occurs in three basic forms:

1. A mixed rock alluvial conglomerate (boulders to clay size) cemented by a mixture of salts
2. Salts filling basement rock (mostly volcanics) fractures and pores
3. Salts filling interstitial space between rock debris on the surface near piedmont layers

Commercially relevant is the conglomerate type, although fracture filling can reach grades of over 60% NaNO₃, but of restricted potential.

A standard section of a current mining face is shown in Figure 1.

Overburden (*chuca* or *chusca*) is commonly a friable desert dust, mainly built up by sulfates and silt. *Costra*, a conglomerate firmly cemented by clays and salt (NaCl), underlies it. In a graded transition below the *costra* is *caliche*. It is petrographically very similar to *costra*, but the cement in *caliche* is a salt mixture containing chlorides, nitrates, sulfates, iodates, borates, and other curiosities such as chromium salts. The bedrock, a similar conglomerate to *caliche*, is called *coba* if uncemented and *conjelo* if cemented. The transition is mostly graded.

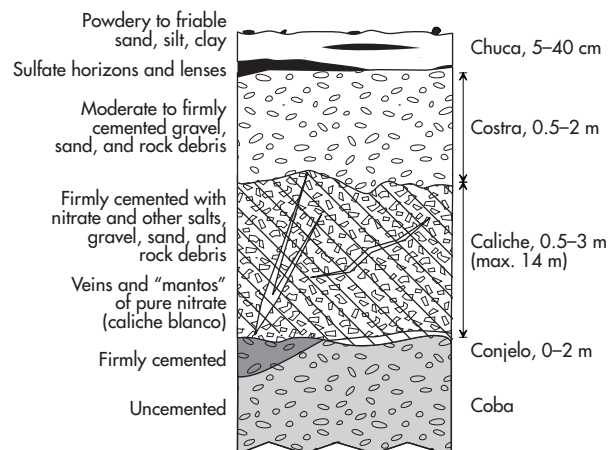


Figure 1. Standard stratigraphical section of a caliche deposit

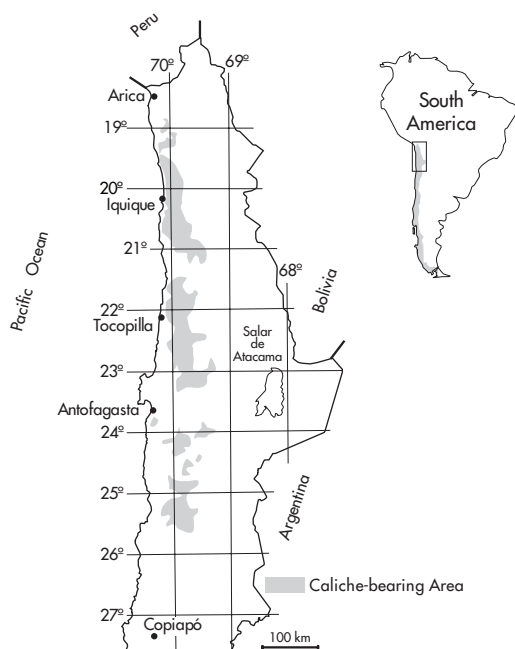
In general, the *caliche*—which is 1–2 m thick and white, brown, or black—consists of a variety of minerals, including nitrate (up to 40%), saltpeter (up to 17%), bloedite, glauberite, polyhalite, darapskite, lautarite, and dietzeite. Table 3 gives the weight percentages for common chemicals used in nitrate production.

Natural nitrate in economic concentrations occurs only in the Atacama Desert of northern Chile, one of the driest areas of the world (see Figure 2). *Caliche*-bearing areas are found within the central depression (central graben), between the coastal range and the pre-Andean range (see Figure 3).

Caliche ore deposits cover 2.8 million hectares in north-central Chile, and SQM holds the right to explore or exploit the mineral resources over roughly 60% of this area. This area contains an estimated 75% of Chile's *caliche* ore reserves. The total *caliche* potential of the Atacama Desert is unknown but is estimated to be several billion tons. In June 2003, SQM published the reserves information shown in Table 4.

Table 3. Weight percentages for common chemicals used in nitrate production

Chemical Name	Chemical Formula	wt %
Sodium nitrate	NaNO_3	6.5–8.5
Sodium chloride	NaCl	4–10
Sodium sulfate	Na_2SO_4	10–18
Calcium	Ca	0.5–4
Magnesium	Mg	0.3–1.3
Potassium	K	0.3–1.5
Potassium perchlorate	KClO_4	0.025–0.034
Borax	$\text{Na}_2\text{B}_4\text{O}_7$	0.4–0.6
Iodates (as iodine)	I_2	0.03–0.06
Lithium sulfate	Li_2SO_4	0.027 (approximate)
Water	H_2O	1–2

**Figure 2. Carlos Theune (left) and Peter Harben (right) observing a typical nitrate-bearing pampas****Figure 3. Geographic distribution of Chilean nitrates****Table 4. SQM's caliche reserves (as of December 2002)**

Mining Area	Proven			Probable		
	t	NaNO_3 , %	I_2 , ppm	t	NaNO_3 , %	I_2 , ppm
Pedro de Valdivia	119.7	7.1	354	300.3	6.9	444
	134.6	7.3	400	469.5	7.2	375
	74.8	6.2	500	582.0	6.5	471
	37.5	3.6	521	19.2	4.8	489
	4.6	6.2	484	234.3	6.9	524
	139.2	7.6	403	93.6	8.0	364
	510.4	6.9	414	1,698.9	6.9	441

TECHNOLOGY

Exploration Techniques

The main exploration techniques for natural nitrate are pitting and drilling, although some research has been done on geophysical methods. Grade and thickness distribution is irregular, requiring drilling patterns up to 400×400 m in the preliminary exploration stage. For evaluation purposes, the pattern is narrowed to as small as 50×50 m.

Although air reverse drilling (using a 5/4-in. tricon bit tool) has shown to be the most cost-efficient technique, grades must be checked by a few pit samplings. It seems that part of the nitrate salts are still blown out as fines through the annular rig space, thereby lowering the true grade. It is a quite complex problem because the difference is related to the drilled depth, so that the deeper the sample the lower the grade difference. It is advisable to elaborate grade correction curves adapted to a given exploration area. Drilling equipment should be mounted on a light all-wheel-drive truck, because the chusca surface can be extremely sticky.

Commonly, samples are taken every meter. The ignition test (Pavilo or Mecha) has proved to be very reliable in detecting where nitrate mineralization ends. This test involves scattering some of the milled sample (or drill dust) over an incandescent cotton rope; if the sample contains nitrates, it sparkles—the denser the sparkling, the higher the nitrate contents.

Nitrate Mining and Processing

Open-pit mining (called *rajos* in Chile) using dragline and power shovels yields an ore comprising 6.5%–8.5% NaNO_3 ; 4%–10% NaCl ; 10%–18% Na_2SO_4 ; 2%–7% Mg , Ca , K , B , and I ; 1–2% H_2O ; and 53%–69% gangue.

Processing is via the closed-circuit Guggenheim method: countercurrent leaching of crushed caliche ore in big vats with a heated leaching solution (at about 40°C), mainly composed of mother liquor from the nitrate crystallization plant, weak brines generated in the washing stages of the leaching cycle, and fresh water, to selectively dissolve out the sodium nitrate. On cooling, the sodium nitrate crystallizes out and is separated by a centrifuge, leaving the mother liquor to be recycled to the leaching vats.

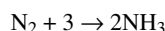
SQM mines about 30 Mtpy of caliche ore from surface mines at Pedro de Valdivia, María Elena, Pampa Blanca, and Nueva Victoria. Typically, the caliche ore is found under a layer of overburden material that is between 0.5 and 1.5 m thick, in seams that are between 0.2 and 5 m thick. SQM processes the caliche ore at Pedro de Valdivia, María Elena, Pampa Blanca, and Nueva Victoria. At the first two production facilities the caliche ore is mechanically crushed to approximately a half inch (12 mm) in diameter, and the crushed ore is then transferred to nearby leaching vats. The crushing process

also produces fines (25%–30% by weight, including those coming from the mine) that after screening are leached separately from the crushed ore. The resulting solution is used to produce sodium nitrate, potassium nitrate (by reaction with potassium chloride at Coya Sur), iodine, and sodium sulfate.

At Pampa Blanca and Nueva Victoria, the caliche ore is heap leached without crushing. Leachates from both operations are treated for iodine extraction. At Pampa Blanca, the waste solutions from the iodine plants are transferred to solar ponds where rich nitrate salts are crystallized. After dry harvesting, the nitrate salts are hauled to Coya Sur to be used in the production of potassium nitrate.

The Haber–Bosch Process

In the Haber–Bosch process (named for its developers Fritz Haber, a German academic chemist, and Carl Bosch, an industrial colleague), natural gas (mainly methane [CH_4]) is compressed to 300–600 psi and desulfurized; in the presence of nickel catalysts at 815°C , the gas reacts with high-pressure steam to yield process gas, a mixture of hydrogen, carbon dioxide, and carbon monoxide. The process gas enters a secondary reformer containing nickel catalysts and injected compressed air; the oxygen in the air is consumed in exothermic reactions with hydrogen, carbon monoxide, and residual methane from the primary reformer. The gas contains sufficient nitrogen from the injected air for ammonia synthesis. The process gas reacts with steam to produce additional hydrogen and converts the carbon monoxide to carbon dioxide, which is separated as a by-product. Traces of carbon dioxide and carbon monoxide are removed by methanation, yielding pure hydrogen. The remaining gas mixture, or “synthesis gas,” consists of hydrogen and nitrogen in the correct ratio for ammonia synthesis, which takes place at high temperature and pressure and over a catalyst of iron oxide promoted by aluminum oxide, with potassium, calcium, or magnesium oxide.



The production of 1 ton of anhydrous ammonia containing 82% ammoniacal nitrogen (NH_3^+) requires 680,000–708,000 m^3 (24–25 MCF) natural gas feedstock and 425,000–453,000 m^3 (15–16 MCF) process gas. This ammonia is the starting point in the production of a range of nitrogen compounds that includes anhydrous ammonia, ammonium nitrate, urea, and ammonium sulfate.

The Haber–Bosch process is arguably one of the most important technological innovations of recent centuries (Smil 2000), and it helped Fritz Haber win a Nobel Prize for his work with nitrogen.

MARKETING

Fertilizer Uses

Fertilizers dominate the consumption of nitrogen compounds, and a diverse range of industrial uses makes up the balance. Nitrogen, a component of RNA and DNA, the genetic blueprints of life, is a primary nutrient (along with phosphorus and potassium) that encourages vigorous plant growth and increases yield. Nitrogen is the most widely used fertilizer nutrient, ahead of phosphorus and potassium. Cereals are estimated to account for 55% of fertilizer use worldwide in the following amounts: wheat (20%); corn (14%); rice (13%); barley (4%); oilseeds such as soybeans, oil palm, sunflower, linseed, and others (12%); pasture and hay at 11%; and vegetables, sugars, roots and tubers, and fibers each consuming 4%–5%. Plants take up elemental nitrogen only in the soluble nitrate or ammonium form (i.e., chemically bonded or fixed nitrogen).

Industrial Uses

Industrial sodium nitrate is used in a variety of industries where it is most often employed as an oxidizer. The main uses are as follows:

- **Adhesives:** used in starch formulations of water-soluble adhesives, wallpaper, and gummed tapes.
- **Ceramics:** used as a fluxing agent in enamel frit.
- **Charcoal briquettes:** added to a mixture of wood by-products, starch, and lignite to promote ignition and burning. The amount added depends on the type of wood and coal used, although it is typically 2%–3%. This market expanded rapidly during the 1980s and now probably stands at about 20,000–25,000 tpy.
- **Chemical compounds:** used as an oxidizer in pesticides, antifreeze, cement, and pigments, among others.
- **Explosives:** used as an oxidizer in water gel, slurry emulsion, and dynamite explosive formulations. Typical slurry explosives contain 10%–15% sodium nitrate, and dynamite can also contain sodium nitrate as an energy modifier.
- **Glass:** used as an oxidizer to remove impurities. Sodium nitrate also has a fluxing action that reduces the melting temperature, which in turn saves energy or improves throughput.
- **Health and nutrition:** used in the production of antibiotics and pharmaceuticals, and as a preservative in curing beef, bacon, and other meats.
- **Metallurgy:** used in heat-treatment salt baths where it changes the metallurgical structure to improve such mechanical properties as hardness and tensile strength. Sodium nitrate is used in the treatment of aluminum alloys, and in secondary refining (recycling), it is used to soften lead and to reduce impurities such as arsenic, antimony, and tin.
- **Water treatment:** used to supply oxygen to control and prevent hydrogen sulfide formation in wastewater that contains organic matter. Sodium nitrate can be used as an ingredient in water-softening agents and as an anticorrosive agent in boiler water.

All indications are that industrial sodium nitrate usage will continue to decline as more companies experiment with new non-industrial sodium nitrate batches. In broad terms, however, there is no one-to-one substitute for industrial sodium nitrate. The compound has unique characteristics that can only be partially replaced by other materials such as calcium nitrate, sodium sulfate, and ammonium nitrate. Although a direct replacement is not readily available, combinations of other batch materials can make replacement of industrial sodium nitrate possible, although these changes require lengthy testing and production changes. For the most part, many of the current users of industrial sodium nitrate have not been shocked enough by price or supply concerns to make the move to replace sodium nitrate. Only the glass industry has a real incentive to eliminate industrial sodium nitrate consumption to reduce oxides of nitrogen (NO_x) emissions.

The industrial market for potassium nitrate is fairly significant when compared with its overall consumption. The major industrial market is the color television (TV), lead/crystal, optical, and electronic glass markets. In TV glass, potassium nitrate is used in conjunction with potassium carbonate as required sources of K_2O needed for properly fluxing cathode ray tube glass in the presence of barium and strontium oxides, which are incorporated to screen out the x-rays generated. The ratio of nitrate to carbonate depends on the relative K_2O unit price between the two, and the limit of NO_x emissions allowed. Traditionally, this ratio has been about 1:3.

TV glass represents about 80% of total glass consumption of potassium nitrate. As a strong oxidizing agent, potassium nitrate is used in the manufacture of explosives and fireworks, and is also employed in making frits and in heat-treating steel and other metals.

Product Grades and Specifications

Ammonia-Based Products

One of the principal commercial forms of nitrogen is ammonia (NH_3), a colorless, nonflammable, liquefied gas with a characteristic sharp, penetrating odor that is highly irritating to the mucous membranes and eyes (it is the active product of smelling salts). Ammonia is the simplest stable compound of nitrogen and hydrogen. It is the source of approximately 97% of nitrogen fertilizer, which is either applied directly to the soil or converted into ammonium nitrate, ammonium phosphate, and other nitrogen compounds.

In manufacturing, ammonia is used to produce synthetic fibers such as nylon and rayon, as a catalyst in the production of synthetic resins, and to prevent coagulation of raw latex rubber. It neutralizes acidic by-products of petroleum refining and has metallurgical applications such as nitriding alloy sheets. Ammonia is a critical part of the ammonia-soda (Solvay) process to produce soda ash, and it is a portable source of hydrogen for welding. The pungent smell of ammonia is common in many household cleansers. Because ammonia is easily liquefied by compression or by cooling to about -33°C and because it absorbs substantial amounts of heat from its surroundings when returning to the gaseous state, it is used as a coolant in refrigerating and air-conditioning equipment. The polarity of NH_3 molecules and their ability to form hydrogen bonds help make ammonia highly soluble in water, forming an alkaline solution of ammonium hydroxide with its characteristic alkaline (basic) properties and ability to combine with many chemicals.

Ammonia serves as a starting material for the production of many commercially important nitrogen compounds. One of the most important is urea, $\text{CO}(\text{NH}_2)_2$, formed when ammonia is treated with carbon dioxide at $132^\circ\text{--}182^\circ\text{C}$ under high pressure; it is used as a direct application fertilizer (46-0-0) or in urea-ammonium nitrate (UAN) solutions, in animal feed, in urea-formaldehyde resin and melamine production, in textile treatment, and in pharmaceuticals. An important form of nitrogen derived from ammonia is monoammonium phosphate, $\text{NH}_4\text{H}_2\text{PO}_4$, or MAP (11-48-0), and diammonium phosphate, $(\text{NH}_4)_2\text{HPO}_4$, or DAP (18-46-0). Its main use is as a fertilizer; it is also used as a food additive.

Ammonia is treated with various mineral acids to produce critical ammonium chemicals. Ammonium nitrate, NH_4NO_3 (33.5-0-0), manufactured from nitric acid, is used in explosives such as ammonium nitrate and fuel oil (ANFO) and nitroglycerine, in the manufacture of glass and frit, as an ingredient in charcoal briquettes, in metal treatment, in water treatment, and as a feedstock in the manufacture of adipic acid, nitrobenzene, and toluene diisocyanate. Ammonium sulfate, $(\text{NH}_4)_2\text{SO}_4$ (21-0-0), from sulfuric acid, is used as a direct application fertilizer, in a blended nitrogen fertilizer containing 24% sulfur, as a fire retardant, in the manufacture of viscose rayon, and as a chemical feedstock. Most ammonium sulfate is a by-product of the production of caprolactam (the intermediate for nylon 6 fiber and plastics), the removal of ammonia from coking coal in the steel industry, and the Sedema process of chemical manganese dioxide production. Ammonium chloride, NH_4Cl , or ammoniac salt, is produced from hydrochloric acid; it is used in galvanizing and soldering fluxes, as an electrolyte in zinc-graphite dry-cell batteries, and in the preparation of alkaline cleansers. Other chemicals derived from ammonia or its derivatives include calcium nitrate, ammonium dichromate, hydrazine and sodium cyanide,

nitric acid, antimony nitrate, cyclohexanone, magnesium nitrate, manganese nitrate, nitrobenzene, nitroglycerin, nitrophosphates, and trinitrotoluene.

Caliche Ore-Based Products

The caliche ore mined in Chile is used as a feedstock in the manufacture of sodium nitrate (16-0-0), sodium potassium nitrate (15-0-14), and prilled (13.5-0-44) and standard potassium nitrate (13.5-0-45); in numerous blended specialty fertilizers used for higher value crops such as vegetables, tobacco, fruits, cereals, sugar beets, and cotton; and for hydroponics or greenhouses. Fertilizer based on 100% nitrate nitrogen is virtually chloride free and slightly alkaline, easy to handle, nonhygroscopic, and 100% water-soluble, making it suitable as a fast-nutrient-release fertilizer. It is reported to help alleviate prolonged greenness and delayed curing in tobacco and to reduce the risk of late season growth, boll shed, and insect damage in cotton. It encourages early maturity, high yields, increased storage life, and transit qualities in vegetables, and it improves the sugar content and facilitates the uptake of Ca, Mg, and K in citrus fruit.

Sodium nitrate, which contains 16% nitrogen and 2.6% sodium plus trace elements such as boron and magnesium, is fully water soluble, making it suitable as a fast-nutrient-release fertilizer. It contains 100% nitrate nitrogen, which is available for root uptake without chemical transformation and can supply the sodium requirements for many crops where the sodium can replace part of the plant's potassium requirement, thereby reducing costs. Sodium nitrate is used, for example, as a quick-acting top-dress nitrogen fertilizer, which strengthens crops and increases their resistance to pests and disease. The main market for sodium nitrate, however, is industrial; it acts as a secondary oxidizer in slurry water gel, emulsion, and dynamite formulations; aids in the removal of glass batch impurities where fine oxidizing conditions are necessary; contributes to steel tempering, heat treatment of aluminum alloy, and the annealing of copper; and acts as a scavenger for secondary lead and as a food additive to preserve color and inhibit botulism.

Potassium sodium nitrate, containing 15% nitrogen as nitrate and 14% chlorine-free potassium, has a high solubility and a slight alkaline reaction in soil. It is quick acting and chlorine-free, and has a balanced nitrogen and potassium ratio of 1:1. Prilled potassium sodium nitrate is used for sidedressing tobacco, vegetables, fruits, and flowers, and for topdressing small grains in early spring.

NPK Specialty Blend fertilizers (produced by SQM) are bulk-blended mixtures with part or all of their nitrogen as nitrate, chlorine-free potassium, and optional secondary or minor element concentrations. These products are manufactured on demand specifically for crops that are sensitive to ammonia or chlorine in the soil. These blends—SQM produces more than 200—are used as base fertilizers during planting of crops such as potatoes, vegetables, and tobacco and as a sidedressing for citrus, coffee, etc.

Packaging

In general, fertilizers are sold in bulk to large farms or agro-companies and in 50- or 25-kg (100-lb or 50-lb) plastic bags to smaller consumers. Potassium nitrate destined for domestic fertilizer usage in the United States is generally shipped bulk in 100-t covered hopper cars, and in palletized 50-kg (100-lb) bags and 1,000-kg (1-t) supersacks. Table 5 shows the typical packaging for sodium nitrate for industrial uses.

Shipments of industrial-grade potassium nitrate to the TV-glass industry are generally in 100-t bulk railcars, whereas shipments to smaller industrial users are primarily in 50-kg bags and 1,000-kg supersacks.

Table 5. Typical packaging for sodium nitrate

Grade	Import Package	Finished Goods Package
Industrial-grade sodium nitrate	Bulk	Bulk, 50 kg, 100 lb, 1 t
Technical-grade sodium nitrate	1-t supersack	50 kg, 100 lb, 1 t
Refined-grade sodium nitrate	1-t supersack	50 kg, 100 lb, 1 t

Transportation

In Chile, nitrate and related products are transported by road or rail to consumers. Because much of the production is exported, there are several important ports, including Iquique and Antofagasta, plus Tocopilla, where SQM operates a dedicated port for bulk or packaged shipments to customers and distributors.

Specifications

Urea contains 46% N; ammonium nitrate, 33.5% N; ammonium sulfate, 21% N; MAP, 13% N and 52% P; DAP, 18% N and 20% P; and aqueous ammonia, a minimum of 29.4% NH_3 . Potassium nitrate has a minimum chemical analysis of 13% N and 44% K_2O (potassium oxide), although most grades sold contain 13.0%–13.8% N and 45%–46% K_2O ; chloride levels are very low, usually less than 0.01%. It is available as a prilled (nominal 6×20 mesh) direct application, and bulk blending and soluble, or as a crystalline (nominal 20×120 mesh) product for liquid fertilizer applications and the manufacture of granulated N-P-K fertilizers. Higher purity forms (slightly lower chloride, sodium, and other metal contaminants) are required for industrial applications.

ECONOMIC OR COMPETITIVE FACTORS

Modern nitrate production is accompanied by iodine production, and in fact iodine may be considered the primary product with the nitrates as coproducts. Crystallized sodium sulfate decahydrate (Glauber salt) is produced from the leaching solutions remaining after the iodine production process and is used to produce anhydrous sodium sulfate.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

Anhydrous ammonia is not a poison and has no cumulative toxic effects on the human body. Ammonia vapor is considered to be “life threatening,” however, when exposure levels reach 2,500–6,500 ppm for up to 30 min or “rapidly fatal” if exposure levels reach 5,000–10,000 ppm for up to 30 min. The U.S. Environmental Protection Agency’s (EPA’s) interim acute exposure guideline levels (AGELs) include an AGEL-2 for ammonia of 160 ppm for 30 min and 110 ppm for 60 min (AGEL-2 is defined as the concentration of an airborne substance at or above which it is predicted that the general population, including sensitive but not hypersusceptible individuals, could experience irreversible or other serious long-lasting effects or impaired ability to escape). Ammonia is not combustible except when its concentration in the air is 16%–25% at 849°C or higher. It does require special handling because anhydrous ammonia turns into a colorless, pungent, hazardous gas under atmospheric conditions. One industry reference for storage and handling is K61.1, written by The Fertilizer Institute (TFI) and issued by the American National Standards Institute (ANSI). In 1990, the U.S. Department of Transportation classified anhydrous ammonia as a nonflammable gas linked to a required “inhalation hazard” label and as a Division 2.2 nonflammable, nonpoisonous compressed gas for domestic shipments. International shipments, however, were classified as a Division 2.3 poisonous gas, consistent with UN regulations. Ammonia is stored in carbon-steel cylindrical

tanks at atmospheric pressure and -2°C , and shipped in tank railcars or trucks under pressure as a liquid, by refrigerated barges and ocean vessels, or by pipeline.

Nitrogen compounds are an environmental concern in that overfertilization and the subsequent runoff of excess fertilizer can contribute to nitrogen accumulation in watersheds, which has been theorized to cause hypoxic zones (such as in the Gulf of Mexico during the summer).

PRICES

Because the choice of fertilizer is an agronomic decision rather than an economic decision, the demand for specialty fertilizers is inelastic with regard to price. If the price of fertilizer increases, the farmer still must purchase it if he intends to continue to grow the crop. This is particularly true for nitrogen, which is soluble and disappears quickly compared with both P and K, which can remain in the soil for some time. Therefore, there may be a slight drop in P and K initially when fertilizer prices rise, but the cutback cannot be maintained for any significant length of time.

Prices are chiefly a result of the supply-and-demand balance. In the case of potassium nitrate, Chile, the United States, and Israel control the volume of supply available on the market. On the demand side, the types of farming and the range of crops produced have an influence on fertilizer use. Tobacco production is declining in the United States but is increasing in China. As with most markets, the actions of China will have a major impact on fertilizer demand and pricing.

Urea is the main nitrogen fertilizer and can be an alternative to the use of nitrate. There will be a price relationship between urea and nitrate at which farmers will decide to switch in either direction. History has shown that nitrate prices are less volatile than urea prices. A price relationship is more evident in the sodium nitrate markets in Chile and China. In Chile, SQM has set the price of sodium nitrate at different levels relative to urea from season to season (mainly from 1980 through 1987), and this has been very useful for establishing a relationship that extends from a 6% share of the nitrogen market for nitrate when its price per unit of nitrogen was 2.5 times that of urea, to 48% of the nitrogen market when its price per unit of nitrogen was 1.1 times that of urea.

Negotiations to sell sodium nitrate to China are based on nitrate at twice the urea price per unit of nitrogen. As a result, most of the negotiations revolve around the urea price to be used in the comparison, which makes the situation challenging for the seller.

Worldwide, the price of potassium nitrate is set by exports from Chile on an f.o.b. port basis in US dollars per ton. These prices peaked at just about \$300/t in 1997. Since then, they declined to less than \$280/t in 1999 and to \$250/t or less based on exports in 2000 and 2003.

For industrial nitrates, price levels are determined by industry type—based on exports, the average price for sodium nitrate was \$180/t f.o.b. Chilean port in 2002 and 2003.

Actual pricing in the United States for most industrial-grade potassium nitrate is \$450–\$500/st delivered to the customer. As the largest consumer, the TV-glass industry pays the lowest price, and smaller consumers pay the higher price. TV glassmakers purchase by 2- to 3-year contracts, with target prices subject to meet-or-release clauses. Other sales are mostly consummated on a spot basis, based on quoted or negotiated prices.

OUTLOOK AND FUTURE TRENDS

Demand Drivers

Western Europe and North America have generally accounted for the bulk of the demand for specialty fertilizers such as potassium

nitrate and potassium sulfate. Latin America and Asia (particularly China), however, hold the key to future demand growth based on population growth and the increasing sophistication of farming. In addition, China is the largest producer of tobacco, which is the largest consumer of specialty fertilizers. Worldwide, specialty fertilizer demand will increase with the increased popularity of fruits and vegetables, the need for intensive farming close to urban areas, and the increased use of innovative farming techniques such as fertigation and micro-irrigation. Demand should also increase as farming in areas with high chloride soils becomes necessary. Periodic fluctuations in demand occur because of factors such as weather conditions in the growing areas (the El Niño effect), changes in government agricultural support policies, commodity price and foreign exchange fluctuations, and changes in the crops grown or in the N-P-K ratios used.

Conventional use of sodium nitrate in explosives, BBQ briquettes, and glass appears to be declining as less nitrate is used per unit of product, and, in some cases, environmental concerns are encouraging elimination. In the glass industry, there is a real push to eliminate industrial sodium nitrate to reduce NO_x emissions. The compound has unique characteristics, however, that can only be partially replaced by other materials such as calcium nitrate, sodium sulfate, and ammonium nitrate. Future growth has to rely on the development of new uses—in particular, water treatment and alternative energy.

Market Channels

Today, as sole suppliers of natural nitrates, Chilean nitrate producers face a situation—driven by market forces—in which they have a very small piece of the fertilizer market, and the only way to grow is to expand into other regions producing the same crops that currently use nitrates. That implies a significant marketing effort intimately related to the distribution channels.

Nitrate producers have to be much closer to the end user than producers of commodity fertilizers. For example, in both Brazil and Chile, PCS Sales (or Canpotex) sells potassium chloride using a sales representative. This company officer and his secretary receive calls from fertilizer importers (6 in Chile and 10 in Brazil) and act as coordinators between the producer (PCS) and the importer for setting the quantity, price, timing, and conditions of a shipment (usually at least 10,000 t of product).

SQM has its own subsidiary (Soquicom) in Chile for the import of any kind of fertilizer and for the sale of nitrates. This subsidiary contracts out a chain of local and national distributors that carry, on consignment, fertilizer products imported and produced by SQM. Soquicom has divided Chile into seven zones, and each has an office that manages sales and produces market intelligence. SQM agronomists in each office work with the local distributors to establish the amounts needed and dates delivery is required. They organize local marketing (directly for big farmers or collectively for the smaller ones), which basically consists of showing them the results of agronomical trials for their areas of interest. SQM's marketing department collaborates with universities and governmental institutions for these trials that are designed to show the advantages of nitrates over other fertilizers. There are also local trials, conducted by the local office in collaboration with large farmers. The local offices also provide information on the competition, both products (calcium nitrate) and fertilizers imported by other companies. They also provide information about developments in local farming and the performance of distributors.

Only a limited number of countries produce nitrates, iodine, and lithium, and therefore a significant proportion is exported: virtually all the natural sodium nitrate exported comes from Chile.

More than 90% of SQM's specialty fertilizers are exported, with a fairly even distribution, to more than 100 countries: approximately 20% is sold in South and Central America, 22% in North America, 19% in Europe, and 21% in the rest of the world. No single customer accounts for more than 4% of specialty fertilizer sales, and the combined sales of the 10 largest customers account for less than 21% of total sales.

Almost all iodine is exported from Chile, including some 2,000 tpy of iodine derivatives that are processed locally.

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Olivine

Peter W. Harben and Corky Smith Jr.

Olivine is a magnesium-iron silicate mineral formed deep in the upper mantle. It is used chemically as a source of magnesia combined with silica and physically for uses requiring hardness and resilience. Relatively few countries and still fewer companies produce it in commercial quantities. Overall, Norway dominates commercial production, and metallurgy dominates consumption.

GEOLOGY

Olivine is a common mineral in the low-silica rocks making up the oceanic crust. It is particularly common in pre-Ordovician to Tertiary basalts and other mafic igneous rocks and is the essential mineral of peridotite. Rock containing more than 90% olivine is known as dunite, named for its type locality in Dun Mountain, Nelson, New Zealand. A medium- to coarse-grained crystalline rock, dunite is generally reddish brown when weathered. Fresh, unweathered dunite is, however, relatively rare because it readily takes up water and alters to oxides and serpentine. Deposits commonly contain 92% olivine, 5% pyroxene, and 1% spinel, chromite, and magnetite, along with 2% secondary minerals such as chlorite, serpentine, talc, vermiculite, and limonite. Olivine also occurs in basic igneous rocks such as olivine gabbro, basalt, and diabase (dolerite). Commercial deposits of olivine, however, are generally restricted to dunite bodies of the alpine type that intruded from the upper mantle into the upper lithosphere along deep faults in partly crystallized form (Harben and Kuzvart 1997). Associated minerals are diopside, spinel, plagioclase feldspars, chromite, magnetite, talc, hornblende, serpentine, iron-nickel meteorites, and augite.

Magnesium-rich olivine forms through the thermal metamorphism of siliceous limestone and dolomite. Fayalite is more common in regionally metamorphosed iron-rich sediments.

Mineralogy

Olivine represents an isomorphous solid solution series of orthosilicate minerals rather than a single mineral and has the general formula R_2SiO_4 , where R is iron or magnesium. The magnesium end member is forsterite, Mg_2SiO_4 , named for Adolarius Jacob Forster (1739–1806), an English mineral collector, and the iron end member is fayalite, Fe_2SiO_4 , named for its type locality at Fayal Island in the Azores. This gives a general designation of $(MgFe)_2SiO_4$ or $2(Mg, Fe)O \cdot SiO_2$. Olivine comprising more than 15% fayalite and less than 85% forsterite is considered unsuitable for most industrial uses: the iron content makes it less refractory because Mg_2SiO_4 melts at 1,890°C compared to 1,205°C for Fe_2SiO_4 .

Chemical and Physical Properties

Olivine (forsterite) is commonly yellowish green with a vitreous luster. It also occurs as light or olive-green yellow. The Mohs hardness is 6.5 to 7.0, the cleavage is poor, and the fracture is conchoidal. The specific gravity is approximately 3.2 when pure Mg_2SiO_4 and rises with increasing iron content.

DISTRIBUTION OF WORLD DEPOSITS

Commercial olivine has two main occurrences:

1. Dunite, a medium- to coarse-grained igneous rock with 90% or more of its volume made up of olivine
2. Serpentine, composed mainly of the mineral serpentine, $(Mg, Fe)_3Si_2O_5(OH)_4$, from kimberlites, ophiolites, and gabbros that originally had large amounts of olivine

Despite their obvious geological differences, the names olivine, dunite, and serpentine are often used interchangeably. Deposits commonly contain more than 90% olivine plus pyroxene, spinel, chromite, and magnetite together with secondary minerals such as chlorite, serpentine, talc, vermiculite, and limonite. Because fresh, unweathered olivine is a rarity, most commercial deposits are based on the less attractive altered serpentine.

The world's production capacity of olivine, dunite, and serpentine is estimated at some 8 Mtpy, of which about half is high-quality olivine almost exclusively from Norway. This source dominates trade via its deep-water ports and a long-standing distribution system. Production elsewhere is mainly based on serpentine, for example, in Argentina, Austria, Brazil, Italy, Japan, Korea, Mexico, Spain, Taiwan, and the United States (see Table 1).

Norway

Olivine production in Norway of approximately 3.5 Mtpy is derived from dunite bodies within the Fjordane Complex, south of Ålesund, in the Sunnmøre-Nordfjord District in the west of the country. These deposits are the largest in the world, estimated to contain 2,000 Mt of olivine within 6 km². The average mineral content of the dunite is 92% olivine, 5% pyroxene and serpentine, 1.5% chlorite, and 1% spinel; the mineralogical composition of the olivine is 94% forsterite and 6% fayalite (Olerud 1995).

The world's largest olivine producer is A/S Olivin, owned by North Cape Minerals AS, which itself is 64% owned by Unimin Corp. and the balance by Franzefoss Bruk AS of Norway. The company owns the Bryggja, Nordfjord, operation (underground)

Table 1. World production of olivine*

Country	Production, ktpy
Australia	80
Austria	20
Brazil	350
China	350–500
Italy	100
Japan	2,000
Mexico	150
Norway	3,500
South Korea	500
Spain	700
Taiwan	400
Turkey	150
United States	100
Total	8,050

Source: O'Driscoll 2004.

* Commonwealth of Independent States olivine production not included because of a lack of reliable data.

and two operations at Åheim (Å Imeklovdaalen), south of Ålesund, comprising More (surface) and Rauber gvik, Romsdal (underground), the latter through Olivin's subsidiary Industrimineraler AS. Bryggja and Rauber gvik have a combined production capacity of 500,000 tpy, whereas the Åheim mine has a capacity of 3.8 Mtpy with output carried via a 4-km-long conveyor in a tunnel to the plant next to the harbor. Slag conditioning in the iron and steel industry accounts for 90% of sales, with the balance used in foundries, refractories, and abrasives. Steinsvik Olivin AS is a potential olivine producer in Norway based on a deposit at Vassbakkedalen, above Steinsvik in Dalsfjord. The deposit is 2 km from the North Sea, and analyses of samples have apparently indicated olivine quality similar to that of Åheim. The total size of the reserves has been estimated at 25 million m³, with MgO content ranging from 46.5% to 49.0%. The project is designed to ramp up from an initial production of 250,000 to 350,000 tpy (O'Driscoll 2004).

Italy

Nuova Cives Srl mines an olivine deposit near Turin in the municipalities of Castellamonte, Vidracco, and Baldissero Canavese in the north of Italy. The 75-km² outcrop area hosts more than 100 Mt of reserves, grading 95% to 97% olivine. The capacity is some 300,000 tpy of crude ore, with the plant at Vidracco capable of producing 250,000 tpy. About 40% is used in refractories and metallurgical applications; 10% in iron ore production; 15% in foundry; 20% in blasting abrasives; 10% in bituminous products, special paints, and ceramics; and 5% in road construction (O'Driscoll 2004).

Spain

In the province of La Coruña, in Galicia in northwestern Spain, Pasek España SA produces about 700,000 tpy of dunite for slag conditioning, refractories, and aggregates. Pasek España is a wholly owned subsidiary of Belgium's Pasek Group and focuses on the refractories market. Pasek also has operations in France and Brazil.

Turkey

Turkey produces about 150,000 tpy of olivine from a number of small- to medium-scale producers. The leading producer is Beyk-

rom Mining Inc. in Beysehir, Konya, with a plant capacity of 150,000 tpy. The main markets are eccentric bottom-tapping (EBT) taphole filler, slag conditioner for steel, refractories, sand blasting, foundry, and also fines for other markets. Beykrom's target markets are in the Mediterranean and Middle East regions. Potential producers include Olivin Mineral AS and Ado Mining.

Japan

Japan is the world's second largest olivine producer, after Norway, with an output of some 2 Mtpy. Much of this is derived from extensive deposits of mostly serpentine in the Horoman Hill region in Hokkaido, which supplies the domestic steel and foundry industry. As many as 30 producers have the capability of producing as much as 5 Mtpy of all forms of olivine, much of which is used in construction. The largest is Toho Olivine Industrial Co. Ltd.'s operation on Horoman Hill on the northern island of Hokkaido, which produces about 300,000 tpy of olivine. This is the largest deposit in Japan, with reserves estimated at 100 Mt.

China

Olivine production in Henan Province in central China is based on deposits of forsterite in southwest Henan, in Xixia County, west of Nangyang, and in Yubian County. The ore body is approximately 7.5 × 1.1 km in size, with ore reserves of more than 100 Mt and mineral reserves of 9 Mt. The more than 30 mining sites have production capacities ranging from 10,000 to 50,000 tpy. Henan olivine production is estimated to be 350,000 to 500,000 tpy of high MgO (47.26%) grades used as a slag conditioner, foundry sand, refractories, and other uses. The main producers are Henan Mines & Refractory Corp. and Nanchuan Minerals Group.

United States

Olivine production in the United States is restricted to the Cascade Mountains of Washington State and the Smoky Mountains of North Carolina. Deposits in Washington are superior in quality but much farther from most markets. Output is modest at about 100,000 tpy.

The center of production in northwestern Washington is at Twin Sisters Mountain in Whatcom and Skagit counties, 32 km east of Bellingham. A 90-km² elliptical body of dunite, the largest in the Cascade belt at 200 billion t, is composed almost entirely of unaltered olivine (W. Moen, personal communication). The geological setting of the area is dominated by three thrust sheets, the youngest of which brings greenschist and phyllite, thought to be pre-Jurassic, over Paleozoic rocks. The Twin Sisters mass is an enstatite-bearing dunite that weathers reddish brown. Unaltered rock consists of olivine, enstatite, chromite, and clinopyroxene. Forsterite is dominant throughout the mass. Unimin Corp. accounts for the bulk of olivine production, working a talus accumulation at the base of Twin Sisters Mountain, and Olivine Corporation operates a mine near Bellingham, Washington. Production capacity is 50,000 tpy. Industry sources report that Olivine Corporation mines about 40,000 tpy of olivine from its Sven Larsen quarry in Whatcom County, which is used to produce olivine foundry sand for manganese steel castings. In addition, some material is shipped to Unimin Corp.'s plant at Hamilton, which produces casting sands and other refractory products.

Several large masses of dunite have been recognized in a belt extending from Watauga County, North Carolina, southwestward to White County, Georgia, a distance of about 280 km. Two main districts, the Webster-Balsam District in Jackson County and the Spruce Pine District in Yancey and Mitchell counties, have historically produced most of North Carolina's olivine. The deposits contain 50% to 90% olivine. The dunite bodies occur in two main forms—lenticular intrusions with the long axis parallel to the regional schistosity and,

more rarely, ring dikes. The core of the bodies, accounting for about half the volume, consists of relatively unaltered olivine; the outer zones and some faulted zones within the core are partially altered to serpentine and talc. The largest of these bodies contains an estimated 300 Mt of dunite, and the mineralogy is remarkably consistent. The now-closed Addie deposit, 56 km southwest of Asheville, North Carolina, consists of a highly laminated dunite alternating with talc, chlorite, and other secondary minerals formed through the action of hydrothermal solutions. Masses of dunite little affected by this metamorphism were the economic zones.

Recent production has been limited to the Unimin Daybrook mine near Burnsville in Yancey County with an output of some 100,000 tpy.

Other Countries

Magnolit GmbH produces some 120,000 tpy of serpentinized olivine from an open pit at St. Stefan ob Leoben in Austria. Because the product contains from 40% to 70% serpentine, it has to be calcined and graded for commercial use.

In Mexico, Regio Cal SA de CV produces about 25,000 tpy of dunite and serpentine at Mag Minas de Tamaulipas, Ciudad Victoria, Tamaulipas.

Black Mountain Mineral (Pvt) Ltd produces 30,000 to 40,000 tpy of olivine from a quarry at Lashaker, some 60 km from Mingora in Swat, Pakistan.

Olivine production in the former U.S.S.R. is centered in the Pamir Mountains.

TECHNOLOGY

The positive relief of dunites and the fact that they support sparse vegetation facilitate prospecting. Core drilling is often difficult because of the presence of serpentinized zones, and therefore percussion drilling with compressed air (the so-called "down the hole" method) is used.

Except for one room-and-pillar underground operation at Briggja in Norway, mining of olivine or dunite is by open-pit methods. Using bench heights of 3 to 9 m, drilling and blasting is generally supplemented by secondary drop-ball work to reduce the size of the boulders. Shovels or front-end loaders load trucks transport the feed to the local plant, where it is reduced to -40 mm material using a primary jaw or cone crusher. The resulting product may be screened to a -40 +10 mm commercial product or reduced further by cone, impact, or roll crushers or by ball mills. Some producers such as those in North Carolina use wet processing and gravity separation. In Australia the dunite is calcined in rotary kilns at 1,650°C to produce grades suitable for refractory and foundry applications.

USES

Olivine is a commercial source of magnesia combined with silica used mainly in metallurgy, where it is utilized as slag conditioner, refractory, and foundry sand, and as a fertilizer. Its physical attributes are appropriate for abrasives, filler applications, and several miscellaneous uses. According to the U.S. Geological Survey (USGS), in 2004, foundry uses accounted for 91% of olivine use in the United States, with sandblasting and other abrasive uses at 5%, and refracting applications at 4% (Kramer 2005). Gem-quality olivine is known as chrysolite (light yellowish-green olivine), evening emerald (olivine's gemstone variety), and most commonly peridot because of the inclusions and cloudy nature of large stones, peridot is the magnesium-rich forsterite with a unique green-yellow color caused by the presence of iron ions plus trace nickel and chromium.

Metallurgy

By far the largest market for olivine is as a slag conditioner in blast and electric-arc furnaces. In addition to conditioning the slag, the olivine controls the basicity through alkali recirculation reduction within the furnace because of the formation of stable magnesium alkali silicates. In addition, its higher reaction temperature reduces low-temperature breakdown and swelling of the burden, thus maintaining permeability and reducing coke consumption. The olivine may be added directly to the blast furnace charge as lump (10 to 40 mm), added as a sinter feed (3 to 6 mm), or mixed with low-silica iron-ore fines and pressed into pellets. Each form has its pros and cons. As a lump added directly to the furnace, olivine can replace some of the limestone and dolomite flux in the reduction of the iron ore. Compared with dolomite, olivine has a higher MgO content (requires less material for a given MgO level), higher MgO:SiO₂ ratio (thus allowing MgO levels to be raised without changing the basicity of the slag), and lower loss on ignition (LOI) of 0.3% to 0.7%, which conserves the energy required to drive off unwanted carbon dioxide.

With an initial sintering temperature of 1,450°C and fusion at 1,665° to 1,743°C, olivine is well suited as a refractory. Added advantages include a low and uniform coefficient of thermal expansion; good resistance to thermal shock, spalling, and slag attack; and a high green strength. Therefore olivine is used in the manufacture of magnesia (forsterite) refractory bricks; in spraying, ramming, and gunning mixes; as EBT tap hole filler for electrical arc furnaces; and in precast refractory linings for incinerators. Because of its ability to minimize generation of harmful gases, olivine sand is used to line siloburners used to dispose of hospital waste and other toxic wastes.

The refractory properties plus its lower free-silica content and strong resistance to metal attack mean that olivine can replace silica sand as a foundry molding sand used for aluminum, brass, bronze, manganese steel, gray iron, and alloy steel. When casting manganese steel and other high-value alloys and copper and aluminum alloys, olivine sand produces a clean surface requiring minimal finishing. Additional benefits include the basicity of olivine, which enhances the bentonite bonding properties, thus reducing clay demand and its low and uniform expansion rate, which eliminates the need for cushioning agents and thus allows recycling. Its angular particle shape tends to use up to 50% more resin for binding compared with rounder silica sand.

Olivine has extremely high heat-retention properties and is used in the brick cores of heat-storage units.

Nonmetallurgical Uses

Olivine's properties of less than 1% free silica, a moderately high Mohs hardness of 6.5 to 7.0, a specific gravity of 3.3, a conchoidal fracture yielding an angular grain shape, and a light-colored dust allow it to be used as a loose-grain airblast abrasive, filtration media, and a weighting agent in concrete oil-production platforms. Olivine may replace silica sand as an airblast abrasive because of the reduced risk of silicosis used in repairing and maintaining ships, railcars, trucks and automobiles, and aircraft and maintaining structural steel such as bridges, oil rigs, boilers, storage tanks, and pipelines.

As a fertilizer and soil amendment, olivine contributes magnesia and iron as nutrients to the soil.

The light color of the dust also allows olivine to be used as a filler in specialty paints, asphalt, mastics, and roofing tile formulations. As a local rock, olivine can be crushed and used as an aggregate used in construction and concrete. Rock wool manufactured from olivine is being marketed in Europe as environmentally

Table 2. Olivine chemical composition

Chemical	Norway, Dunite	Norway, A/S Olivin Standard	Norway, A/S Olivin Refractory	Austria, Magnoliithe	Italy, Nuova Cives	Sweden, Handol	United States (Washington), Olivine Corp.	United States (North Carolina), Unimin	Japan, Toho
MgO	47–51	48–50	49–51	48 min*	41–43	46	49.4	50.5	47 max†
SiO ₂	41–43	42–43	41.5–42.5	42	42–44	41	41.2	40.1	42 min
Fe ₂ O ₃	6.5–7.7	6.8–7.3	6.5–7.0	10.5 max	1.2–2.7	8.2	7.1	6.7	2
Al ₂ O ₃	0.5–1.0	0.5–0.8	0.4–0.5	na‡	na	na	na	na	na
CaO	0.05–0.06	0.05–0.10	0.05–0.10	0.4 max	1.5–2.6	0.8	0.2	0.2	0.4
Oxides§				na	na	2	1.8	1	8.5 max
LOI	0.2–1.5	0.7–1.5	0.2–0.5	na	na	1.8	0.7	0.7	2.5 max

Adapted from Harben 2002.

* min = minimum.

† max = maximum.

‡ na = not available.

§ Al₂O₃, TiO₂, MnO, Cr₂O₃, NiO, CaO, K₂O, Na₂O.

Table 3. Nuova Cives sizing and applications

Sizing	Market Application
30–60 mm	Rail ballast
10–25 mm, 10–45 mm lump	Blast furnaces
3–18 mm, 8–18 mm	Metallurgical and road construction
2–2.5 mm, 2.5–5.5 mm, 5.5–7 mm	Taphole fillers and in EBT/OBT,* basic refractory, backing sand redressing
10–2,500 µm	Foundry, gunning and ramming mixes in spray linings for tundish facings, water filtration, waste furnace, preparation of special basic paints for moulding, ceramic frits, waterproofing and bituminous products, anticorrosive and anticorrosive paints
0.1–0.35 to 1–2.5 mm	Blasting abrasives, water-jet cutting

* OBT = obround bottom-tapping.

friendly (or perhaps “green,” because the very name is derived from the Latin *oliva*, meaning *olive*, alluding to its olive green color). Night storage heaters have electric elements that heat up blocks of dense material such as olivine with a high specific heat capacity and cased in layers of insulation so that the heat escapes slowly.

Future Uses of Olivine

Olivine is a candidate for sequestering CO₂ emissions generated from burning fossil fuels. The concept of mineral sequestration involves the reaction of CO₂ with minerals to form geologically stable carbonates, i.e., mineral carbonation. One example would be to activate or pretreat the serpentine and olivine, which is placed in a solution of water, NaCl, and sodium bicarbonate to react with CO₂ at a high temperature. This method allows for 80% carbonation in less than an hour and forms magnesite (MgCO₃), silica (SiO₂), and water, which acts as the harmless storage unit. In principle, 1 t of olivine can dispose of approximately 0.67 t of CO₂ in an exothermic reaction that releases 90 kJ/mol.

1. $(\text{Mg, Ca})_x\text{Si}_y\text{O}_x + 2y + z\text{H}_2\text{O} + x\text{CO}_2 \rightarrow x(\text{Mg, Ca})\text{CO}_3 + y\text{SiO}_2 + z\text{H}_2\text{O}$
2. $\frac{1}{3} \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \frac{2}{3} \text{SiO}_2 + \frac{2}{3} \text{H}_2\text{O} + 64 \text{ kJ/mol}$
3. $\frac{1}{2} \text{Mg}_2\text{SiO}_4 + \text{CO}_2 \rightarrow \text{MgCO}_3 + \frac{1}{2} \text{SiO}_2 + 90 \text{ kJ/mol}$

The current pretreatment methods of heating or fine grinding are too energy intensive for practical use. Consequently, groups such as the Arizona State University (ASU) Carbon Sequestration Research Team (which is a member of the CO₂ Mineral Sequestration Working Group that is managed by the Fossil Fuels Division of the U.S. Department of Energy), are examining alternative methods.

Specifications

Typically, olivine contains 45% to 51% MgO plus 40% to 43% SiO₂; 7% to 8% Fe₂O₃; 0.2% to 0.8% CaO; and 1.8% to 2% Al₂O₃ + TiO₂, MnO, Cr₂O₃, NiO, and CoO. LOI is critical because this indicates the presence of hydrated minerals such as chlorite and serpentine. Table 2 gives the chemical analysis of some commercial olivine products. Sizes range from lump or aggregate (10 to 45 mm) to sand, to flour (–200 or –325 mesh).

Blast furnace-grade lump (10 to 40 mm) is for direct feed to the blast furnace and 0 to 6 mm or 0 to 3 mm to the sinter stream with an average MgO content of 47% to 48%. Foundry-grade olivine is mainly American Foundry Society (AFS) 20, 30, 60, 90, 120, and flour; for brass, bronze, and aluminum, it is AFS 100, 140, and 180. Filler grade runs 0 to 0.8 mm and 0 to 0.02 mm and fertilizer grade runs <0.1 mm.

Table 3 gives sizing from Italy as an example.

ECONOMIC FACTORS

Environment, Safety, and Health

One important attribute cited for olivine for use as a foundry sand or airblast abrasive is its low free-silica content. Any mineral product with a crystalline silica content of 0.1% or more, however, is generally regulated under U.S. Occupational Safety and Health Administration (OSHA) Hazard Communication Standards or similar standards, so they require a cancer warning label.

Substitutes and Recycling

Olivine competes with several minerals in several markets:

- As a slag conditioner against dolomite
- As a magnesia source (45% to 51% MgO) against magnesite (47.8% MgO) and dolomite (20% MgO)
- In abrasives against specular hematite, garnet, silica sand, and slag
- In fertilizers against dolomite, caustic magnesia, and magnesium sulfate

Theoretically, as an airblast abrasive, spent olivine can be recovered, cleaned, resized, and reused to offset the higher initial costs compared with silica sand or slags. In practice, not much olivine is recycled, and the higher price is thus justified by OSHA considerations and reduced liability. Reclaiming mold and core sands in foundries has increased because of escalating purchasing and disposal costs.

Future Trends

The iron and steel and metal foundry industries largely influence demand for olivine, and they in turn depend on consumer durable-goods sales and construction activity, both of which are tied to gross domestic product (GDP) and population growth. Iron and steel production tends to be strong during periods of economic expansion and slows down in line with the economy. In addition, demand for foundry sand has been reduced by the advent of continuous casting in the steel industry. On the other hand, consumption as an airblast abrasive and a foundry sand may be encouraged by cost competitiveness as well as OSHA regulations that discourage the use of silica sand (and chromite in foundries). Nevertheless, the limited sources of production, wide range of competitive materials, and relatively low selling price restrict olivine to local or regional markets, most notably in Scandinavia and Japan. Access to low-cost transportation is critical and is the main reason why Norway has been a successful exporter and producer.

Prices

Delivered prices for olivine depend on quality, packaging, and freight charges, with the low end of the range at commodity-like levels. Prices (in US dollars) quoted in *Industrial Minerals* in 2005 for the United States are approximately as follows:

- Ex-works foundry: \$60 to 110/t (AFS 30 to 180, bulk), \$77 to 125/t (AFS 30 to 180, bags)
- Flour: \$117/t (bags)
- Aggregate: \$50 to 78/t (bulk)
- Europe CIF (cost, insurance, and freight), crushed, for sinter pellets, blast furnace: \$13 to 19/t (bulk)
- Dry graded, refractory aggregate, ex-works: \$72 to 80/t (bags)
- Foundry and blasting sand, ex-works: \$78 to 84/t (bags), \$65 to 84/t (bulk)

- Sand for tundish spray: \$100 to 110/t (bags)
- EBT taphole filler, dry, ex-works: \$85 to 95/t (bags)

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Perlite

James M. Barker and Ken Santini

INTRODUCTION

The expanding properties of perlite have been known for almost 2,000 years (Allen 1992). Called perlstein in Germany in the 1800s (Evans 1993), perlite was originally identified by its vitreous, pearly luster and characteristic curved (onionskin texture) perlitic fractures (Breese and Barker 1994). Textures of perlite range from classical (onionskin) to granular (most common commercial type) to pumiceous (lower density). Defined as having 2 to 5 wt % combined water, perlite occurs worldwide in young, glassy, rhyolitic, high-silica volcanic rocks generally less than 60 million years old.

Modern perlite production began in 1946 in Superior, Arizona, and soon thereafter in New Mexico with a trade organization, the Perlite Institute, in place by 1949 (Allen 1992). Crushed and sized crude perlite expands or “pops” into anhydrous glass foam when heated quickly to plasticity at about 600° to 900°C while releasing steam from combined water. Very fine perlite is expanded into microspheres typically less than 100 µm in diameter.

Industry may refer to any volcanic rock that expands as “perlite.” This includes obsidian (<2 wt % water), bloated in Japan, and pitchstone (>5 wt % water), expanded in Eastern Europe. The low density and porous texture of expanded perlite plus its low thermal conductivity, high sound absorption, and chemical stability give it many valuable commercial properties, especially in the construction industry (Breese and Barker 1994).

GEOLOGY

Perlite is one of the natural volcanic glasses containing combined water. These include obsidian, perlite, pitchstone, and hydrated volcanic ash or “pumicite” (Breese and Barker 1994). Perlite (2 to 5 wt % water) is hydrated volcanic glass formed over a few million years or so by the chemical weathering of obsidian at or near the earth's surface. The obsidian precursor to perlite originally contains ~0.1 to 0.4 wt % water because lava is nearly anhydrous at surface or near-surface pressures as water is evolved rapidly from the melt (Fisher and Schmincke 1984).

The water in obsidian is increased by gradual diffusion of meteoric water or sometimes other waters, such as thermal spring, phreatic or connate, into the high-silica (~70% to 75% SiO₂) rhyolitic (acidic) glass. Reincorporation of magmatic water from microvesicles and voids is also possible soon after cooling. The tension developed by the volume increase caused by this hydration results in the arcuate or concentric fractures typical of onionskin

perlite. Alkali-rich obsidian is hygroscopic, so alteration to perlite is inevitable but moderated by climate and wettable surfaces within the perlite body (Chamberlin and Barker 1996). Thus, perlite is not a primary igneous rock, although remnants of the primary obsidian or rhyolite may remain.

Semiarid climates are more conducive to retaining hydrated volcanic glass because it is not removed by the intense chemical weathering in a humid climate with its rapid flushing of glass dissolution products (see Lorenz and Muller [1982] for a tropical perlite).

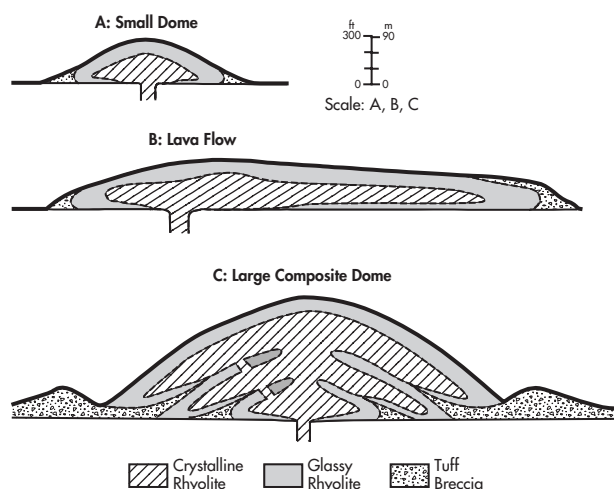
Perlite is often described as metastable over geologic time. Although technically true, the reaction takes billions of years in the absence of water. Volcanic and impact glasses on the moon are still pristine after 4 billion years (Carmichael 1979), suggesting that the idea of devitrification of perlite deposits should be put to rest for practical purposes (Chamberlin and Barker 1996). The primary form of glass in older rocks is perlite, often recrystallized, if glass is preserved at all (Fisher and Schmincke 1984). Perlite dated as Devonian (391.0 ± 3.8 Ma by ⁴⁰Ar/³⁹Ar) is known from Gaspé Peninsula, Quebec, Canada (M. Heizler, personal communication, Argon Lab, New Mexico Bureau of Geology and Mineral Resources). Other deposits are Jurassic or Cretaceous but most are Tertiary.

Extreme viscosity of high-silica lava favors formation of very-thick glassy chill zones on the lava surface. The eruptive history of the parent volcano determines the potential size of the perlite resource (Figure 1).

The best resource is the glassy top of a permeable (microvesicular) high-silica lava flow. Steep-sided high-silica lava domes typically are larger and more common than flows but yield less perlite because their complex, multi-vent cooling histories form interleaved mixtures of glass and rhyolite (Chamberlin and Barker 1996). Formation of perlite is a very complex process that requires a long chain of fundamental or essential events. If one event is omitted or is incomplete, no commercial perlite will form (Figure 2).

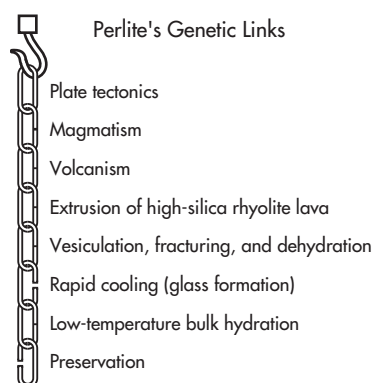
Because perlite textures are a continuum based on many interacting volcanic processes, they often do not fit nicely into classification “boxes.” Common textures of perlite used by industry are pumiceous (least dense), granular, and onionskin (most dense). Most commercial perlite mined is now granular or pumiceous.

Pumiceous perlite is at the margins of the deposit and is typified by frothy, open vesicles that can show flattening and distortion because of compression and flowage shear. Obsidian cores and



Adapted from Chamberlin and Barker 1996.

Figure 1. Diagrammatic cross sections of a small dome (A), lava flow (B), and large composite dome (C). The composite dome shows several overlapping volcanic events which complicate commercial production compared to a single lava flow or small dome.



Adapted from Ohle and Bates 1981; Chamberlin and Barker 1996.

Figure 2. A sequential list progressing from top to bottom showing fundamental and essential geologic processes in the formation of commercial perlite. Open links show where the chain is most likely to be broken.

perlitic fractures, if present, are generally restricted to dense vesicle wall junctions and may not be visible in outcrops. Pumiceous perlite is friable and may not core or mill well.

Granular perlite has a sugary texture and blocky fracture. Collapsed vesicles impart a silky luster to surfaces that are nearly parallel with flow banding. Well-developed perlitic fractures are rare. Granular perlite typically cores and mills well.

Onionskin has well-developed curved perlitic fractures, initially used to define perlite, and pearly-to-resinous luster. Widely spaced vesicles are present but are highly collapsed. Remnant obsidian nodules may be abundant as isolated grains or as pods of varying dimensions. The obsidian grains in the onionskin zone may be gradational or abrupt and can rapidly increase toward the interior of the unit or laterally into subzones in which hydration of the glass is incomplete. Although onionskin perlite mills and cores very well, it is a limited resource in most deposits.

OVERVIEW OF WORLD PERLITE DEPOSITS AND ACTIVITIES

References used in this section are Kuzvart (1984), Harben and Bates (1990), Breese and Barker (1994), Harben and Kuzvart (1997), Kendall (1999b), Roskill Information Services (2000, 2005), Barker et al. (2002), and Harben (2002), as well as U.S. Geological Survey (USGS) country reports, numerous *Industrial Minerals* articles, personal communications with companies, and site visits by the authors. Note that S&B Industrial Minerals, hereafter called S&B, is very active throughout the world. With 35 mines, plants, and distribution centers in 13 countries, S&B is the largest single supplier of crude perlite in the world.

Table 1 shows approximate world production through 2003, which averaged about 2.9 Mtpy from 1999 to 2003, increasing from a world total of about 2 Mt in 1995 (Coope 1997).

Although deposits of perlite are widespread worldwide, they often are not developed and are available only as market conditions allow. Examples include the El Rosario deposit, 1 of 18 in El Salvador (Lorenz and Muller 1982). Barker et al. (2002) list at least 100 deposits in North America alone. While perlite mining and associated expanding operations are discussed in this section, the numerous operations that only expand are not covered.

Algeria

Algeria is believed to have a producer near Maghnia (BGS 2005).

Argentina

Perlite deposits in Argentina are in the north in Salta Province and west-central in Mendoza Province. Production in the 1990s varied from 9.4 to 27.6 ktpy (Kendall 1999a), mostly for domestic use as filter aids and insulation (Roskill 2000, 2005; BGS 2003). Production was 19,725 kt in 2003 and has ranged from about 17 to 21 ktpy in the early 2000s (BGS 2005). In 1997, three companies (Granulterm y Cia., Perfiltra, and Minaclar) produced perlite (Kendall, 1999a).

Perfiltra of Buenos Aires was established in 1967 under the name of Silflo Argentina as a subsidiary of Johns Manville Corporation but is now an independent. It mines perlite (~76% SiO₂) from deposits in the Argentine Andes at San Antonio de los Cobres in Salta Province. The company processes crude perlite and expands at San Antonio de los Cobres, Banda del Río Salí, Tucumán Province, and Rosario, Santa Fe Province. Perfiltra produces expanded perlite for construction, cryogenic and pipe insulation, filtration, and horticulture. In 2004, it produced 8.5 kt for filtration and 2.5 kt for horticulture.

In the early 1980s, Multiquim began mining perlite at 3,900 m in Salta Province. Most of the perlite mined in the 1980s was exported, but in 2005 the majority is expanded at a plant in Rosario. Although the major end uses are agriculture and construction, some is used for stone-washing denim, cryogenic insulation, industrial absorbents, ambient temperature insulation, abrasives, and filtration.

Armenia

Armenia has three perlite deposits (72.60% to 74.84% SiO₂) that have been mined, with reported combined reserves of about 320 Mt (Troitsky, Petrov, and Grishae v 1998). A fourth deposit at Vorotan is very large but uneconomic because of lack of transportation.

Perlite occurs in Upper Tertiary to Quaternary volcanics that consist of basalt overlain by trachytic-rhyolitic flows. The upper part of the flows includes acidic rocks such as rhyolite, obsidian, and perlite (usually onionskin). The perlite displays a gradual transition to rhyolite and obsidian with textural differences resulting from variations in the cooling of the acidic lavas (Harben and Kuzvart 1997).

Table 1. World production of perlite, t

Country	1999	2000	2001	2002	2003	Comments
Algeria	na*	na	na	na	na	Probable producer
Argentina	21,008	17,521	17,916	17,152	19,725	
Armenia	90,000	140,000	16,618	147,242	175,990	
Australia	3,886	6,675	6,214	8,300	9,440	Year begins July 1
Bulgaria	12,700	16,700	12,300	10,500	16,800	
China	450,000	500,000	550,000	600,000	750,000	All years estimated
Georgia	5,000	5,000	5,000	5,000	5,000	All years estimated
Greece	777,898	817,825	840,660	850,000	850,000	
Hungary	140,787	151,069	89,900	72,196	145,000	
Iceland	na	na	na	na	na	Probable producer
India	383	274	176	283	279	Year begins April 1
Iran	15,069	28,000	20,000	20,000	20,000	Year begins March 21
Italy	60,000	60,000	60,000	60,000	60,000	All years estimated
Japan	260,000	250,000	250,000	250,000	255,000	
Mexico	61,596	68,702	80,297	85,703	35,000	
Morocco	na	na	na	na	na	
Mozambique	na	na	na	na	na	Probable producer
New Zealand	2,000	2,000	3,000	3,000	5,000	All years estimated
Philippines	22,500	4,600	61,300	8,500	15,200	
Russia	45,000	45,000	45,000	45,000	45,000	All years estimated
Slovakia	19,460	17,022	14,910	18,635	15,000	
South Africa	1,200	1,200	1,200	1,200	1,200	All years estimated
Thailand	6,050	5,600	8,500	7,600	9,500	
Turkey	147,818	149,426	154,515	151,902	136,683	
Ukraine	25,000	25,000	25,000	25,000	25,000	All years estimated
United States	711,000	672,000	588,000	521,000	493,000	
Approximate total	2,878,355	2,983,414	2,850,506	2,910,413	3,087,817	Average = 2,942,101

Adapted from Roskill Information Services 2000, 2005; Barker, Santini, and Alatorre 2003, 2004; Barker and Santini 2005; BGS 2005; Bolen 2005.

* na = not available.

The mined deposits are Aragats (mined by Grefco Minerals about 80 km from Yerevan), Dzhraber (mined by Amperlite), and Fontan-Dzhraber. In 1998, Dicalite Armenia (a subsidiary of Grefco Minerals) purchased Aragats and acquired large high-grade reserves, plus a mine and plant. Most production is supplied to the Dicalite plant in Belgium.

Total Armenian production reached 700 ktpy in the 1980s with exports to Russia and Western Europe. After Armenia left the Soviet Union, production and export of perlite declined. During the mid-1990s, there were no exports to Russia, but these resumed in 1997. Production of perlite fell to about 17 kt in 2001, then rebounded to about 17.6 kt in 2003 (BGS 2005).

Australia

Minor production of perlite in Australia occurred as early as the 1970s (Allen 1992). Since 1990, production has remained below 10 ktpy and in 2003 was 9,440 kt (BGS 2005). Perlite is produced in Queensland at Numinbah Valley, Nychum, and Nerang.

At Numinbah, Australian Perlite (a subsidiary of Solvay Interlox) produced approximately 4 kt in early 2005. The crude perlite is trucked to Sydney for expansion.

The Nychum deposit, which may contain a 700-Mt resource, is now produced by Chillagoe Perlite (formerly James Meyer) about 50 km northwest of Chillagoe, feeding a plant west of Cairns.

Fernz Minerals (part of Orica Chemicals) mines about 5 ktpy at Nerang and expands in Banksmeadow, New South Wales.

Perlite deposits in New South Wales are on the southern margin of the Nightcap range. Deposits at Port Stephens, Stroud, and Gloucester are less than 2 m thick.

Bulgaria

Perlite (~73% SiO₂) was discovered in 1921 at Broken Mountain near Jebel about 25 km southwest of Kardjali and at Svetoslav near Cold Well Lake (Petrov 1994). The perlite deposits occur in acidic volcanics of Oligocene age (Petrov 1994). Both sites were evaluated during the 1950s, and production of perlite commenced in 1960. Since 1998, Bulgarian production has ranged from 10 to 17 ktpy, with 16.8 kt in 2003 (BGS 2005).

Bentonite AD is the only producer in Bulgaria and mines the Broken Mountain deposit. Proven reserves are about 800 kt. Perlite from the mine is transported about 12 km to a 70-ktpy plant. Processed perlite is supplied for glass manufacture and to the construction industry. In October 2003, S&B acquired a majority interest in Bentonite AD.

Canada

All perlite consumed in Canada is imported, whether in crude or expanded form. Nearly 95% of expanded perlite in Canada is utilized

in horticultural applications. The remainder is consumed in loose insulation and other uses. In 2003, U.S. and Greek exports of crude perlite to Canada were, respectively, 27,735 and 37,869 kt. Greek imports by S&B have exceeded those from the United States since 2001 (Roskill 2005). In British Columbia, 20 occurrences of perlite are known (White 1990, 1991).

In 1953 and the 1980s, the Francois mine near Burns Lake produced perlite (Giles and Poling 1991). Production from 1949 to 1953 was 1,597 t (BC Geological Survey 2005a) but the mine is not active at present. The abandoned Francois mine exploited a 2-m-thick bed of perlite that is in sharp contact above and below with rhyolite and typically exhibits onion-skin texture. Approximately 300 m north of Burns Lake a similar perlite bed, about 15 m thick, is exposed along an access road. The perlite at both locations is considered to be Eocene or Oligocene in age (Hora 1984).

Until 1987, Aurum Mines operated the Frenier mine about 60 km west of Clinton. Volcanic rocks at the site are correlated with the Eocene Kamloops Group and consist of rhyolitic tuff, rhyolite flow, perlite, and breccia. The flows are approximately 25 to 30 m thick and contain onion-skin perlite. Based on drilling, proven reserves are about 450 kt, and the inferred resource is 3.8 Mt, based on a specific gravity of 2.3 (BC Geological Survey 2005b). Frenier perlite was trucked about 400 km to Fraser for crushing and expansion. Production from 1983 to 1987 totalled 6.5 kt before the company filed for bankruptcy. In late 2003, BBF Resources shipped a 180-t bulk sample of Frenier perlite to a plant in the Vancouver area for pilot-plant testing to ascertain the recoveries of specific sizes of perlite. Subsequently, 40 t of horticultural perlite was shipped to one company for expansion tests, and another company tested a finer-grained product. BBF Resources dropped the project in 2004.

In Quebec, perlite on the Gaspé Peninsula is Devonian in age, making it one of the oldest explored perlite deposits in the world. Minor development occurred in the early 2000s, but the majority of the deposits near Mount Tuzo are not considered to be economically viable, although Perlite Canada may have mined some material during the mid-1990s (Roskill 2005).

Chile

In 2004, the Harborlite Chile mine and expansion plant in Santiago produced 8 kt of filter-aid and aggregate products. The filter aid is used domestically by the wine industry and is exported to wine producers in Mendoza, Argentina. Other deposits are near Concepción and at the Puelche Volcanic Field in the Andes of central Chile along the border with Argentina (Hildreth et al. 1999). A glassy, marginal zone of crumbly dark-gray perlite a few meters thick is exposed in patches around the edge of the otherwise devitrified rhyodacite body that has been glaciated.

China

Perlite occurs in more than 200 deposits in 17 provinces. Of these, 21 deposits have been explored in some detail. Listed here are perlite reserves in excess of 250 Mt (Lu 1998; O'Driscoll 1994c). China has more than 40 producers of crude perlite—all mines are open pit—and more than 300 producers of expanded perlite, mostly used for thermal insulation (O'Driscoll 1994a). The British Geological Survey reported that Chinese production of crude perlite in 2002 was 600 kt (BGS 2005), which may be understated because other Chinese statistics show 550 kt of exports above domestic consumption. The major recipients were South Korea (267 kt) and Japan (183 kt). The 2003 production of crude perlite in China was at least 750 kt.

The largest producer, at more than 300 ktpy, is Xinyang Shangtianti at Xinyang in Henan Province. The deposit (72% SiO₂) is in Cretaceous volcanic rocks as lenses (Lu 1998), which are in the

middle of the lava flows, underlain and overlain by rhyolite and bentonite. Most of the perlite lenses are 50 to 800 m long, 50 to 550 m wide, and 10 to 60 m thick.

S&B holds a 25% interest in Xinyang–Athenian (XAMCO) in Henan Province, one of China's largest operations. The remaining 75% ownership is the local government. Through Sino Hellenic Industrial Minerals Co. (SHIMCO), S&B operates a 150-ktpy facility producing crude perlite and expanded products. SHIMCO's major markets are China, South Korea, Taiwan, and Japan.

Commonwealth of Independent States

Perlite occurs at 21 deposits in seven former Soviet republics. Perlite production is conducted in Armenia, Ukraine, Russia, and Georgia, discussed in separate sections. Deposits are also found in Kazakhstan (Semeitau deposit), Azerbaijan (Kechaldag deposit), and Tajikistan (Tashkesken deposit), although no production is reported (Troitsky, Petrov, and Grishaev 1998).

Georgia

JSC Perlite mines the Paravand deposit (Troitsky, Petrov, and Grishaev 1998) that occurs in volcanic flows 20 to 195 m thick, associated with obsidian and rhyolite (Harben and Kuzvart 1997). From 1997 to 2003, production was about 5 ktpy (BGS 2003, 2005). Reserves are 30 Mt, of which approximately 2.5 Mt are suitable for filter aids.

Greece

Perlite deposits are found in mainland Greece at Trace and on several islands, including Milos, Kos, Yali, Chios, Kimolos, Lesvos, and Nissiros (Coope and Manos 1986; Hatjilazaridou, Chalkiopoulou, and Grossou-Valta 1998). Since 1997, crude-perlite production has ranged from about 695 to 850 ktpy (BGS 2003, 2005). Exports have been mainly to Canada, Germany, Israel, Italy, Netherlands, Spain, the United States, and a few others.

S&B mines perlite at two locations on the island of Milos: Trachylas (74.4% SiO₂) in the north and Provatas (74.71% SiO₂) in the south. Milos Island is part of a volcanic arch extending from the Attica region near Athens to the west coast of Turkey. Late Pliocene to Late Pleistocene acidic volcanism produced tuff, pumice, tuffite, and ignimbrites, along with domes and lava flows of andesite, dacite, and rhyolite. The last activity produced rocks weathered to perlite, presently exploited by S&B (Harben and Kuzvart 1997).

The Trachylas perlite is harder, and Provatas is softer. Of the 1,069 Mt estimated in 1991 for Milos reserves, approximately 17% are at Trachylas, and about 83% are at Provatas. Perlite at both locations is mined from open pits to feed a plant at Tsigrado (upgraded in 2003). Crude perlite is trucked to the processing plant at Voudhia Bay for further sizing to –3 mm, followed by drying and screening prior to storage in silos to await final shipment. The capacity of the S&B processing plant on Milos is about 650 ktpy. Most of the perlite produced is exported, although some is shipped to an expansion plant at Ritsona, which is 90 km north of Athens. Bulk shipments of 8 to 15 kt are destined for continental Europe, and 25-kt shipments for North America. Perlite products in containers go to the Far East and for special cryogenic projects elsewhere. In 2003, expanded perlite from S&B Greek and Spanish operations amounted to 240,000 m³.

Perlite sales from S&B are supported by “just-in-time” warehouses in China, Europe, and North America. Just-in-time refers to a process where suppliers deliver product to the warehouse only when it is needed, avoiding the necessity of storing large amounts of inventory. In 2003, four new just-in-time warehouses were opened in Central Europe and one in the United States.

In the mid-2000s, Greek exports of crude perlite increased from 462 to 650 ktpy worldwide, because of increased market penetration in North America. At the same time, European sales have decreased, mainly because of a loss of 100 ktpy in construction products in Germany.

Armstrong Industries, a producer of ceiling tiles, is S&B's major customer in the United States. Its plants in Mobile, Alabama, and Pensacola, Florida, began taking perlite in 2003 from a warehouse in Mobile.

Aegean Perlite has mined on the northeast side of Yali, between the islands of Kos and Nissiros in the southeast Aegean Sea. Capacity of the open pit is 250 ktpy; perlite is air-dried before crushing and sizing. Production by Aegean Perlite commenced in 2002, when about 80 kt was produced from Yali.

Bouras produces approximately 30 ktpy of perlite from Milos, mainly for the German market, and also has operations on Kos.

Hungary

Hungarian perlite deposits are in the Tokaj Mountains of Zemplén Province at Pálháza (close to the Slovakian border), Erdőbénye, Abúszántó, Telkibánya, and Mádl (Shackley 1990; Roskill 2005). They occur in a 2,000-m section of Tertiary andesitic volcanics (Shackley 1990; Harben and Kuzvart 1997). In a 2000 estimate, reserves were about 2.8 Mt. Production has ranged from approximately 72 to about 175 ktpy since 1998 (BGS 2003, 2005). Approximately 30% of production in 2002 was exported mainly to Austria, Germany, and Poland.

Perlit-92 Kft (Kendall 1994), the sole producer in Hungary, is owned by Duna-Dráva Cement és Mészmuvek Kft, which is part of the German Heidelberger Zement group. Perlit-92 Kft has mined perlite (68% to 75% SiO₂) at the Pálháza deposit, first mentioned in the 18th century, since the mid-1950s and controls a deposit at the village of Bózsza (5 km from Pálháza). The grayish-black ore is in a distinctive columnar form (Kendall 1994). Mining is by drilling and blasting in an open pit (2.4-Mt resource) and trucked to a nearby 200-ktpy plant. Mine-run perlite is crushed, dried in a rotary kiln, and further sized before being screened into at least 15 grades and stored in silos.

Iceland

Iceland has several perlite deposits with commercial potential. A deposit in the Prestahnúki Mountains, about 100 km from Reykjavík, is reported to contain 48 Mt of perlite. The deposit originated in the Pleistocene by a rhyolite eruption under a glacier (Harben and Kuzvart 1997). Although the deposit is 50 km from the nearest harbor, access is easy only during the summer. Limited production of perlite may have occurred from this deposit, but no current information is available. Another perlite deposit is at Seydisfjörður on the east coast and close to a possible deep-water anchorage.

India

Perlite deposits are in Gujarat State, in parts of the Saurashtra, Kutch, Kheda, Sabarkantha, and Vadodra districts. Past production was by Raj Minerals, which may not be operating in 2005. Production has been very small and highly variable since 1990, ranging from 15 to 452 tpy (BGS 2003, 2005).

Iran

Perlite occurs at Khalkhal in Ardebil Province. Production, probably by Roudsaz in Tehran, has ranged from about 15 kt to about 28 kt in recent years (BGS 2003, 2005). At least 11 deposits are listed in the National Geoscience Database of Iran (www.ngdir.ir/MiningInfo/

[OrbadyInfo.asp](#)) in the states of Azarbaijan-e-Sharqi: near Miyaneh [6 deposits], Salmas [1], and Tabriz [1], Ardebil (Nir [1]), and Tehran (Damavand [2]).

Italy

Since the mid-1990s, perlite production has been about 60 ktpy (BGS 2003, 2005), and domestic consumption is estimated to be 70 to 80 ktpy. Exports of crude perlite are to France, Germany, United Kingdom, and others.

Western Sardinia contains the largest perlite deposits in Italy and is the only production site. The perlite occurs in Tertiary acidic volcanic rocks of the Mount Arci Complex on the northeast side of the Campidano Rift Valley at Morgongiori and Pugifiari. Perlite textures range from pumiceous to granular to onion-skin. Silica content varies from ~68% to ~73% (Jebson and Allen 1986). Ceca Italiana mines at Pugifiari, with most of the perlite being used by its plants at Pioltello (near Milan) and Sale rno. Sarda Perlite (51% S&B) mines near Morgongiori, and its 120-ktpy processing plant is at Torre Grande near the port of Oristano.

In the 1980s, VIC Italiana ceased mining on the island of Ponza, west of Naples.

Japan

Perlite is produced in the Kushiro, Kitakata, Tomioka, Yamaguchi, and Chiba regions. Recent annual production has ranged from 240 (2002) to 290 ktpy since the late 1980s (O'Driscoll 1994b; BGS 2003, 2005). More than 20 mines extract perlite from Miocene–Quaternary acidic volcanic rocks (Harben and Kuzvart 1997). Approximately 200 ktpy are imported, mainly from China, and about 15 ktpy of domestically produced perlite is exported, mainly to South Korea.

With approximately 45% of total production, Mitsui Mining and Smelting (formed in 1990) is the largest producer. Its mines are at Mikata (Hyogo Prefecture), Kitakata (Fukushima Prefecture), and Sagayamauchi (Sagami Prefecture). The Kitakata mine is Mitsui's largest, at approximately 50% of annual production, with Mikata producing 20% and Sagayamauchi 30%. Mitsui's expansion plants are at Funabashi (Chiba Prefecture), Kitakata and Omuta (Saga Prefecture), and Osaka (Osaka Prefecture).

Perlite is also mined, processed, and expanded by Toho Perlite at Wadatoge, Nagano Prefecture; by Nippon Perlite at Tsuruoka, Yamagata Prefecture; and by Shinano Perlite at Shinano, Nagano Prefecture.

Macedonia

Perlite is found in Tertiary volcanics close to the border with Greece. The major area is at Nižde Mountain where perlite is associated with Pliocene latite in the Gradesnica deposit. Development was active in the late 1990s with production expected to reach 80 ktpy (Harben and Kuzvart 1997), but none occurred.

Mexico

Mexican production has ranged from about 50 ktpy to about 97 ktpy since 1997 (BGS 2003, 2005). Major production in Mexico by Termolita and Compañía Minera Oriental totaled about 35 kt in 2003. This reflects a sharp decline in mine production resulting from a decrease in the market in Mexico and a reduction of unsalable perlite grades because of efficiency improvements at the mines (Barker, Santini, and Alatorre 2004). Sonora and Chihuahua also have minor production.

Termolita started operations in 1970, and production in 2005 was about 25 kt, mostly for domestic use. Some perlite is exported to the United States. The Leticia mine, 25 km west of the city of

Durango, Durango state, in north-central Mexico, supplies about 25 ktpy of crude perlite to an expansion plant 600 km east in Monterrey, Nuevo Leon. Proven reserves are large and mainly onionskin. Termolita has four expanders in operation (two horizontal, one vertical, and one portable for cryogenic) with a yearly capacity of 1.32 million bags containing 0.125 m^3 of expanded perlite.

Grefco Minerals owns 49% of Cia Minera Oriental and Dicalite de México. Cia Minera Oriental extracts perlite from the 35-ktpy open-pit Dimesa mine at Oriental (Puebla), approximately 24 km northeast of Mexico City and supplies Dicalite de México's three expanders (two horizontal [800 kg/hr] and one vertical [2,500 kg/hr]) in Mexico City. It also expands perlite at the mine to supply Dicalite de México, which ships to all states in Mexico and to Latin America.

Industrias de Perlita mines at El Prieto for its expansion plant in Ciudad Juárez y Asencion, Chihuahua. Aislantes del Pacifico mines at Ciudad Obregon, Sonora.

Morocco

The Tiedennit perlite deposit mined by Perlite Roche is east of Tangier in Nador Province. Reserves are about 38 Mt, of which 2 Mt are proven. The Moroccan government, via the Bureau du Recherche et de Participations Minières, owns 20% of Perlite Roche. The remaining 80% is owned by Roche Invest (Moroccan Canadian), which can process 20 ktpy. The main market for Perlite Roche is acidity control during phosphate production. An associate company, Roche Perlite, began expanding in 2001 using an Incon furnace at Berrechid near Casablanca.

Mozambique

Mozambique may currently produce perlite near Muguene, (west of Maputo) in the Lebombo Mountains that extend into South Africa (BGS 2005). The perlite is associated with obsidian and bentonite in the Karoo Supergroup. At Muguene South, the reserves of perlite are 100 kt (proven) and 400 kt (probable). At Muguene North, the reserves are 250 kt (proven) and 1 Mt (probable). The bulk density from Muguene is 0.109 g/cm^3 (6.84 lb/ft^3). A small furnace with small output operated in the 1960s (Cilek 1989).

New Zealand

Perlite occurs in Quaternary rhyolitic domes and flows (Christie et al. 2000). Large deposits occur in the Rotorua-Taupo Volcanic Zone of North Island. Other deposits are on Great Barrier Island northeast of Auckland and at Coromandel. Deposits at Great Barrier Island and Paku Island (both North Island) are Pliocene; at Kinleith and Atiamuri (North Island), Pleistocene-Holocene; and at Gebbies Pass (Banks Peninsula, South Island), Miocene (Harben and Kuzvart 1997).

Production has ranged from about 1.8 to 3.3 ktpy in recent years with minor production as early as the 1970s (Allen 1992). Industrial Processors of Waitakere, West Auckland, mines about 2 ktpy at Atiamuri, north of Lake Taupo, southwest of Rotorua, and 100 km southeast of Hamilton. The perlite is in a small glassy rhyolite dome on the margin of a much larger lithic rhyolite dome within the Taupo Volcanic Zone. The perlite is crushed and screened at the Fulton Hogan Atiamuri sand-processing plant. Material expanded in Auckland is well suited to cryogenic insulation and filter aids.

Peru

Cia Minera Agregados Calcareos of Lima produced perlite in the past but ceased in the 1990s.

Philippines

Perlite deposits are found in Legaspi City, Bagumbagan, Bicol, and the Calayan Islands. Philippine production has ranged from about 4.6 ktpy to about 61 ktpy since 1997 (BGS 2005) with minor production as early as the 1970s (Allen 1992). Exports are mainly to South Korea and Taiwan and less to Thailand and other countries. Philippine exports of crude perlite ranged from 5 to 8 ktpy in the early 2000s.

Induplex is a private company, sold by Dicaperl in the mid-1990s, that retains rights to use the Dicalite trademark. Induplex mines perlite at Legaspi and has a processing plant close to the mine. Its Cavite plant, about 8 hr by road from Legaspi, produces expanded perlite, at up to 15 ktpy.

In 1985, United Perlite acquired Trinity Lodge Mining, established in 1968. United Perlite mines in the Bicol region about 600 km south of Manila and markets products through UBS Marketing, concentrating on filter aids for sugar, coconut oil, and pineapple processing.

Russia

Perlite occurs in Buryatia, on the Kamchatka Peninsula, in Pribalkalie, near Baikalsk, at Pri morskoy krai, Magadan oblast, Chita oblast, Khabarovsk krai, and the Kuril Islands. Reserves in Buryatia are 30 Mt. JSC Perlite of Zaigraevsky raion mines the Mukhor-Talinskoe deposit in Buryatia, and JSC Kamchatskstroimaterialy mines the Nachikinskoe deposit on the Kamchatka Peninsula. Perlite production is 45 ktpy (BGS 2005), including 5 ktpy exported mainly to Japan.

At the Mukhor-Talinskoe deposit, Cretaceous volcanics resembling a highly eroded cone have a central core of rhyolite surrounded by glassy rocks. Weathering has produced secondary minerals such as zeolites, cristobalite, and monmorillonite. The Nachikinskoe deposit occurs in the center of a ring structure, probably an old extrusive caldera of an andesite volcano. Perlite in the lower zone is 2.5 to 10 m thick; the upper part is largely composed of rhyolite and obsidian (Harben and Kuzvart 1997).

Saudi Arabia

Onionskin and granular perlite occur at Harrat Shama (Tafil) and Jabal Shama on the Red Sea coast, about 100 km south-southeast of Jiddah (Laurent 1993), in Tertiary rhyolite flows and breccias (Jeffrey 2002) of the Miocene Liyyah Formation (Laurent 1993). The perlite has been explored and tested, with mixed results, but has not been produced. Perlite is also found at Jabal al Abyad, 130 km north of Al Madinah, associated with acidic volcanic centers. Preliminary testing yielded noncommercial results.

Slovakia

Perlite occurs in Tertiary volcanic rocks (Harben and Kuzvart 1997) at Lehôtka pod Brehmi, Jastrabá, Mala Bará, and Byšča. Total reserves are 30.5 Mt and extend into Hungary. Production ranged from about 19 kt in 1999 to about 15 kt in 2004 (BGS 2005).

Kerko-Perlit mines all of Slovakia's perlite at Lehôtka pod Brehmi, which is processed nearby. Approximately 80% is exported, mainly to the Czech Republic.

South Africa

Perlite (71.72% to 72.36% SiO_2) occurs in the Lebombo Mountain Range, Natal, in Jurassic acidic volcanic rocks as lenses and layers, and has a granular texture (Harben and Kuzvart 1997). These deposits occur near the Mkuze Game Reserve in KwaZulu-Natal around Nxwala Hill along the border with Mozambique. Drilled in

the mid-1970s, proven reserves of 3 Mt were shown in irregular lenses (Strydom 1998). Prately Perlite Mining, sole producer in South Africa, selectively mines Nxwala (Griffiths 1989). The perlite is crushed, dried, classified, blended, and expanded at its Krugersdorp plant for horticulture and construction. Annual production from this resource is approximately 1.2 kt or less (Skillen 1995). In addition, about 10 ktpy of crude perlite is imported from Turkey.

Thailand

Perlite deposits are found in Lopburi Province. Thai production has ranged from about 550 tpy to about 9.9 ktpy since 1997. About 7.6 kt was produced in 2004 (BGS 2005).

Turkey

Turkey has more than half the world's perlite reserves (Houssa 1999). Evaluations of the perlite place the resource at as much as 4,000 Mt (Ozgur 1997). The Turkish government calculated perlite reserves at 5.7 Mt. An estimated 2.8 Mt of this reserve are in eastern Turkey near Erzurum and Karas and extending into Armenia. Other deposits are in western Turkey near Ankara, Izmir, Manisa, Dikili, Bergama, and Çanakkale.

Reported production of crude perlite varies widely by agency. Since 1997, production has been increasing and ranges from about 105 ktpy to about 250 ktpy and in 2004 was about 137 kt (BGS 2003, 2005). Domestic consumption is low (20 kt in 1996; Ozgur 1997), so approximately 75 % is exported to Western Europe including Italy, Belgium, France, Spain, and the United Kingdom. Other importing countries include Brazil, India, Russia, Saudi Arabia, South Africa, and South Korea. After starting in 1961, total exports ranged from about 100 ktpy to 200 ktpy in the early 2000s.

Turkish perlite sells for approximately 40% less than Greek perlite because Turkish exports to Western Europe are mainly for filter aids that sell for less than construction and horticultural perlite. Producers include Eti Mine Works, Harborlite Aegean Endustri, S&B, Per&Tas, and IPM Group.

Eti Mine Works consists of two state-owned mines producing perlite (72 % to 76% SiO₂) at Menderes (Mezarkaya mine) and Manisa (Karagöl II mine). These operations feed a 145-ktpy crushing and screening plant at Izmir, which also has the ability to produce annually 130,000 m³ of expanded perlite and 2,500 m³ of micronized perlite.

Harborlite AS, formed in 1995 from Ege Endustri Mineralleri Sanayi AS, mines near Bergama, feeding a processing plant in Dikili that has an annual capacity of 100 kt. Much of the crude perlite is exported to affiliates in Europe.

IPM Perlit (IPM) mines perlite at Kocaköy, Deveboynu, Bademalan, Maruflar, Damsitepe, and Seleme, encompassing 8,000 ha containing approximately 25 Mt of reserves (*Industrial Minerals* 2004). In 1999, IPM formed Diperlit Filter Mining and Industry to produce and sell to domestic and international markets from an 80-ktpy processing plant at Yayıntaş, Bergama, in Izmir Province. Most production is for the Western European filter-aid market. While large shipments by IPM go through the port at Nemrut Bay, smaller bulk shipments are through Dikili with container/bagged shipments via the port at Izmir.

S&B has owned most of Pabalk Mining and Saba Madencilik since 1995. Pabalk mines near Biga in Çanakkale and supplies perlite to Saba Madencilik, which operates a 40-ktpy processing plant approximately 3 km from the port of Karabiga, where all processed perlite is exported.

Table 2. United States perlite production and imports, kt

Activity	1999	2000	2001	2002	2003	2004*
Production	711	672	588	521	493	510
Imports	144	180	175	224	245	190
Exports	(47)	(43)	(43)	(42)	(37)	(40)
U.S. consumption	808	809	720	703	701	660
U.S. average price†	33.40	33.78	36.31	36.45	38.20	35.22

Source: Bolen 2005.

* Estimated.

† US\$/t.

Perlitas Istanbul Perlit Sanayi ve Ticaret mines about 40 ktpy at Bergama. Its processing plant at Bergama can produce 50 ktpy of crude perlite, mainly for filter-aids manufacture.

Per&Tas mines in Izmir.

Ukraine

The Shinoi-Varna deposit (72.98% SiO₂) near Zakarpattia is mined by JSC Beregovsky, the only commercial producer. Since the mid-1990s, production has been about 24.3 ktpy, far below capacity of about 340 kt. Three grades of crude perlite are produced. The finest grade is used in ceramic tiles, whereas coarser grades are used in construction and horticulture. Two undeveloped deposits in the same area are Arlovskoe and Fogoshskoe with reserves of 66 Mt and 28 Mt, respectively.

United Kingdom

Perlite occurs in northwest United Kingdom and on the Isle of Arran. Perlite deposits in Northern Ireland at Sandy Braes, County Antrim, have estimated reserves of 10 Mt. About 13.8 kt were produced between 1951 and 1968 by British Gypsum. Antrim Perlite evaluated this deposit in the mid-1990s and was issued a prospecting license in 1997. Progress has been hampered by lack of a local market.

The United Kingdom is a major importer of crude perlite, averaging approximately 65 ktpy in the early 2000s, mainly from Germany, Italy, Netherlands, and Turkey.

United States

Total U.S. production in 2004 was 510 kt, an increase after five consecutive years of decline (Table 2; Barker and Santini 2005). Recent extensive discussion of North American deposits can be found in Austin and Barker (1995, 1998), Chamberlin and Barker (1996), Kendall (1999b), and Barker et al. (2002).

Exports to Canada and the Pacific Rim partially offset imports. After a record 245 kt in 2003, imports from Greece to the Eastern and Gulf coasts of the United States declined about 22%. The market for Greek imports remains protected by high rail rates from western U.S. plants. Minor imports by Termolita from Mexico persist. In 2004, Noble Materials was sold to Grefco (Dicaperl), and in 2005, Basin Perlite was sold to Harborlite (World Minerals), and World Minerals was sold to Imerys.

Overall U.S. consumption declined about 6%, a decrease for the fifth consecutive year since 2000. Since 2000, consumption dropped about 18% mainly because of lower demand in construction (Bolen 2005). The average price of perlite in the United States declined about \$3.00—to \$35.22—in 2004.

End uses of expanded perlite, including microspheres, was construction, 62% (64% in 2003); horticultural aggregate, 13%;

Table 3. Estimated 2004 production of processed perlite sold by the four largest producers in the United States

Perlite Operation	Production,* 1,000 st	Production,† kt	Percentage of Total
Harborlite, No Agua, New Mexico	216	196.0	38
Harborlite, Superior, Arizona	50	45.5	9
Dicaperl, Socorro, New Mexico	130	118.0	23
Dicaperl, No Agua, New Mexico	5	4.5	1
Cornerstone, Oregon	110	100.0	20
Harborlite, Utah	21	19.0	4
Other	30	27.0	5
U.S. total	560	510*	100

* Estimated.

† Calculated and rounded from estimates.

fillers, 10%; filter aids, 9%; and other, 6% (Bolen 2005). Crude perlite was produced by eight companies in seven western states operating 10 mines (Table 3). Sales remain strong for very coarse horticultural perlite (hort) or very fine perlite for microspheres.

Development of microspheres continues to meet customer demands in the 2000s for ever lower density and specific shapes or treatments. Worldwide microspheres production is by five U.S. companies: Harborlite (Utah), Therm-O-Rock West (Arizona), Therm-O-Rock East (Pennsylvania), Silbico (Illinois), and Dicaperl (Colorado, Nevada, and Oklahoma). Only Harborlite Utah and Dicaperl control their own sources of perlite.

Arizona

Middle Tertiary flow-banded rhyolite partly underlies low hills on the northern flank of Picketpost Mountain and a few miles to the east. Intercalated with the rhyolite is onion-skin perlite (~71% to 75% SiO₂) that locally exceeds ~200 m in total thickness (Welty and Spencer 1987; Austin and Barker 1995). The Harborlite mine is in Pinal County ~3 km southwest of the processing plant at Superior and includes the former Nord operations. Onionskin is mined from a 2- to 15-m bed that has a trace of pumiceous perlite and contains black obsidian (Harben and Kuzvart 1997). Production was 45 kt in 2004 and is particularly well suited for filter aids. About 98% is used "in-house" at Harborlite expansion plants and about 2% is used in aggregate.

California

American Perlite mines and processes perlite 11 km from Big Pine near Fish Springs in the Owens Valley, Inyo County. A Recent volcanic dome, ~65 m in height, is elongated east to west and capped by layered, vesicular pumiceous perlite (74.5% SiO₂) locally with dark-gray to black obsidian (Austin and Barker 1995).

Production in 1997 was about 36 kt of granular perlite from an ~25-m ore zone. About 75% to 80% was trucked to Southern California for lightweight aggregate in fiberboard and approximately 20% to 25% for horticultural purposes.

Idaho

During the late 1980s, National Perlite Products (Oglebay Norton) mined the Wrights Creek deposit, which is located approximately 40 km south of Pocatello, Idaho and contains about 10 Mt perlite (75% to 76% SiO₂), pumice, and rhyolite as part of a caldera com-

plex. A dacite plug underlies part of the perlite yielding near vertical dips (Austin and Barker 1995).

The crude perlite was expanded at Malad City, 40 km south of the mine, until 1994. Several owners subsequently tried to reopen the operation. During 2000, Idaho Minerals purchased perlite from other producers in an attempt to enter the perlite business using the Malad City plant while it evaluated the mine at Wrights Creek. This operation was inactive in 2005.

New Mexico

New Mexico continues to be the major producer in the United States with production at No Agua Peaks and Socorro. The Socorro deposit is mined by Dicaperl, and the operations at No Agua include mines and processing plants owned by Harborlite and Dicaperl. Both companies have additional processing and truck or rail loading facilities 37 km north in Antonito, Colorado.

The U.S. Gypsum mine at Grants had minor production throughout the 1990s (<10 ktpy). The granular perlite on the flank of East Grants Ridge consists of a domal complex of perlite, obsidian, and rhyolite flows (Weber and Austin 1982) about 3.3 million years old (Barker et al. 1989). The operation was put on the market in 2001 and due diligence was performed, but no sale was made. The plant was dismantled, the mill and mine were reclaimed, and the lease from the railroad was dropped in 2003.

The Dicaperl mine is about 5 km southwest of Socorro in Socorro County on the southeast flank of Socorro Mountain (part of a caldera complex). The Miocene volcanic glass hosting the granular perlite is about 7.85 million years old and is part of a high-silica (74.35% SiO₂), high-potassium rhyolite. The perlite, which is in a faulted dome, is at least 200 m thick in places, so reserves are substantial (Weber and Austin 1982; Austin and Barker 1995; Chamberlin and Barker 1996). Rippers and scrapers feed a conveyor belt to the processing plant for drying, grinding, air classifying, and storage in silos. Production of about 250 ktpy in the early 2000s dropped to 118 kt in 2004. Dicaperl produces 8 to 10 grades blended as needed to customer specifications and shipped by rail to in-house and customer expanders mainly for ceiling tile and horticulture.

The Dicaperl El Grande mine, part of the Nu-Alexite deposit, is on the western side of No Agua Peaks, a few miles north of Tres Piedras in Taos County. The deposit is a Pliocene (~4 million years old) glassy lava flow (75.97% SiO₂), weathered to granular perlite (Austin and Barker 1995; Chamberlin and Barker 1996). Obsidian is locally abundant. Mining is by ripping, scraping, and occasional blasting before the short transport to the plant. Mined perlite is passed over a grizzly and through a jaw crusher before entering a rotary dryer, followed by grinding and screening. Past output of this mine, which had been the third largest perlite mine in the United States, was about 180 ktpy. In 2004, when 5 kt was produced, Dicaperl put the El Grande mine at No Agua Peaks on standby for campaign mining. About 80% of past production was used in the construction market, about 10% for horticulture, and 10% mainly for at least seven grades of filter aids.

The Harborlite No Agua mine, approximately 3 km east of U.S. 285 and in the eastern No Agua Peaks adjacent to Dicaperl, was the largest perlite producer in the United States in 2004 (Table 3). This deposit was originally owned by the Schundler Company (a perlite and vermiculite processor in New Jersey) followed by Johns Manville until it came under the control of World Minerals, Inc. in 1991. The dissected rhyolitic dome (from one to four domes) (Naert 1974; Breese 1984; Whitson 1982; Chamberlin and Barker 1996) and flows are Pliocene (about 4 million years old) with locally abundant obsidian. Mining, in several open

pits over the years, is by ripping and occasional blasting of perlite, which is then moved by front-end loaders into trucks that haul it to the mill for drying, grinding, and classifying into seven grades, and then to silos for storage. Perlite is pulled from silos for blending or on-site expansion or to meet customer specifications and then discharged into pressure-differential railcars at Antonito. A small amount is trucked. Most is shipped to ceiling tile and construction end users or Harborlite expansion plants.

Many perlite deposits in New Mexico have been evaluated since the 1950s, but none has been mined for sustained periods. The Brushy Mountain pumiceous perlite deposit is about 16 km east-southeast of No Agua Peaks and was most recently mined by Silbrico until the early 1980s. The perlite is a vitrophyric breccia ~22 million years old (Oligocene/Miocene) with associated rhyolite flows (Weber and Austin 1982). The large amount of fine waste plus transport over gravel roads made this relatively remote operation unprofitable. Scharkan (1992) investigated three deposits at McDonald Ranch and Wallace Ranch, both of which have been drilled and tested, and at Schwartz. The Leitendorf Hills pitchstone, about 15 km south-southwest of Lordsburg (Weber 1963), is very large and was mined briefly in the early 1950s (Flege 1959), but the variability and high expanded density of the pitchstone have hindered development since.

Nevada

Nevada has large perlite resources, and several have been mined extensively. The largest past producer was the Hollinger mine near Pioche in Lincoln County. Perlite production in Nevada in 2002 was restricted to relatively small-scale mining of three deposits for niche markets.

The Tenacity mine of Wilkin Mining and Trucking, about 40 km west of Caliente in Lincoln County, is an open-pit operation that exploits a blue-gray onionskin perlite of Miocene age. The top of the mined interval has obsidian in irregular patches (Austin and Barker 1995). Wilkin operates a small expansion plant in Caliente, about 50 km east of the mine. Production has been as high as 3.6 ktpy, principally for the horticultural market in Southern California. In 2004, the company shipped about 1.6 kt.

At the Eagle-Picher 6.6-ktpy plant, about 11 km northeast of Lovelock at the Eagle-Picher Colorado diatomite operation in Pershing County, production in 2004 was ~4 kt. The screening and expansion plant came online in 1994 with one furnace feeding captive filter-aid (12 grades) operations. Crude perlite is from the Popcorn mine in Churchill County, 55 km south of Fallon and about 130 km south of Lovelock, with reserves estimated to be 1.4 Mt. Granaria Holdings of the Netherlands is the controlling shareholder of Eagle-Picher, which was for sale in 2005.

In 2001, Noble Materials began mining from a deposit a few kilometers east of the Popcorn mine for microspheres production in Fallon. The microspheres were sold in sizes that averaged between 30 and 70 μm . In 2002, the company ceased mining in Nevada and switched to Cornerstone perlite from Oregon (USGS 2002a) and Harborlite perlite from New Mexico. The Noble operations in Nevada and Oklahoma were sold to Dicaperl in 2004.

Oregon

Cornerstone Industrial Minerals, part of Seven Peaks Mining, runs the Tucker Hill perlite mine about 55 km northwest of Lakeview in Lake County. The perlite varies from onionskin (minor) to granular, the preferred ore with less obsidian. Proven reserves are 4.9 Mt, and indicated resources are more than 30 Mt. The perlite is mined using blasting in an open pit and crushed to -1.25 cm . It is trucked to the processing plant at Lakeview where it is further crushed, dried, and

screened to produce 11 standard plus custom grades of crude perlite stored in silos for blending, if required. Shipments are mainly by rail or truck (Speltz 1998) to expanders near Portland, principally on contract to Armstrong World Industries in St. Helens. The 2005 production of Cornerstone was ~112.5 kt, mostly for horticulture but also for ceiling tile and industrial insulation. About 75% of the sales were to the western United States, western Canada, and the Pacific Rim; the rest was sold to customers mainly in the eastern United States and eastern Canada (Barker, Santini, and Alatorre 2004).

Supreme Perlite, established in 1954, periodically mines at Dooley Mountain in Baker County, east of Portland. Processed perlite is shipped to its expansion plant in Portland and to other end users. Supreme sells several grades to the construction and horticultural markets. In the past, most perlite that Supreme expanded in Portland came from No Agua, New Mexico.

Utah

The crude perlite and microspheres plants of Basin Perlite are at Milford, Utah, about half way between Las Vegas and Salt Lake City, on the main line of the Union Pacific Railroad. Harborlite Utah produces crude perlite products (horticulture, construction) and microspheres. It also supplies microspheres feed to both Therm-O-Rock East (New Eagle, Pennsylvania) and Therm-O-Rock West (Chandler, Arizona); the latter produces microspheres for Harborlite Utah through a tolling agreement. The microspheres are shipped to Harborlite Utah's joint-compound customers in Arizona, Malaysia, and Mexico, which include U.S. Gypsum, the world's largest producer of joint-compound (from the Harborlite Utah, Therm-O-Rock West, and Therm-O-Rock East plants). Therm-O-Rock East produces microspheres for customers in the eastern United States and eastern Canada.

The Basin deposit, in the Mineral Mountains about 18 km northeast of Milford (USGS 2002b), occurs in the Quaternary Bailey Ridge Flow, which is subdivided into three lithologic units: lower rhyolite; middle rhyolite and obsidian; and upper obsidian and perlite, which hosts the Basin open pits (now dormant). Perlite is up to 27 m thick, and total reserves or resources are approximately 25 Mt (Santini 2003). Mining was by contract as campaigns (14 to 36 kt) in open pits by ripping with a bulldozer or excavator, followed by crushing and screening. The 23-tph plant had a capacity of 91 ktpy, where drying and crushing produced 10 standard sizes stored in silos for blending, if needed; Basin typically blended ~20% to 30%. Basin shipped in bulk and in various packaging, including 910-kg supersacks and 151-L barrels for foundries. Harborlite Utah now processes perlite from the Black Rock Desert 65 km to the north in the former Basin plant.

Fine perlite for microspheres is pneumatically conveyed from the perlite plant to the microspheres plant. The perlite is roller-milled and air-classified before discharging to a vertical expansion furnace. Uncoated microspheres are produced and shipped in bulk or in 227-kg supersacks. Basin also produced coated microspheres as needed.

EXPLORATION

Deposits of perlite occur commonly throughout the world, and geologically the outlook is excellent for discovery and development of new resources. The competitive pressure exerted by existing producers within market areas will impair the ability of new sources to supply the same markets and end users. This is especially true in the United States.

Fundamental strategy for the exploration for perlite requires an integrated approach incorporating the recognition of geologic

occurrence and lithologic and temporal modeling. Perlite is usually associated with Tertiary to Quaternary high-silica volcanic rocks and flows/domes, which provide general parameters to guide regional reconnaissance for new resources. Rhyolitic complexes of Oligocene to Middle Quaternary age have proven to be successful target areas for initial field reconnaissance. The glasses within this age range are old enough to have hydrated extensively and are young enough to have escaped extensive erosion. More recent glasses are likely to be incompletely hydrated and to have less commercial potential as sources for high-quality perlite. The hydrated glass selvages of flows and extrusive domes are often extensive and can be easily mined using low-cost open-pit methods, making this occurrence type an attractive target for exploration. The perlitic tuffs and breccias often associated with domes and flows offer additional resources.

The study of many deposits provides useful lithologic and textural models that have been developed for exploration and evaluation of deposits. Models help guide the placement (and termination) of drill holes and mine planning. Though the presence and the development of textures and zonation are variable among deposits, the features exhibited at the No Agua deposit in New Mexico are commonly observed in flow/dome occurrences throughout the world. Although no single model can be applied to all occurrences (Chamberlin and Barker 1996), the rock types, textures, and zonation as described at No Agua provide a useful basis for geologic mapping and for the uniform comparative description and interpretation of deposits.

Traditional methods used for exploration of perlite deposits include detailed mapping to identify source vents and flows, core drilling, and trenching. Detailed mapping is employed to delineate basic rock types, perlite textures, and contaminants such as clay, caliche, rhyolite, and obsidian. Mapping and modeling can be used in conjunction with geophysical techniques for the prediction of trends and the location of the concealed portions of perlite bodies. Core drilling and trenching are used to assess continuity and quality of perlite. Optimum spacing and placement of drill holes is based on the variability of lithology and quality within individual deposits. The core diameter must be large enough to ensure high core recovery and to provide sufficient samples for evaluation. If perlite quality is uniform and geology is well known, cuttings from percussion, rotary, or reverse-circulation drilling can be used instead of core.

MINING

Throughout most of the world, the lower cost of surface mining relative to underground mining drives producers to use open-pit methods. Most perlite mines use either ripping or blasting, or both. If the perlite is soft and friable, brecciated, or extensively jointed, ripping is employed with significant cost savings. Blasting is required where perlite cannot be readily broken using rippers, but care must be taken to achieve fragmentation without production of excessive fines or oversized material. Once broken and sometimes crushed, the perlite is loaded on trucks or conveyor belts by front-end loaders, excavators, or scrapers for transport to the processing plant. Selective mining is used to minimize rhyolite or obsidian. If perlite textures vary, it is often blended to produce consistent milling characteristics and to meet market specifications.

PROCESSING

Perlite processing follows three main lines: crude, expanded, and microspheres. Crude perlite and expanded perlite are the main products. The expanded perlite is divided into foam (multicellular) and microspheres (mostly unicellular).

Table 4. Size distribution for some Basin Perlite products

Product*	Sieve Size Range	Major End Uses
PQP-100	-6 +12	Horticulture
PQP-120	-12 +30	Horticulture, ceiling tile
PQP-130	-12 +50	Ladle topping, loose-fill cavity insulation, masonry
PQP-145	-16 +50	Loose-fill insulation, masonry
PQP-150	-30 +100	Fire-resistant insulation
PQP-160	-50 +100	Ceiling tile, fire-resistant insulation
PQP-170	-50 +200	Pipe insulation
PQP-180	-100 +200	Cryogenic insulation
PQP-192	-200	Soap
PQP-200	-200	Ceramics
PQP-500	-100	Joint compound

Adapted from Basin Perlite literature.

* Most of these products are blended from various bins per customer specification.

Crude Perlite

The size of the expanded perlite particle is determined mainly by the particle size of the feed to the furnace. The final particle-size distribution will vary among producers, but basic milling and classifying processes include primary and secondary crushing, drying, classification, tertiary crushing, and dust collection. Crude perlite, usually stockpiled, is reduced in size through jaw crushing prior to drying. Following drying, particle size is further reduced through additional crushing and sized over vibrating screens. Variants on this general procedure include the use of gyratory cone crushers for primary crushing, and impact mills, rod mills, hammer mills, gyrodisks, and roll crushers in secondary and tertiary crushing. The basic perlite size grades are stored in silos and can be blended to meet the specifications of customers (Table 4).

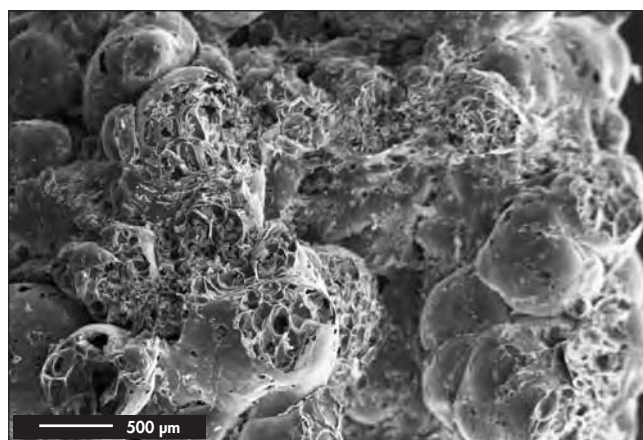
Processing has changed in recent years to favor some particle sizes over others. This market-driven size preference is illustrated by the shortage of horticultural grade material (hort) and the ramp-up in microspheres production in the early 2000s. Plants were, as much as possible, reorganized to favor coarser grades (jaw crusher feeding a cone crusher, for example) and to enhance fines production. Some middle grades may become unsalable under certain market conditions and are wasted when this strategy is used.

Expanded Perlite

Foam (Multicellular)

When heated to softening, perlite can expand to as much as 40 times its original volume. Expansion is generally achieved at temperatures that range from 600° to 900°C in one of two basic furnace types: the stationary vertical expander or the rotary horizontal expander. Both operate on the same principle. Crushed and sized perlite is rapidly introduced into a hot zone, where volatilization of the combined water within the glass is coincident with the softening of the glass. The resulting frothy particle (Figure 3) exhibits extremely low-density, high surface area and light or white color.

The stationary vertical furnace is the more widely used of the two furnace types (Jackson 1986). Sized perlite, which may or may not be preheated, is gravity-fed through a side port into the hot zone where expansion occurs. The expanded particles are carried by updraft into the cyclone collection system. Expanded particles pass through the hot zone and drop from the system, while shattered fines are carried upward and are collected in the baghouse.



Courtesy of New Mexico Bureau of Geology and Mineral Resources.

Figure 3. Expanded horticultural perlite showing thin-walled multicellular grain

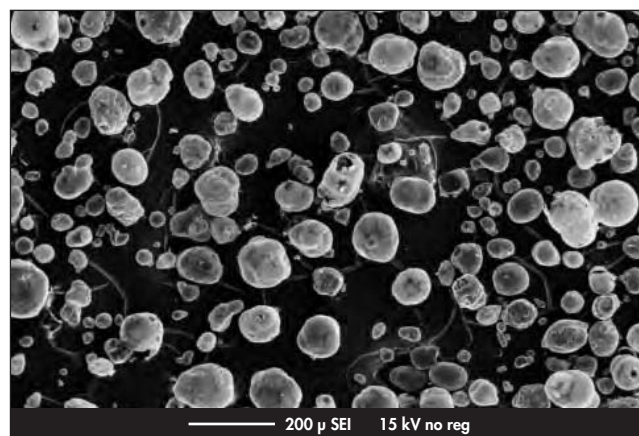
Within a rotary horizontal furnace, the feed falls into the hot zone toward the top of the flame. As in the vertical furnace, the feed may or may not be preheated before introduction into the hot zone. As the furnace rotates, the feed travels by lifters and spirals down the length of the tube, and the expanded product is drawn by draft into the cyclone and baghouse system. Following the cyclone sizing, the product may be milled and classified for use as filter aid or may be surface treated for other applications. Final products are bagged, then loaded as bulk into railcars or trucks (of ten pressure differential) or into containers.

The densities and particle strengths of the expanded perlite required by the end user vary by application. The final density and recovery of the product as well as the fuel efficiency of the expander can be improved through preheating the furnace feed (Jackson 1986). For vertical furnaces, preheating is achieved in an external, separate heater. In horizontal furnaces, the feed is preheated as it is transported between the inner and outer shells of the furnace to the hot zone where expansion occurs. Preheating the coarser grades can be important because of the relationship between the ratio of volume to surface area of the particle, heat transfer, and residence time in the hot zone of the furnace (Jackson 1986). Although some flexibility of finished product properties can be achieved through adjustment of furnace conditions and through preheating, it is important to note that all perlites do not expand alike. Kadey (1983) has written that perlite containing excessive combined water is likely to shatter upon expansion, whereas perlite containing less water is likely to produce higher-density products. Perlite is also classified as live or dead based on its expansion characteristics (Murdock and Stein 1950). A typical value of 3.2% to 3.7% combined water in perlite seems to work best in most situations.

Microspheres (Unicellular)

Feedstock for microspheres production is crude perlite. At one microspheres operation, the former Basin Perlite in Utah, the general processing method was as follows:

1. Crude perlite was pneumatically conveyed from bins to the microspheres plant.
2. The perlite was ground in a roller mill to $-75\ \mu\text{m}$ (-200 mesh) and passed through a double whizzer that returns oversize ($+75\ \mu\text{m}$) to the roller mill for regrinding.



Courtesy of New Mexico Bureau of Geology and Mineral Resources.

Figure 4. Uncoated perlite microspheres expanded from very-fine crude perlite. The glassy, spherical, hollow particles consist of one or more microcellular bubbles with intact walls. Note the holes or "blow-outs" on the prominent particle near the center of the scanning electron microscope (SEM) photo and on a few other particles.

Table 5. Physical properties of selected Silbrico microspheres products

Grades	Sil-32	Sil-42	Sil-35	Sil-43
Oil absorption ASTM-D-1483, grams oil per 100 cc	30	36	38	40
Hygroscopic moisture m	0	0	0	0
Surface Hardness	7.0	7.0	7.0	7.0
Thermal conductivity, $\text{Wm}^{-1}\text{K}^{-1}$	0.36	0.40	0.41	0.43
Color	White	White	White	White
Dry bulk density, kg/m^3	112	136	145	168
Average particle size, μm	75	45	40	35
Effective particle density (in resin), kg/m^3	179	250	250	303
Particle size range, μm	1–300	1–210	1–150	1–150
Fusion point, $^{\circ}\text{C}$	1,260	1,260	1,260	1,260

Adapted from Silbrico Corporation literature.

3. The $-75\ \mu\text{m}$ material was jet-stream classified to $-75 + 10\ \mu\text{m}$ ($-200 + 1250$ mesh) with an average particle size of 25 to $30\ \mu\text{m}$.
4. This material was fed to a 4.5 ktpy (3-shift) vertical furnace for expansion.

The expansion furnace burned natural gas, and operated at a temperature range of 480° to 600°C . Upon expansion, glassy, spherical-shaped hollow particles were produced, which consisted of one or more microcellular bubbles (Figure 4). This product (BASIN 500) had a particle size of 100% -100 mesh ($160\ \mu\text{m}$), an average particle size of 250 mesh ($60\ \mu\text{m}$), and a bulk density of 112 to $144\ \text{kg/m}^3$.

Depending on customer requirements, the microspheres could be surface modified with either silicone or silane. These coatings increase the hydrophobicity (water repellency) of the microspheres. The finished product was then conveyed to storage bins for shipment to customers.

See Table 5 for additional information on physical properties of microspheres.

Table 6. End uses of crude and expanded perlite in North America*

Type	Category	Application	Remarks and Properties
Expanded	Formed	Insulating board	~70% perlite + cellulose + binder
		Ceiling tile	~75% perlite + cellulose + binder
		Pipe insulation	Perlite + sodium silicate + fiber
	Construction	Wallboard	Decreases shrinkage, reduces weight
		Loose fill	Wall cavities (silane or silicone)
		Masonry fill	Masonry block fill (silicone or asphalt)
		Plaster aggregate	Reduced rebound when gunned
		Concrete aggregate	Yields 15–50 lb/ft ³
		Joint compound	Enhanced workability (microspheres)
		Door core	Fireproofing; door liner ~75% perlite
		Coatings	Sprayed; texturizer
		Cryogenic	Fills annular space between tank walls
		Carrier	Cosmetics
		Filter aid	Food, beverages, liquids; Blunt 1994
		Horticultural	Retains water, aeration; Blom 1994
		Hay	With 50% bentonite, binding hay cubes
		Filler	Plastics, sealants, caulks, adhesives
		Animal litter	Poultry litter, animal feed
		Textile	Gentler stonewashing of fabric
Crude	Stone	Decorative	Landscaping; golf sand traps
	Abrasive	Sandblasting	Silica substitute; polishes and cleansers
	Foundry	Ladle topping	Insulating crust and coagulant of silica
	Silica	Acid treatment	CaF ₂ scavenger in phosphates
	Pottery	Flux	Feldspar substitute
Research	Surface charge	Activated perlite	Expanded and crude; Dogan, Alkan, and Cakir 1997.
	Microspheres	Fluidized bed	Sodeyama et al. 1996, 1997a, 1997b.
	Synthetic	Zeolite	Christidis, Galani, and Marcopolous 2000.
	Substitute	Feldspar	Mogilski 1990; Bozadgiev 1995.

Adapted from Meisinger 1985; Shackley and Allen 1992; Breese and Barker 1994; Gunning 1994; Austin and Barker 1995, 1998; Bolen 1998, 2000; Englert 2000; Kendall 2000; Barker et al. 2002.

* About 97% of perlite produced in the United States is expanded, of which 71% is used in construction.

Table 7. Typical particle size distribution of selected microsphere products (shown as percent retained on each sieve)

U.S. Sieve	Sil-32, wt %	Sil-42, wt %	Sil-35, wt %	Sil-43, wt %
+50 mesh	2	Trace	0	0
–50 +100	15	5	Trace	Trace
–100 +200	33	25	12	5
–200	50	70	88	95

Adapted from Silbrico Corporation literature.

END USES

In the United States in 2004, perlite end uses were construction products, 62%; horticultural aggregate, 13%; fillers, 10%; filter aids, 9%; and other uses, 6% (Bolen 2005). Worldwide, construction is by far the dominant end use (Englert 2000).

The commercial physical properties of expanded perlite include low bulk density, physical resilience, chemical inertness, low thermal and acoustical conductivity, fire resistance and nonflammability, and water retention. Crude perlite ranges from light gray to black in outcrop. In contrast, the most distinguishing characteristic of expanded perlite, other than low density, is brilliant white color. Even in end uses where color is not paramount, white is the preferred

color, even at a cost penalty. The brilliant white of expanded perlite offers aesthetic advantage in light colored, visible surface coatings.

The greater hardness of perlite, its chemical resistance, and porosity are important in horticulture when soils are wet for prolonged periods or where drainage, aeration, and water retention are required. Addition of perlite to dry soils aids retention of water. The high brightness of finely ground perlite applied to the surfaces of seed blocks reflects light to the underside of seedlings and promotes rapid and sturdy growth. Typical specifications (Chang 2002; Harben 2002) for crude perlite by mesh size and end use are shown in Table 4. Many end uses are summarized in Table 6 and are described in works by Kendall (2000), in which Table 2 lists valuable perlite characteristics related to application; and by Barker et al. (2002); and Harben (2002).

Microspheres

Perlite microspheres are inert, nontoxic, low density, white, micron-sized functional fillers (Table 7).

Used mainly in joint compound as part of wallboard installation, perlite microspheres provide the following properties to joint compound:

- Reduce weight and shrinkage
- Lessen cracking and sagging

- Reduce drying time
 - Enhance workability
 - Improve impact resistance, nailing, stapling, and sanding
- Non-joint compound end-use applications include the following:

- Textured and acoustical coating mixes
- Cultured marble
- Adhesives and sealants
- Wall-patching compounds
- Stucco
- Auto body putty
- Thermo-set castings
- Syntactic foam
- Sheet molding (SMC) and bulk molding compounds (BMC)
- Rotational molding
- Fiber-reinforced product (FRP) spray and hand lay-up
- Tub and shower enclosures
- Specialty coatings
- Block filler paints

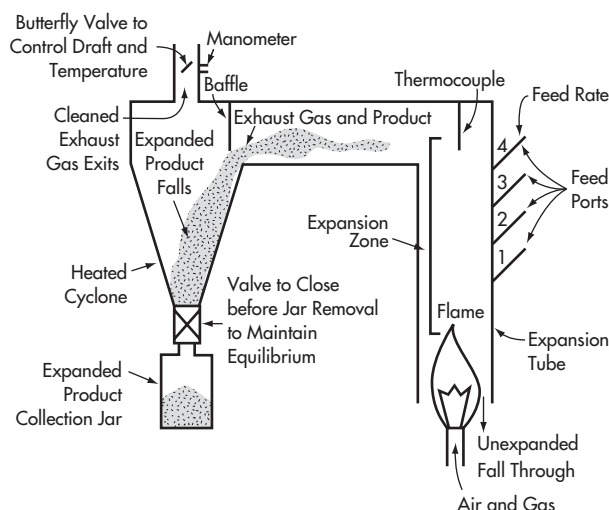
TESTING

Perlite deposits are evaluated for suitability in four main end uses: horticulture, construction, filter aids, and fillers/extenders. Basic testing of expanded perlite, done for exploration, usually is loose weight (expanded density, furnace yield [mass balance]), sieve analysis of expanded perlite, brightness, and sinters. Additional end-use specific tests (Giles and Poling 1991) may be performed later. For example, a special grinding regime and chemical tests are added to filter-aid-grade perlite testing, owing to its use in the food industry. Tests for filter aids are given in the *Perlite Institute Handbook* (Anon. 1984), the U.S. Food Chemical Codex, and Breese and Barker (1994).

Facilities for testing perlite, both crude and expanded, are sparse on a commercial, cost-effective, or readily accessible basis. Little information or data are accessible regarding perlite testing of many products (Barker, Hingtgen, and Bowie 1987; Barker and Harris 1990). To maintain quality and performance standards, the Perlite Institute, formed in 1949, assembled a comprehensive testing procedure and specification manual, which includes tests developed by the Perlite Institute, as well as specifications established by the American Society for Testing and Materials (ASTM). The *Manual of Test Methods* (Perlite Institute 1984) is available through members of the Perlite Institute in Harrisburg, Pennsylvania, via its Web site. Barker et al. (1987) and Breese and Barker (1994) give descriptions of testing equipment, procedures, and calculations; some are adapted slightly from the Perlite Institute tests.

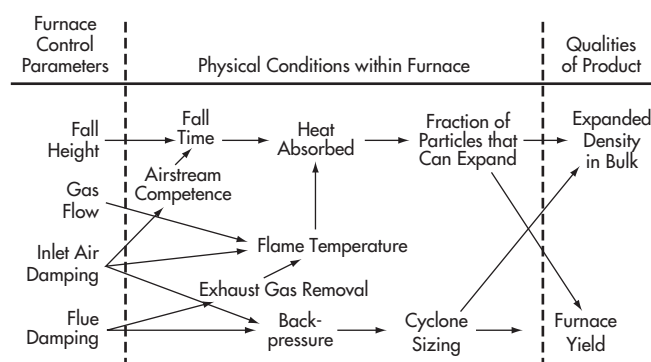
Perlite testing is not an exact science. Interpretation of results requires experience, and scaling up from laboratory results demands caution. Scale-up problems abound in designing full-scale plants based on bench-scale expansion tests. No correlation has been demonstrated between bench-scale expansion tests using horizontal furnaces and similar tests in commercial plants (Kadey 1983). Scaling up from vertical furnace bench testing to full-scale testing has better correlation, but full-scale testing must be done prior to investment in mining or processing of perlite.

Use of perlite microspheres is relatively new, and testing procedures and specifications are often kept confidential. For use in joint compound, bulk density and particle-size distribution are the main criteria (Table 5). An important test for all end uses is crystalline silica content so that compliance related to health regulations can be determined.



Adapted from Barker and Harris 1990.

Figure 5. Schematic diagram of a laboratory perlite furnace showing feed ports above the flame and expanded perlite in the cyclone. Note the location of thermocouple for measuring expansion temperature.



Adapted from Barker and Harris 1990.

Figure 6. Interactions between control settings, furnace conditions, and product quality in a perlite furnace

Expansion

Efficient expansion of perlite particles is highly dependent on their surface-area-to-volume ratios. A narrow, unimodal size distribution is preferred for testing. The small size of laboratory expansion-furnace tubes (typically 1 to 2 m long) makes it sensitive to feed particle size (Figure 5). Expansion in a 1-m tube is best using the -50 +100 mesh fraction at 700°C, although the -30 +50 mesh fraction can also be used at higher temperature of up to 800°C.

Perlite expansion is a function of its composition (especially water content), fluxing agents (calcium, sodium, and potassium), feed rate to the furnace, fines in the feed, softening temperature, furnace temperature, and particle residence time in the flame. Additional factors affecting perlite expansion are humidity, barometric pressure, and ambient air temperature (Figure 6). Seasonal variation and reaction to changing elevation if the furnace is moved are measurable. Ambient conditions at the furnace location (temperature, humidity, combustion, air flow, etc.) are additional variables. Perlite expansion is thus more art than science and is highly operator dependent.

More heat must penetrate some perlite particles to achieve good expansion. These tend to produce particles with round, multiple cells and thick bubble walls that retain their integrity, useful in construction and horticulture. Preheating the perlite feed, increasing the furnace temperature, and/or optimizing feed size are possible ways to mitigate this or decrease energy use. Other perlites are more responsive to furnace heat and tend to shatter when expanded, producing bubble-wall shards forming better filter aids (Blunt 1994). Either outcome provides a commercial product.

Expansion and testing of perlite is done under varying conditions, so a standard must be used. The higher the expanded density of an unknown perlite sample compared to the standard, the more energy-intensive perlite production will be. Test results can also be reduced to the ratio between an unknown sample and the standard to dampen some of the variability or can be normalized on the standard. Finally, as many variables as possible should be controlled, especially by using the same technician to do the tests.

Commercialization

Laboratory-expanded perlite is handled differently than commercially expanded perlite. Laboratory perlite is carefully moved between containers in small amounts compared to large tonnages of expanded perlite air-classified in plants. The laboratory material has less size reduction from handling and has lower expanded density and fewer fines for otherwise identical expanded perlite. Commercial feed, and hence product, often is not sized as accurately as the material tested in laboratories. These relationships must be considered when scaling up to commercial production. The density to which a perlite expands affects many of its commercial properties, so the expanded density is crucial to assigning a given perlite to its most favorable end uses.

Test results generally cannot be interpreted separately. Scaling up from laboratory results must be done with caution. Pilot-plant testing must be done prior to construction of commercial processing facilities.

PERLITE PRICES

The perlite market is sensitive to trends in the construction and horticulture sectors. Expanded perlite comprises the majority of worldwide consumption. Historical perlite production and average prices in the United States are given in DiFrancesco and Bolen (2004), and recent data are in Table 2. All prices are free on board (f.o.b.) plant with transportation additional.

Crude Perlite

Crude perlite is used as an expanded furnace feed, slag coagulant, abrasive, metal cleanser, and silica source. Typical prices for crude perlite range from US\$27.50/t to US\$449.50/t. In the early 2000s, horticultural perlite reached US\$95/t.

Expanded Perlite

Most of the market for expanded perlite is in construction-related products such as roof insulation board, acoustical ceiling tile, pipe insulation, concrete, and plaster aggregate. Prices for expanded perlite range from US\$190 to US\$660/t.

Microspheres

Prices for microspheres depend on packaging and on whether they are coated with silicone or silane. Pricing ranges from US\$0.44 to US\$0.66/kg, or US\$440 to US\$660/t.

TRANSPORTATION AND PACKAGING

Expanded perlite bulks out before it tons out against the carrier weight limit, so most perlite is shipped unexpanded. Imports usu-

ally arrive by ship at ports with convenient road or rail access to expanding plants. In the United States and Canada, shipping to customers is generally by rail, and, as in Europe, the perlite is expanded locally for use nearby. Ocean freight exports from Greece to the United States began in 1983 and continue.

Fine grades of perlite are often moved in bulk in pressure differential (PD) railcars or truck trailers. Perlite is distributed in several packaging sizes and types. Bags and various supersack systems are common. Overseas, perlite is shipped packaged in containers.

Filter aids are shipped expanded in bags as light as 7.5 kg. They are usually handled pneumatically in bulk and require less line pressure and pump horsepower than competing products. Perlite is easily fluidized for unloading (Blunt 1994).

Microspheres

Customers purchase microspheres in 0.12-m³ plastic-lined bags (16 to 22 kg) or in 227-kg supersacks. Microspheres are shipped in bulk by PD truck (bulks out at approximately 6 t) or PD railcar (bulks out at approximately 23 t). Some producers, like the former Basin Perlite, also ship packaged microspheres offshore utilizing containers.

ECONOMIC AND COMPETITIVE FACTORS

No tariff is applied on perlite imported into the United States, where the depletion allowance is 10%.

Substitutes

Expanded perlite competes with polystyrene, vermiculite, and pumice as an ultra-lightweight aggregate, thermal and acoustical insulator, and bulking agent. The resilience of perlite is preferred for concrete under wet conditions. In cryogenic applications, where the insulating material must have low thermal conductivity, perlite dominates the market. The worldwide availability of perlite deposits and expansion facilities and lower price make it more competitive than vermiculite where physical resilience or brightness is paramount.

In horticulture, perlite, polystyrene beads, and vermiculite can be used selectively in different market segments. In loose-fill insulation, polystyrene beads and vermiculite are competitive.

Pumice must be shipped in its natural, lightweight form and hence is less competitive (Evans 1993) because of the very high transport costs, although higher grain-strength benefits aggregate use.

Filter aids have long been dominated by diatomite. The irregular and platy particles of milled perlite perform well in rotary vacuum filters and in filter-aid applications needing high flow rates without high clarity.

Environment and Regulation

Perlite is composed of amorphous volcanic glass with trace crystalline materials such as quartz and feldspar. Quartz is present in low amounts in perlite, generally ranging from <1% to 5%. The crystalline silica in perlite occurs primarily as alpha and beta quartz and sometimes as cristobalite or tridymite, which are more reactive in the body than alpha and beta quartz (Sax and Lewis 1988). When perlite is mined, processed, or utilized, some of the crystalline silica may become airborne, but little of this occurs as respirable dust (<5 to 10 µm in diameter). The relationship of pulmonary fibrosis in workers exposed to crystalline silica dust for widely varying lengths of time is well documented (Sax and Lewis 1988), and the perlite industry has addressed these health issues for many years. Perlite dust is treated and regulated as a nuisance dust with appropriate exposure limits enforced.

In 1987 and 1988, the International Agency for Research on Cancer (IARC), under charter by the World Health Organization, reviewed literature regarding the health effects of crystalline silica

(IARC 1987, 1988). IARC then classified crystalline silica as a Class 2A (probable carcinogen) in humans. This finding was based on limited evidence in humans and sufficient evidence in animals (Miles 1998; SME 1998) and only applies to inhaled (respirable) crystalline silica, not to dust that is ingested or contacted. The carcinogenic risk of crystalline silica was revisited in 1996 with a recommendation and reclassification of quartz and cristobalite as Group 1 (carcinogenic in humans) published in 1997 (IARC 1997). Silica regulation has ensued as many nations, including U.S. federal and state agencies, consider the findings of IARC when writing health-related legislation.

The regulation of silica in perlite and other materials is complex and ever changing. Miles (1998), SME (1998), and Health Council of the Netherlands (SZW 2003) provide an overview. The U.S. regulations presuppose that untreated mixtures of products and crystalline silica present the same hazard as any component of the mixture comprising more than 1% by weight or volume. If a component is a suspected carcinogen, then the threshold becomes 0.1% by weight or volume, and a carcinogenic warning label is required if this value is exceeded. Dilution of the mixture to below the threshold level of 0.1% can eliminate the need for labeling. Thus, the two key values for crystalline silica in perlite are 0.1 and 1.0 wt %.

The industry has responded to silica regulations by mobilizing several organizations, mandating protective equipment wear by workers, updating material safety data sheets (MSDSs), dust reduction and monitoring, development of test methods suitable to the 0.1 and 1.0 wt % thresholds, and training. Even though crystalline silica is of concern, perlite dust is not harmful itself (Cooper and Sargent 1986) and is now treated as nuisance dust. Fugitive dust generated on windy days is often noticeable in communities surrounding perlite processing.

The crystalline silica content of perlite filter aids must be determined prior to the pilot-plant stage of development. The crystalline silica content of both crude and expanded perlite is regulated as a carcinogen. Testing for crystalline silica is done routinely using x-ray diffraction (XRD) methods (Barker and McKee 1990; Hamilton and Peletis 1990; McKee, Renault, and Barker 1990; Miles and Hamilton 1991; Miles and Harben 1991; Renault, McKee, and Barker 1991, 1992; SME 1998; Miles 1998). Key levels are 0.1 wt % and 1 wt % crystalline silica. The total crystalline silica along with the amount of quartz, cristobalite, and tridymite should be determined. The crystalline silica from perlite is usually diluted during end use and rarely presents a problem unless very high concentrations are found. Perlite is very well suited to XRD detection of trace crystalline silica because it is mostly amorphous volcanic glass. Other methods of analysis for crystalline silica include x-ray fluorescence (XRF), optical petrography, electron microscopy, wet chemistry, heavy liquid separation, solubility, and infrared absorption.

FUTURE TRENDS AND OUTLOOK

The perlite industry continues to mature. Growth is slow but steady, and consolidation into fewer and larger firms has begun in North America. S&B has penetrated markets aggressively worldwide and is clearly the industry leader in the mid-2000s. The perlite industry in the United States continues to undergo rapid change and increased competition.

Microspheres

The demand for perlite microspheres in North America is expected to increase as the wallboard market grows. As construction practices change outside of North America, such as from lathe and plaster to wallboard, the international market for perlite should grow significantly.

In addition, some joint compound producers project a higher growth rate for "lightweight" joint compound compared to "standard or all purpose" in the western United States. This is being driven by (1) an increased use of lightweight joint compound and (2) commercial and residential construction growth in this region of the United States. Lightweight joint compounds have a higher microspheres content (>30 wt %) than all-purpose joint compounds (<15 wt %). Producers have performed R&D for producing a super-lightweight joint compound that will require a "lower bulk density" perlite microspheres product.

Non-joint-compound end uses for perlite microspheres should continue to grow, as the producers begin to direct more market development in this area. Also, R&D efforts by producers and consumers will probably result in new end-use applications.

The North American joint compound market for perlite microspheres is estimated by wallboard producers to be approximately 55 ktpy. Annual growth rate for the next few years is projected at about 2.5% to 3.0%. The major consumers of perlite microspheres for joint compound production are U.S. Gypsum (>50%), National Gypsum, Hamilton Materials, BPB Gypsum, Lafarge Gypsum, and Georgia-Pacific Gypsum. U.S. Gypsum has 20 joint compound plants in North America: 13 in the United States, 5 in Canada, and 2 in Mexico. In addition, it has a plant in Malaysia. Smaller producers in the United States include Magnum Products, Murco Wall Products, Freeman Products, Southern Wall, Solids Products, Supro, Tool World, Custom Building Products, Kadex, Welco Manufacturing, and Century Industries.

Non-joint-compound consumption is not known, because it is a fragmented market (i.e., a wide variety of end uses). However, industry estimates place it at about 15 ktpy.

Silica

Crystalline silica in general is tending toward an asbestos- or arsenic-style debate (Chajet 2004). In the face of large declines in silica mortality, various government and private groups are proposing very stringent silica exposure rules. Silica deaths declined to less than 180 deaths in 2000 (compared to about 1,800 in 1969), owing to reductions in exposure set in place years ago. This trend suggests that silica mortality may be on the verge of elimination in the next few years as deaths approach zero. An opposing trend is the massive increase in silica-related lawsuits, including at least 35,000 in 2003 alone (Chajet 2004). U.S. Silica has a total of more than 32,000 silica claims (Ulizio 2004), mostly in Mississippi (57%) and Texas (33%), which are states favorable to these types of lawsuits. As summarized by Chajet (2004), the situation is as follows:

- Restriction of the "sophisticated buyer" defense is developing for producers delivering in bulk to commercial customers.
- Product information may need to be supplied to customer employees at supplier expense.
- A silica health insurance exclusion is being applied to renewals and new policies.
- Temporary or contract workers must be protected from harm.
- Companies are reviewing hazard information to ensure that all high-risk workers (both those employed by the company and those who work for its customers) are informed.

Drastically lower silica thresholds have been proposed and are likely to be implemented, perhaps at great cost to the perlite industry.

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Phosphate Rock

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INTRODUCTION

Phosphorus is essential to plant and animal life. It provides the material for skeletal bone structure in animals and for cell membranes in both plants and animals. The largest and least expensive source of phosphorus is obtained by mining and concentrating phosphate rock from the numerous phosphate deposits of the world. The principal use for this phosphate rock is the manufacture of fertilizer ingredients for food-crop nutrition and the production of animal feed supplements for use in promoting healthy and quick skeletal growth for meat-producing livestock.

Phosphorus is also the second most abundant mineral in the human body, after calcium. This mineral is essential for the healthy formation of bones and teeth and for processing many of the foods that are consumed. It is also a part of the body's energy storage system and helps maintain healthy blood sugar levels. Phosphorus is also found in substantial amounts in the nervous system. Regular contractions of the heart are dependent on phosphorus, as are normal cell growth and repair.

Phosphate deposits are widely distributed throughout the world, with major economic ore bodies located in the United States, Morocco, China, Russia, South Africa, Jordan, and Australia. These deposits are generally surface mined, with a minor portion mined underground. The United States is currently the world's largest producer of phosphate rock, accounting for 25% to 30% of world production; Florida and North Carolina account for about 85% of this. The gradual decline in U.S. production and increases elsewhere could soon lead to the United States, Morocco, and China producing about equal amounts of phosphate rock.

Untreated phosphate rock, which is a substituted calcium phosphate containing minor amounts of carboxy, hydroxy, and fluoride ions, is only slightly soluble in groundwater and therefore provides little available phosphorus for plant nourishment. More than 90% of the phosphate rock consumed in the United States is used to manufacture wet-process phosphoric acid by reaction with sulfuric acid. This phosphoric acid is then used to produce various fertilizer ingredients, animal feed supplements, and some other phosphorus chemicals. The phosphatic fertilizer ingredients include diammonium phosphate (DAP), monoammonium phosphate (MAP), and triple superphosphate (TSP). DAP and MAP are produced by reacting the phosphoric acid with ammonia, and TSP is obtained by reacting the phosphoric acid with phosphate rock. Recent information indicates that 50% of U.S. phosphoric acid production is exported as either commercial acid or a reacted fertilizer

ingredient, and this accounts for more than 50% of global interregional trade in phosphates, 90% in MAP and 75% in DAP.

The world phosphate market began to recover in 2002, following more than 2 years of weak market conditions caused by lower fertilizer demand, excess capacity, and changes in global supply patterns. Adverse economic conditions significantly affected producers in the southeastern United States that rely heavily on export sales. Since late 1999, three phosphate producers filed for bankruptcy, two phosphate plants in Florida closed permanently, and several other plants and mines temporarily closed or reduced their output. Domestic production of phosphate rock and phosphoric acid, and fertilizer export shipments, increased in 2002. Although the United States has remained the largest global supplier of phosphate fertilizers, its share of the world DAP export market fell from about 65% in 1998 to less than 50% in 2002 (Prud'homme 2002). The current recovery, however, has been accompanied by increased prices for raw materials such as ammonia and sulfur, and so profit margins remain slim.

World production of phosphate rock was estimated to reach 138 Mt in 2003 (Jasinski 2004). Low-grade sedimentary phosphate ores containing calcareous impurities such as calcite or dolomite in addition to siliceous gangue must be beneficiated to meet the expected continuing demand. For more than 65 years, flotation has been successfully applied to both sedimentary and igneous phosphates with siliceous gangue (Houot 1982). Meanwhile, calcination was the only technique used for upgrading sedimentary phosphates with carbonate gangue anywhere other than China and Utah, in the United States (Abdel-Khalek 1982). Calcination has several recognized drawbacks; these include the high energy consumption (Elgillani and Abouzeid 1993) and the lower acidulation reactivity of the calcined products (Abdel-Khalek et al. 1994). As a consequence, some plants no longer use the calcination process, such as the El-Hamrawien phosphate plant on the coast of the Red Sea in Egypt. It is therefore important to develop an alternative technique to upgrade the sedimentary phosphates with carbonate gangue minerals.

In Florida, phosphate mining and processing changed only incrementally during the past half century. Current practice begins with huge draglines removing the overburden and dumping it in spoil piles adjacent to the mine pit. The phosphate ore (matrix) is scooped out, placed in earthen wells, slurried with high-pressure water, and pumped to the beneficiation plant. At the plant, the matrix is washed to complete disaggregation, screened to produce a

Table 1. Phosphate rock world mine production, reserves, and reserve base, kt

Region	Mine Production			Reserves [†]	Reserve Base [‡]
	2002	2003	2004 [*]		
Australia	2,025	2,290	2,300	77,000	1,200,000
Brazil	4,850	5,600	5,650	260,000	370,000
Canada	1,000	1,000	1,100	25,000	200,000
China	23,000	24,500	25,000	6,600,000	13,000,000
Egypt	1,500	2,140	2,150	100,000	760,000
India	1,250	1,180	1,200	90,000	160,000
Israel	3,500	3,210	3,000	180,000	800,000
Jordan	7,180	6,760	6,800	900,000	1,700,000
Morocco and Western Sahara	23,000	23,000	23,000	5,700,000	21,000,000
Russia	10,700	11,000	11,000	200,000	1,000,000
Senegal	1,500	1,470	2,000	50,000	160,000
South Africa	2,910	2,640	2,600	1,500,000	2,500,000
Syria	2,400	2,430	2,400	100,000	800,000
Togo	1,280	1,480	1,500	30,000	60,000
Tunisia	7,750	7,890	8,000	100,000	600,000
United States	4,830	35,000	37,000	800,000	2,000,000
Other countries	36,100	5,000	3,500	1,000,000	4,000,000
World total (rounded)	135,000	137,000	138,000	18,000,000	50,000,000

Source: USGS 1998–2004.

* Estimated

† That part of the reserve base that could be economically extracted or produced at the time of determination. The term *reserves* need not signify that extraction facilities are in place and operative. Reserves include only recoverable materials; thus, terms such as *extractable reserves* and *recoverable reserves* are redundant and are not a part of this classification system.

‡ That part of an identified resource that meets specified minimum physical and chemical criteria related to current mining and production practices, including those for grade, quality, thickness, and depth. The reserve base is the in-place demonstrated (measured plus indicated) resource from which reserves are estimated. It may encompass those parts of the resources that have a reasonable potential for becoming economically available within planning horizons beyond those that assume proven technology and current economics. The reserve base includes those resources that are currently economic (reserves), those that are marginally economic (marginal reserves), and some of those that are currently subeconomic (subeconomic resources).

pebble product (1 × 19 mm), and then hydrocycloned to remove fine phosphatic clay (passing 150 mesh), which is collected in clay settling ponds. The remaining flotation feed (16 × 150 mesh) is upgraded using the Crago double float process, which consists of high solids conditioning with fatty acid/fuel oil at about pH 9.0 to 9.5; flotation of the phosphate mineral; acid scrubbing of the concentrate to remove the reagents; and, finally, flotation of the residual fine sand from the phosphate mineral using an amine. Virtually all the phosphate rock produced is acidulated with sulfuric acid in nearby chemical plants, and the resultant phosphogypsum precipitate is filtered from the phosphoric acid and stored in large gypsum ponds and stacks.

Several problems are becoming more serious in Florida, and these will require changes in the not-too-distant future if the state is to maintain its leadership role in phosphate rock and fertilizer production:

- As mining progresses to the southern and western parts of the state, the phosphate matrix contains less pebble product, is becoming lower grade, and is more contaminated with dolomite.
- Because of increased environmental concerns, mining and production permits are much more difficult to obtain and have tighter restrictions on land use, water consumption, waste disposal, and reclamation of clay ponds.
- Because of recent bankruptcies, government entities are more concerned about environmental liability, especially as related to clay ponds and phosphogypsum stacks and ponds.

The technical problems have been recognized for a number of years, and measures have been taken to address them, although economic solutions are not all at hand. The political pressures are more surprising and will perhaps dictate the acceptance by industry of compromises that will lead to higher capital and operating costs for future and continuing operations. One of the leaders in calling attention to and attempting to solve these pressing problems is the Florida Institute of Phosphate Research (FIPR), which is supported by a portion of the severance tax paid to the state by the mining companies. Most of the funds expended by FIPR support contract research, which is awarded based on proposals submitted by companies, universities, and consultants, although there are a small number of internal research projects as well. Among the projects funded through FIPR are those addressing phosphate rock mining and mineral processing, fertilizer chemical processing, environmental concerns, and mined land and gypsum stack reclamation.

PRODUCTION AND TRADE, RESOURCES AND RESERVES Phosphate Rock

The current, most concise, and authoritative statistics on phosphate rock production and identified reserves worldwide can be found in the U.S. Geological Survey (USGS) *Mineral Commodity Summaries 2004*; these are summarized in Table 1.

Table 2 lists phosphate rock production by country from 1994 through 2003.

The industrial revolution of the nineteenth century provided a ready supply of sulfuric acid. This, coupled with the development

Table 2. Phosphate rock production by country and year, kt

Country	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004*
United States	41,100	43,500	45,400	45,900	43,968	40,600	38,600	38,600	36,100	35,000	37,000
Australia	21	5	1	1	1	2	977	1,893	2,025	2,209	2,300
Brazil	3,937	3,888	3,823	4,270	4,421	4,100	4,900	4,900	4,850	5,600	5,650
Canada	na†	na	na	na	na	na	300	800	1,000	1,000	1,100
Mexico	547	622	682	714	756	951	1,052	787	na	24,500	25,000
China	24,100	19,300	21,000	24,500	30,980	25,100	19,400	19,400	23,000	2,140	2,150
Egypt	632	765	808	900	1,076	na	na	na	1,500	1,180	1,200
India	1,237	1,332	1,432	1,500	1,730	na	na	na	1,250	3,210	3,000
Israel	3,961	4,063	3,839	4,047	4,067	4,100	4,110	4,110	3,500	6,760	6,800
Jordan	4,217	4,984	5,355	5,896	5,967	6,000	5,510	5,510	7,180	23,000	23,000
Morocco and Western Sahara	19,764	20,200	20,855	23,367	23,587	24,000	21,600	21,600	23,000	11,000	11,000
Russia 8,000		9,000	8,500	9,900	12,074	11,100	11,100	11,100	10,700	1,470	2,000
Senegal	1,587	1,500	1,340	1,300	1,503	1,800	1,800	1,800	1,500	2,640	2,600
South Africa	2,545	2,822	2,655	2,732	2,961	2,900	2,800	2,800	2,910	2,430	2,400
Syria	1,203	1,551	2,189	2,392	2,496	2,100	2,170	2,170	2,400	1,480	1,500
Togo	2,149	2,570	2,731	2,200	2,253	1,700	1,370	1,370	1,280	7,890	8,000
Tunisia	5,699	7,241	7,167	7,068	7,959	8,000	8,340	8,340	7,750	35,000	37,000
Other countries	6,960	9,029	10,100	11,500	11,000	9,500	11,300	11,300	4,830	5,000	3,500
World total (rounded)	127,000	130,000	135,000	144,000	150,857	141,000	133,000	133,000	135,000	137,000	138,000

Source: USGS 1998–2004.

* Estimated.

† na = not available.

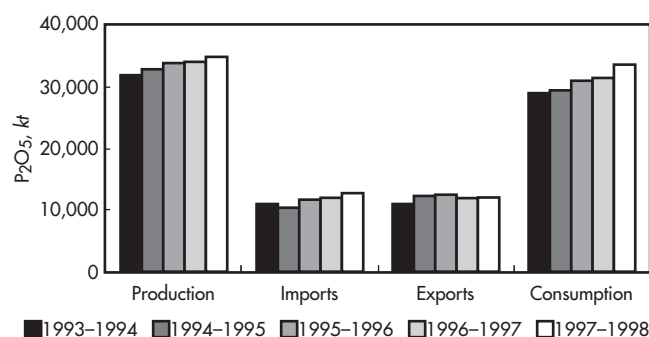
of the rich phosphate deposits of Florida, North Carolina, Tennessee, and North Africa, was the main basis for the phosphate industry in Europe, North America, and Oceania. Today, the United States, China, and Morocco produce about two thirds of the world's phosphate rock. Morocco alone accounts for one third of the international trade in phosphate rock. China has emerged in the past decade as the third largest producing nation, whereas the countries of the former U.S.S.R. saw their share decline to 8% from nearly 25% of the world phosphate fertilizer production because of the collapse of their domestic markets.

Globalization is reflected in the increase in international trade. Although phosphate rock trading has declined from almost 40% in 1980 to about 25% today from its country of origin, if processed phosphates are included, about 60% of the phosphate is exported. Morocco and the United States account for nearly half of these exports, with the United States exporting more than 50% and Morocco more than 95% of their respective phosphate production. The top three rock exporters include Morocco, Jordan, and the former U.S.S.R., accounting for about 50% to 60% of the world rock exports. Togo and Syria also export all or most of their production.

Processed Phosphate

Figure 1 shows world production, imports/exports, and consumption of phosphate fertilizers (in tons of phosphate [P_2O_5]) for five crop years.

Thirty years ago, the main form of traded P_2O_5 was phosphate rock, which was processed in superphosphate and compound fertilizer plants, predominantly in the developed world. Over the last 30 years, the role of phosphate rock as an export carrier of P_2O_5 has declined sharply as vertically integrated industries have been developed at or close to the site of rock mines. World phosphate rock exports fell from 53 Mt of product in 1979 to 27 Mt in 1993 but subsequently increased to stabilize at about 30 Mt. The U.S. industry, for example, was exporting about 10 Mt of rock on average from 1966 to 1986; this was reduced to a few thousands tons in



Adapted from FAO 1999.

Figure 1. Production, imports/exports, and consumption of phosphate fertilizers, 1993–1998**Table 3. World trade in processed phosphates**

Processed Phosphates	1986–1988, Mt	1999–2001, Mt
Phosphoric acid	3.8	4.6
Ammonium phosphate	4.2	8.7
Triple superphosphate	1.6	1.5
Total	9.6	14.8

recent years. Correspondingly, world trade in processed phosphate products increased substantially (Table 3). Almost all the phosphoric acid plants in Western Europe have closed, for economic and environmental reasons.

As is indicated in Table 3, ammonium phosphate as MAP and DAP accounts for most of the increase in processed phosphate trade. Table 4 shows production data from major producers (countries) of phosphate fertilizer.

Table 4. Leading producers of phosphate fertilizer, kt

Country	1995–1996	1996–1997	1997–1998	1998–1999	1999–2000	2000–2001	2001–2002
United States	10,500	10,900	10,765	9,000	8,500	7,300	7,600
China	6,017	5,747	6,405	6,700	6,400	6,700	7,400
India	2,626	2,615	3,090	3,200	3,400	3,700	3,900
Russia	1,933	1,575	1,777	1,700	2,000	2,300	2,400
Brazil	1,265	1,305	1,353	1,400	1,400	1,500	1,400
Morocco	936	979	921	958	955	1,122	1,230
France	668	682	687	489	450	318	277
Tunisia	741	790	673	782	870	885	892
Spain	413	478	488	530	459	439	432
Mexico	427	433	469	479	515	435	352
South Africa	373	397	378	378	391	267	264
Jordan	335	308	279	338	336	234	277
Republic of Korea	421	409	438	421	421	421	327
World Total	33,847	34,020	34,925	33,328	33,093	32,200	33,545

Adapted from FAO 1999.

Table 5. Leading exporters of phosphate fertilizer, t

Country	1995	1996	1997	1998	1999	2000	2001
United States	5,838,000	5,679,000	5,519,506	5,730,693	5,471,252	4,401,601	5,119,642
Morocco	817,800	872,200	849,173	826,060	862,420	1,045,100	1,160,500
Tunisia	686,400	705,000	671,500	728,360	800,300	865,600	875,100
China	114,000	174,000	135,000	148,000	211,000	289,000	347,000
Republic of Korea	198,712	199,933	198,000	228,000	187,983	215,613	189,300
Poland	175,000	151,000	216,500	229,900	212,500	196,200	188,973
South Africa	108,500	162,800	118,400	115,800	154,100	83,600	86,900
Germany	97,000	102,000	107,000	80,000	86,000	94,000	83,000
Finland	51,000	50,000	45,000	41,000	47,000	50,000	55,000
France	57,300	59,700	52,300	52,100	48,500	33,000	27,000

Table 6. Major importers of phosphate fertilizer, t

Country	1995	1996	1997	1998	1999	2000	2001
China	2,936,000	2,482,000	3,012,400	2,892,000	2,699,900	2,211,500	1,786,400
Brazil	338,030	445,783	702,604	691,405	621,124	1,119,696	1,146,619
India	686,270	218,500	715,900	986,100	1,532,400	423,100	494,562
Australia	614,300	649,800	707,000	699,000	672,000	661,000	600,000
France	612,600	561,200	573,900	574,700	576,900	510,000	509,000
Italy	459,000	475,000	489,000	457,000	467,000	402,000	436,000
Pakistan	272,772	381,206	415,731	434,656	416,500	369,000	429,300
Germany	409,000	368,000	376,000	388,000	412,000	361,000	316,000
Argentina	197,200	388,700	272,000	295,000	394,300	341,126	312,824
United Kingdom	349,000	348,000	277,000	276,000	317,000	279,000	279,000
Vietnam	159,000	201,400	192,600	160,900	65,900	314,000	291,000
United States	181,000	167,000	187,091	142,835	186,911	195,941	237,191
Japan	336,000	326,000	334,000	320,900	339,700	346,500	131,000
Iran	283,700	242,400	244,400	217,100	260,900	336,322	168,251

Total world exports of phosphate fertilizers increased from an average of a few million tons during the 1970s to the current level of about 13 Mt. Indeed, there has been a general tendency for processed phosphates to substitute for phosphate rock in the international trade. The United States is the leading exporter of phosphates, with about a 40% share of world trade (see Table 5).

From the mid-1970s to the early 1980s, most of the increase in processed phosphate trade was in the form of phosphoric acid, but subsequently it was DAP, which accounted for most of the increase.

Asia is the most important importing region for ammonium phosphates, followed by Western Europe and Latin America (see Table 6). Chinese DAP imports account for roughly one quarter of

the world trade. Although its DAP imports are relatively small considering its population, India is the world's leading importer of phosphoric acid for use in DAP production.

GEOLOGY

Mineralogy

Generally, phosphate minerals are found in igneous, metamorphic, and sedimentary deposits. In sedimentary marine ores, the phosphate is usually a carbonate fluorapatite. In igneous deposits, the phosphates have compositions close to that of fluorapatite. In some deposits, Ca-Fe-Al and Fe-Al phosphates are associated with apatite (McClellan and Germillion 1980). Currently, the apatites recovered from igneous and metamorphic rocks have commercial importance, but such apatites supply only a small fraction of the world market. On the other hand, sedimentary phosphates have been, and no doubt will continue to be, the major source of commercial raw material for the phosphate industry.

These sedimentary apatites, because of their widely differing modes of chemical composition, display large variations in physical forms and types of associated gangue. Accordingly, these ores fall into one of the following three principal categories (Lehr and McClellan 1973):

1. Siliceous ores. In this type, the major gangue mineral is quartz, chalcedony, or opaline forms of silica. The Bone Valley deposit in central Florida, the upper unit of the Hawthorn Formation in north Florida, and the upper zone of the Hawthorn Formation in central Florida belong to this type. Phosphate ores in Australia and Senegal also fall under this category.
2. Carbonaceous ores. This type of ore consists of phosphatic limestones or calcareous phosphates in which calcite, dolomite, or ankerite is mixed with the phosphate, or which occurs as intercalated seams. These include the lower zone of the Hawthorn Formation in central Florida; most of the phosphate deposits in Hubei and Guizhou provinces, China; the Kara Tau Formation in Russia; a majority of the Mongolian deposits; and some of the Moroccan phosphates.
3. Clayed phosphates. These phosphate ores are associated with gangue minerals containing mainly clays and hydrous iron and aluminum oxides. These gangue minerals are concentrated mostly in the silt and clay size ranges. Most of the phosphate ores in Morocco and Western Sahara, Tunisia, and Togo contain up to 40% clay, whereas the Florida phosphate matrix is composed of one third each of clay, phosphate, and sand.

Geology—Sedimentary

Bateman (1951) gave an enlightening description of the phosphate cycle, summarized here. The sedimentary cycle of phosphorus is quite interesting. Dissolved phosphate enters the soil and is abstracted by plants. It then passes to the bodies of animals and is returned to the soil via their excreta and bones, accumulating into deposits. Phosphate in the deposits may undergo dissolution and end up in the sea, where phosphorus is accumulated or deposited by sea life, embodied in to sediments and returned to the land upon uplift. Some of the phosphorus in the sea is consumed by fish life and passes into birds, whose subsequent excreta have built up great phosphate deposits on some islands of the Pacific. Sedimentary beds of phosphate are formed only under marine conditions in the form of phosphorite. These beds have been formed from early to recent geologic periods and extend with remarkable regularity over thousands of square miles, as in the Bone Valley formation in Florida and the

Qulad Ab doun plateau (Khouribga) in Morocco. Sedimentary deposits of marine origin are sparingly fossiliferous and oolitic.

The high-quality phosphate deposits of the world have been formed by the process of sedimentation, including those of Algeria, Tunisia, and Morocco. These deposits require minimal treatment to produce the most desirable phosphate rock. The Moroccan deposits occur as horizontal beds along with limestone, marls, and clays in which there are 3 to 4 beds up to 2.5 m thick. Deposits in the western United States underlie parts of Utah, Wyoming, Idaho, and Montana, and extend into Canada. The beds are in the Phosphoria formation of Permian age, and the chief bed is about 1.5 m thick. Other major sedimentary phosphate deposits are found in Egypt and Russia. The large phosphate deposits of Florida are generally classified as sedimentary, although they are not strictly sedimentary beds, but pebble deposits derived from a sedimentary phosphate bed. The guano deposits of the Pacific islands are also not sedimentary.

Geology—Igneous

The important igneous phosphate deposits are found in certain intrusive complexes of alkalic rocks. Unlike sedimentary deposits, igneous phosphates generally occur as ringlike structures with limited area extent (generally, 1 to 20 sq mi). Commonly near the center are veins and larger bodies rich in carbonates (calcite, dolomite, siderite, and ankerite) formed either in a molten condition or by metasomatic processes. These carbonate deposits are called carbonatites. Apatite of economic interest can be in the carbonatites or in the alkalic rocks located outward from the central carbonatite. In carbonatites, apatite may be in a weather-enriched surface mantle, or in the unweathered rock (Lefond 1983).

Among the more economically important igneous apatite deposits being exploited commercially are the Khibina nepheline syenite massif near Kir ovsk in the Kola Peninsula in Russia, the Jacupiranga alkalic complex in Brazil, and the Palabora carbonatite in South Africa.

The most important deposit of igneous apatite mined today comes from Kola; the output is more than 9 Mtpy of concentrates with a P_2O_5 grade of 39% from an ore assaying 18% P_2O_5 , 23.1% SiO_2 , and 13.3% Al_2O_3 in a bonded phase of nephelinitic syenites.

Other important igneous phosphate ores are present at Phalaborwa in South Africa. The igneous complex comprises a suite of intrusive alkali rocks that intruded granite gneiss to form three coalescing and concentric lobes. The complex is about 7 km long and varies from 2 km to 4 km wide. The outermost zone consists of syenite and the intrusion is a feldspathic pyroxenite. The next zone consists of an apatite-bearing phlogopitic pyroxenite. Foskor operates an open pit for apatite extraction in a corner of this zone. The apatite varies from 0% to 30% P_2O_5 , averaging 7%, with the principal gangue minerals of diopside and phlogopite. The pyroxenite zone is followed by the foskorite zone, which consists of magnetite, serpentine, and apatite, assaying 6% to 11% P_2O_5 . Originally within the foskorite zone was a carbonatite core hill, which now has largely been excavated and is the large open pit of the Palabora Mining Company (PMC). In 1979 Foskor and PMC reached an agreement in which PMC would extend their open pit, with Foskor sharing the cost, and in return Foskor would receive certain types of ore mined by PMC. Foskor now produces phosphate rock from three sources: pyroxenite ore, foskorite ore, and PMC tailings (Schmidt 1999).

The Brazilian apatites also represent an important source of igneous phosphate ores. They are included in carbonatites (with simple carbonates as in Jacupiranga or as more complex ones with iron carbonates, phlogopite or vermiculite, titanium minerals, barytine, pyrochlore, etc.). The P_2O_5 contents are comparatively low, from 5% for Jacupiranga to 15% for Araxa.

DISTRIBUTION OF MAJOR DEPOSITS

Several excellent references are available on this topic. For mining-oriented discussion of world phosphate deposits, the *World Survey of Phosphate Deposits* (British Sulphur Corporation 1987) is a good resource. For geology oriented information, the best resource may be *Phosphate Deposits of the World* (1986). Only the major phosphate deposits are briefly described in this chapter.

The Americas

Canada

Potentially economic phosphate reserves in Canada are found in Ontario and Quebec. There are also widespread occurrences of phosphate rock of various ages in the Rocky Mountains of British Columbia. The Kapuskasing Phosphate Operations, Canada's first-ever phosphate mine, ranks as one of the highest-grade phosphate mines in the world. Located in the Cargill Township about 40 km southwest of Kapuskasing, this mine has been developed to supply high-quality, low-cost phosphate rock to Agrium's facility in Redwater, Alberta.

According to Pressacco (2004), the local geology consists of a core complex of multiphased carbonatite rocks that are surrounded by a ring of pyroxenite. These two rock types are in turn situated within quartz diorite gneisses that form a large portion of the Kapuskasing structural zone. The carbonatite host rock is subdivided into sovite and rauhaugite. The sovite is a medium to coarse grained, white, banded rock in which calcite is the dominant carbonate species. Sovite includes accessory minerals such as phlogopite, magnetite, clinohumite, apatite, olivine, pyrrhotite, and amphibole. Apatite can reach 15% abundance in this rock type (Sage 1988). In contrast to the sovite, the rauhaugite appears as a massive, fine-grained, dense rock, beige or tan in color, in which dolomite is the dominant carbonate species. Phosphate values in the rauhaugite can reach 14% (Pressacco 2004).

The high-grade ore at the Kapuskasing Phosphate Operations is derived from the weathering and dissolution of the soluble minerals in the host carbonatite rock (e.g., phlogopite). This process has left behind a residue of the insoluble minerals, largely apatite crystals, which is termed *residuum*. This residuum forms above the host carbonatite, and is in turn covered by glacial deposits of lacustrine clays and boulder tills of the Pleistocene age. Limited data suggest that this weathering took place during the late Cretaceous period.

Mexico

The major phosphate resources in Mexico are the Miocene phosphate deposits of Baja California. Roca Fosforica Mexicana SA de CV (Rofomex) started up one phosphate mine in Baja California Sur in 1981 and another in 1982. The combined production of these operations was expected to lift Mexico from a position of almost total dependence on phosphate rock imports in 1980 to self-sufficiency in 1985. That goal has not yet been achieved: Mexico still imports about 200,000 tpy of phosphate fertilizer.

The first of the new Rofomex mines is located at San Juan de la Costa on the Gulf of California. It produced its first concentrates in January 1980. The design capacity of the San Juan de la Costa mine is 730,000 tpy of concentrates grading about 31% P_2O_5 from combined open-pit and underground mining operations that extract ores grading 18% P_2O_5 . At Santo Domingo, on the Pacific shore of the Baja California peninsula, Rofomex constructed a mine that could produce 1.5 Mtpy of concentrates by dredge mining a beach sand deposit that grades about 4.5% P_2O_5 at a cut off grade of 3% P_2O_5 .

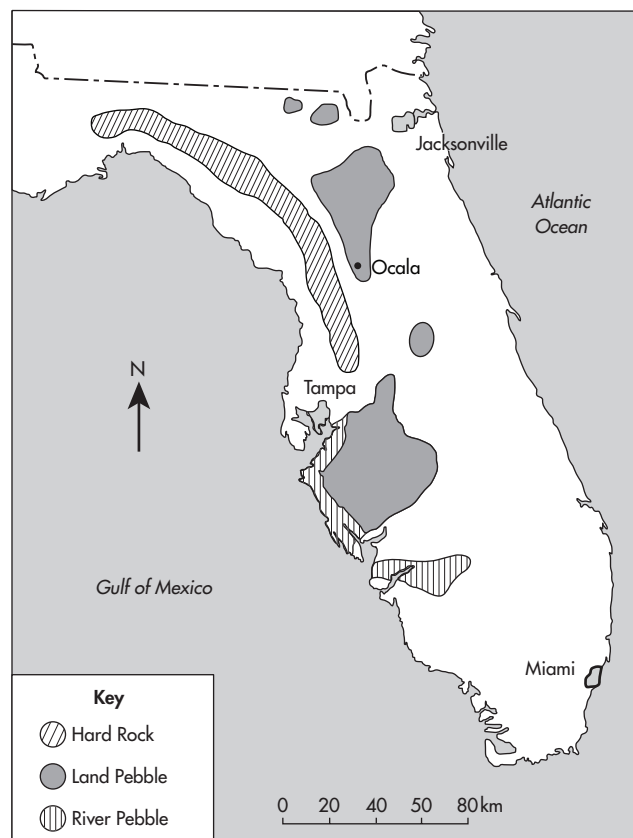


Figure 2. Distribution of phosphate deposits in Florida

Over the long run, Mexico has a substantial phosphate resource to draw on in Baja California Sur, a part from the two deposits being developed. Other phosphate occurrences are located at San Hilario, Santa Rita, Tembabiiche, La Purisima, San Jose de Castro, and San Roque. Of these, the deposit at San Hilario has been the most extensively explored, with drill indications of substantial rock tonnages grading 11% to 13% in weathered cap rock and 14% to 18% in unweathered rock under 30 to 80 m of overburden. In the Santa Rita area, possible economic concentrations of phosphates occur in recent sediments under almost no overburden, but these remain to be more intensively explored.

United States

Florida. The phosphate deposits in Florida fall under three major categories: land pebble, river pebble, and hard rock (Figure 2). The river pebble has long been mined out, and hard-rock mining ceased 40 years ago. Current mining activities are concentrated on two of the largest land pebble deposits, the Bone Valley and Hawthorn formations. The Bone Valley Formation is of Pliocene age, covering six counties in central Florida, roughly 60 mi (97 km) long and 30 mi (48 km) wide. Although this formation was known as one of the richest phosphate deposits in the world, the high-grade ore (matrix) has been almost depleted, with some mines processing flotation feed analyzing as low as 3% P_2O_5 . As a matter of fact, most phosphate ores in central Florida are being extracted from the southern extension of the Bone Valley deposit. As is shown in Table 7, phosphate matrix in the southern extension can be divided into an upper zone and a lower zone (El-Shall and Bogan 1994). The lower zone is highly contaminated by dolomite (Table 8).

Table 7. Analysis of central Florida phosphate matrix

Upper Zone													
Location		Pebble				Feed				Phosphatic Clay			
		Wt %	P ₂ O ₅	% PL*	B	Wt %	P ₂ O ₅	% PL	B	Wt	P ₂ O ₅	% PL	B
Area	A	10	27	59		68	5	9		22	12	26	
B		8	28	63		70	8	17		22	10	22	
C		15	28	63		70	7	15		15	6	13	
Average		11	28	62		69	7	13		20	9	20	
Lower Zone													
Area	A	10	16	35		51	8	17		39	2	4	
B		5	19	45		66	7	15		29	2	4	
C		9	16	35		57	7	15		34	2	4	
Average		8	17	38		58	7	15		34	2	4	

* BPL = bone phosphate of lime (derived by multiplying percent P₂O₅ by 2.185).

Table 8. Average chemical analyses—pebble fractions, wt %

Zone	P ₂ O ₅	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	Na ₂ O	F	Insol
Upper	27.8	41.8	0.52	1.10	0.99	0.57	3.50	12.0
Lower	17.0	35.8	6.19	1.30	0.80	0.43	2.10	13.90

The Hawthorn Formation, on the other hand, is of Miocene age. The upper unit of this formation is similar to the Bone Valley Formation in terms of main mineral components. This deposit is roughly one third the area of the Central Florida deposits, but much less in total tonnage.

Today, five companies mine or process phosphate in Florida: Cargill Crop Nutrition, CF Industries, IMC Phosphates, PCS Phosphate, and U.S. Agri-Chemicals.

North Carolina. In the late 1950s, a phosphate deposit was found beneath a large portion of Beaufort County in the Miocene Pungo River Formation. Subsequent exploration delineated a mineable ore body that contained about 2 billion tons of phosphate ore. North Carolina deposits lie beneath strata ranging in thickness from 13.6 to 75.8 m. The P₂O₅ content varies from 2% to 21%. Reserves in the Beaufort County area are among the largest in the United States, constituting 1,813 km² of phosphate deposits. North Carolina is now the second-leading phosphate producer behind Florida. The phosphate is produced by Potash Corporation of Saskatchewan, which purchased the assets of Texasgulf, Incorporated, in 1985. Phosphate production is from the large open-pit Lee Creek mine near Aurora in Beaufort County. The major portion of the output from this mine is used in nearby chemical facilities to produce phosphoric acid, TSP, and DAP. Deposits of phosphorite also occur off North Carolina's coast in the northeast Onslow Bay District and the Frying Pan Shoals District. The lower part of the Pliocene Yorktown Formation contains phosphorite in the Aurora phosphate district and represents a potential resource. Further exploration may lead to production from these deposits.

Western States. The Permian sediments of Montana, Utah, Wyoming, and Idaho cover about 350,000 km². These reserves are estimated to total 1.6 billion tons at 24% P₂O₅, and constitute about 30% of U.S. reserves and 3% of the world total.

Mining can be traced back to 1904, when an underground operation near Montpelier, Idaho, was started. Large-scale phosphate mining began in 1921 by Anaconda Co. in Conda, Idaho.

J.R. Simplot entered in 1946 by opening the Gay open-pit mine on Fort Hall Indian Reservation, 50 km north east of Pocatello,

Idaho. The Smoky Canyon mine was developed in the mid-1980s. In 1992, the Gay mine was closed.

The phosphate mining industry in Idaho has a unique economic advantage compared with other hard-rock mining in the state and phosphate mining in the United States in general, perhaps because of its proximity to some domestic markets and low production costs. Idaho production of phosphates accounts for more than 12% of the national production. Currently four open-pit operations produce more than 5 Mtpy of ore. The mines deliver ore to two fertilizer plants and two elemental phosphate plants. All four sites are reportedly experiencing selenium releases associated with their waste dumps (Blanchard et al. 2002). These mines are Astaris's Dry Valley mine, J.R. Simplot's Smoky Canyon mine, P4 Production's Enoch Valley mine, and NuWest's Rasmussen Ridge mine.

Today five companies mine or process phosphate in Idaho: J.R. Simplot Company, Monsanto, Rhodia, NuWest Industries (Agrum), and Astaris (formerly FMC).

Phosphate rock processing at Vernal, Utah, began in 1961. J.R. Simplot recently acquired this operation. The ore consists of a hard-rock sedimentary stratum of the Phosphoria Formation of Permian age. The ore is covered by up to about 30 m of overburden, comprising Lower Franson limestone (10 m), Mackentyre shale (10 m), and Upper Franson limestone (10 m), and rests on the Weber sandstone. Exploration drill holes indicate ore thickness of 4 to 6 m, assaying 16% to 22% P₂O₅ and 1.9% to 3.3% MgO. The ore minerals have been identified as collophane, dahllite, and francolite, all carbonate-apatite minerals. Collophane is the most abundant, occurring as pellets of 75 to 500 µm, averaging 150 µm. Pellets are cemented with calcite and dolomite with some chert, clay, and massive collophane. Local fracturing and faulting facilitated weathering. Oxidation of the minor amounts of sulfides in the ore attacked and weathered the carbonate cement, so the weathered ore is easier to grind (Allen 1993).

Brazil

Brazil is the only significant phosphate rock producer on the South American continent. The Brazilian phosphate deposits are of igneous

nature, accounting for 2.6% of the estimated worldwide reserves. The extensive mineral prospecting from 1975 to 1985 nearly tripled the Brazilian rock phosphate deposits. Phosphate production during that period also saw its highest increase (1,207%). Most (87%) of phosphate deposits in Brazil are in the Cerrado region, which covers eight provinces.

One of the largest mines in the Cerrado region is the Tapira mine in the northern portion of the Tapira ultramafic alkaline-carbonatitic complex, in the west of Minas Gerais state (southeastern Brazil). Known reserves of this deposit are about 1.2 billion tons, with an average grade of 8.2% P_2O_5 .

Peru

Peru has one of the 10 largest phosphate deposits in the world, the Bayovar deposit, which is about 1,000 km north of Lima in the Sechura Desert. It has reserves of more than 800 Mt. Except for a pilot-plant operation, this deposit has remained untapped since its discovery, mainly because of the lack of infrastructure in this remote desert area. The government of Peru reannounced the auction of the Bayovar phosphate deposit in December 2000, after several postponements over the past years. The government hoped to gain US\$600 million in proceeds from the privatization of the property. Firms that were listed as being interested in acquiring the property include 65 companies, among which are IMC Global Inc.; Oswal Chemicals & Fertilizers Ltd. of India; FOSKOR of South Africa; Jua Paulo Quay of Spain; and Hermasa E. Interocea, Ipiranga, and Serrana, all of Brazil.

Africa

Morocco. Morocco not only has the world's largest phosphate reserve base but also enjoys high-grade, easy-to-process deposits. The deposits, all sedimentary, were first discovered in 1908. In 1920, the Office Cherifien des Phosphates (OCP), a government organization, was created for exploitation and sale of phosphate rock. The first phosphate rock was produced in 1922. Since then, OCP steadily increased production, reaching 1 Mt in 1939 and the current level of more than 20 Mtpy.

The Moroccan phosphorite resources are hosted in late Cretaceous, Palaeocene, and Eocene marine sediments. Sequences comprising clays, marls, li mestones, and che rts contain several phosphate-rich beds. OCP currently operates four operations, as shown on Figure 3. Morocco is also moving toward increasing exports of processed phosphate. Its phosphate fertilizer exports increased from less than 10 0,000 tpy during the 1970s to the current level of more than 1 Mt, and phosphoric acid exports more than tripled from 1990 (631,800 t) to 2000 (1,547,800 t).

Western Sahara. Since the "liberation" of the former Spanish Sahara by Morocco in 1975, phosphate mining in this region has been under the auspices of OCP. The Bou Craâ deposits were estimated to be about 1,600 Mt, with half the reserve containing 31% P_2O_5 .

Tunisia. Tunisia is the second largest phosphate producer in Africa, turning out about 8 Mt of rock on average in recent years. The phosphate deposits of Tunisia are all sediments, ranging in age from Maastrichtian to Lutetian, found in the Metiaoui Formation in the southern part of the Tunis Basin. Two distinct deposits compose the sediments in this basin—the anticlinal deposits of the Gafsa region and the perched synclinal deposits of the Tebessa-Thala region. More than 90% of the phosphate rocks are currently mined from the Gafsa region. Another potentially important region is represented by the Thanetian phosphate beds, east of Gafsa. Approximately 500 Mt of Tunisian phosphate rock are currently classified



Adapted from Mining-Technology.com 2004.

Figure 3. Locations of major phosphate deposits in Morocco

as mineable. Figure 4 shows where most of the phosphate deposits are located, with circled hammers indicating mining operations.

Algeria. The most important phosphate deposit in Algeria is the westward extension of the Tunisian Gafsa Basin, which is shown in Figure 4. With a resource of about 1,000 Mt and the current mining rate of about 1 Mtpy, Algeria certainly has the potential to produce phosphate for many years to come.

Egypt. The three major phosphate deposits in Egypt are located near the Red Sea, in the Nile Valley, and in the Western Desert. These are all sedimentary, medium grade (20% to 28% P_2O_5), with a total reserve base of 760 Mt. The current phosphate rock production from a few mines averages about 1.5 Mt.

Senegal. Sedimentary phosphate rock occurs at several areas in Senegal. Most of the high-grade deposits are concentrated in the west. Senegal is blessed with extensive reserves of exceptionally high quality phosphate. Marketable phosphate from Taïba (with a standard of 79 BPL), which has been mined since 1960 in Ndomor Diop and more recently in Keur Mor Fall, is famous around the world. The phosphate ore is buried under a layer of sand 30 to 40 m deep. The thickness of the ore seam is between 7 and 10 m. The ore is made up of marketable phosphate, sand, clay, or mud and flint.

Togo. Since the beginning of large-scale mining of phosphate deposits at Akoumpe (in the southeast) in 1963, phosphate mining has become Togo's most important industry, with an annual production of more than 2 Mt. The phosphate beds vary in thickness from 2 to 6 m, while the overburden of sand and clay ranges from 7 to 30 m. The two phosphate mines in Togo produce one of the highest grade phosphate rocks, analyzing 36% P_2O_5 with minimal amount of Mg, Al, and Fe.

South Africa. Though not as famous as its gold and diamond mining industries, South Africa's phosphate mining industry has met domestic needs for phosphate plus some exports for quite

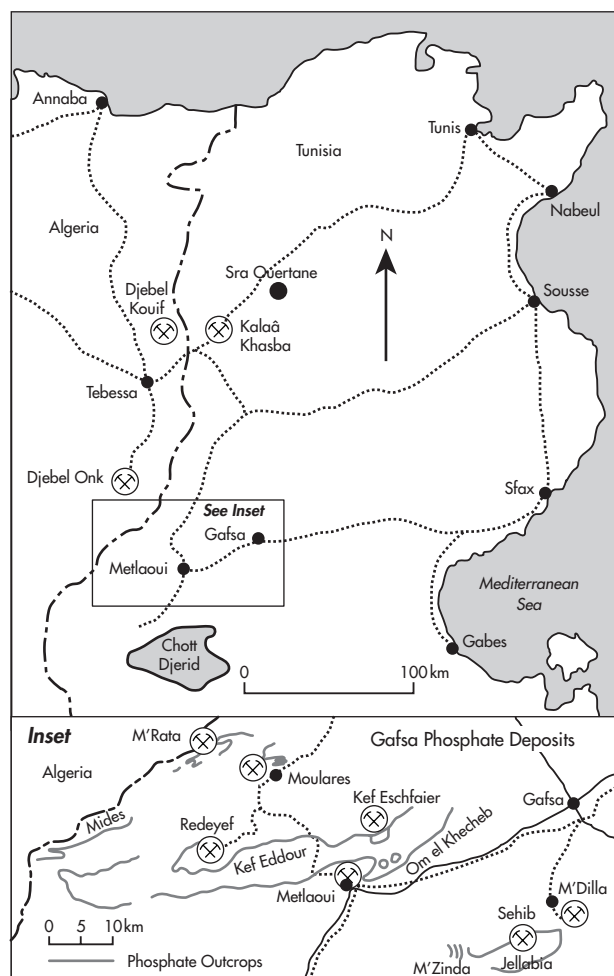


Figure 4. The Gafsa phosphate deposits in Tunisia

some time and may play an important role in the international market in the future, because its phosphate reserve base ranks fourth in the world. The majority of South Africa's phosphate deposits are of igneous nature. The deposits are generally of low to medium grade with high Fe and Al contents. Figure 5 shows the most important phosphate complex operated by Foskor. The Palabora deposit, in northern South Africa, was originally exploited as a source of copper and iron in the seventeenth century by a tribal group of the Monomotapa Empire that wandered south from Central Africa. The associated phosphate resource was commercially mined in the early 1930s by South Africa Phosphates, Ltd., which mined high-grade apatite pockets and sold this as a fertilizer product but soon went bankrupt because of the less expensive Moroccan phosphate rock imports. The state acquired claims and leases and a company, which became known as Phosphate Development Corporation, Ltd., and eventually Foskor, Ltd., and began mining in the early 1950s. Gradually the fertilizer producers adapted their processes to the use of the igneous phosphate rock produced, and in 1976 a significant expansion enabled production for an export capability. At present, approximately one third of the phosphate rock is used domestically, one third is exported as rock, and the remainder is acidulated for phosphoric acid and fertilizer ingredients for export.

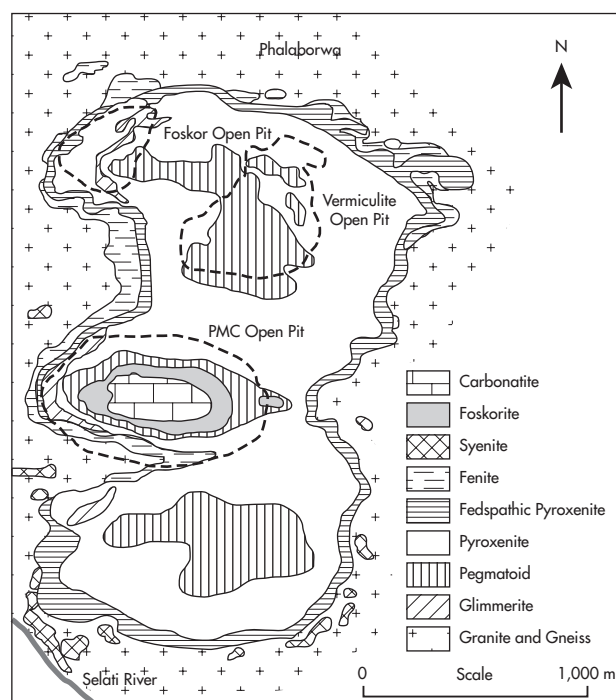


Figure 5. The Igneous Phosphate Complex in South Africa

Middle East

Israel

Nearly all phosphate deposits in Israel are located in the Negev Desert. Substantial resources of phosphate rock occur in the northern Negev region. Arad-Rotem, which was the largest deposit, has 300 Mt, and the Zohar, Zin, and Arava deposits have 250 Mt, 150 Mt, and 150 Mt, respectively. These deposits are associated with flint beds in shallow water sediments, with the phosphorite horizon ranging up to 20 m. The main mineral constituents are francolite and calcite, with small amounts of gypsum, clay, quartz, iron oxides, halite, and dolomite. Israel mines more phosphate than it can consume domestically and exports phosphoric acid to India, Italy, and Turkey, and phosphate rock to Brazil (about 42%), France, Ireland, Italy, the Netherlands, Spain, and the United Kingdom.

Jordan

It may not be exaggerating to say that phosphate deposits can be found anywhere in Jordan. Phosphate deposits are Jordan's primary natural resource and a major source of export income. Estimates of Jordan's proven, indicated, and probable reserves range from 1.5 billion to 2.5 billion tons. Conservatively speaking, Jordan could produce phosphate at its present rate for hundreds of years. In recent years, Jordan produced about 7 Mtpy of phosphate rock, a majority (about 85%) of which was exported as raw rock. In 1985, the Jordan Phosphate Mines Company closed the country's original phosphate mine at Ar-Rusayfah near Amman because of declining rock grade. This left major phosphate mines in operation at Al Hasa and Wadi Abu Ubaydah near Al Qatranah in central Jordan, and a new high-grade mine at Ash Shidiyah, 40 km south of Maan. Reserves at the new mine were estimated to be more than 1 billion tons. The principal phosphate deposits in Jordan are sedimentary type, ranging in age from Campanian to Eocene.



Figure 6. Map showing Hubei, Guizhou, Hunan, Sichuan, and Yunnan provinces, which have major phosphate occurrences

Saudi Arabia

Saudi Arabia is a “sleeping giant” in terms of phosphate mining potential in the Middle East, with phosphate resources estimated up to 3,000 Mt averaging 18% to 21% P_2O_5 . The largest phosphate formation is the Sirhan-Turayf sedimentary deposit, which extends into Jordan, southern Iraq, and Syria. The best explored and largest deposit is at Al Jalamid, which has measured reserves of 213 Mt averaging 21% P_2O_5 and a stripping ratio of 2.3:1. Indicated resources amount to a further 187 Mt, with 19.7% P_2O_5 and stripping ratios of 5:1 or less. The second important deposit is in the Umm Wu’al North Area with a total resource of 537 Mt averaging 19.35% P_2O_5 with a stripping ratio less than 5:1.

Syria

Syria is another Middle Eastern country with a significant phosphate reserve, nearly 800 Mt. Most of the potentially economic deposits are located in the central part of the country. The richest deposits analyze 31% to 34% P_2O_5 . Phosphate mining started in 1971, and production has reached about 2.5 Mtpy.

Asia

China

China’s phosphate deposits are all over the map with more than 250 areas (Figure 6). The five major formations, in Hubei, Guizhou, Hunan, Sichuan, and Yunnan provinces, account for 75 % of

China’s phosphate reserve. The Wengfu phosphorite deposit located in central Guizhou province is a super large ore deposit occurring in Late Sinian (Latest Precambrian) rock. The phosphorites are hosted in the Doushantuo Formation. In ascending order, the Doushantuo Formation can be divided into four members: a “bottom bed,” mainly dolostones; a “lower ore bed” of phosphorites; an “interbed” with dolostones and cherts; and an “upper ore bed” of phosphorites. In the Kunming Area of Yunnan Province, the main phosphate ore horizon is the Upper Phosphorite averaging 5.8 m, which is made up of dolomitic, fine grained, and siliceous phosphates. The siliceous portion does not require complicated beneficiation and is of high grade. There are three major phosphate beds in the lower Doushantuo Formation, a significant portion of which contains 5% to 8% MgO.

Mongolia

There are two phosphate reserve basins in Mongolia. The first area, the Khulosgul basin, was discovered in the north of the country by geological exploration work from 1963 through 1986. The Zabkhan phosphate basin was discovered in the west of the country from 1987 to 1997 (Dorjpalam and Amgalan 1998). As the result of a broad geological exploration work in Mongolia since 1963, more than 50 deposits have been discovered in the two basins, with estimated total reserve base of approximately 5.7 billion tons. If this is true, Mongolia would be placed second in Asia

in terms of reserves. The KPB phosphate basin covers 30,000 km² and has an estimated reserve of 4.5 billion t. Some of these phosphate deposits are excellent in grade, analyzing over 30% P₂O₅. Mg content, however, is high in most of the ores.

Because of the lack of infrastructure and environmental concerns, phosphate mining in Mongolia may not happen in the near future.

India

The use of phosphatic fertilizers in India has maintained a steady upward trend. The current annual domestic demand of apatite and rock phosphate is about 4 Mt, with domestic production meeting hardly 35% of the total demand. This trend will not change dramatically, because India's phosphate reserve is disproportionately small. The inadequate phosphate resources, together with insufficient capacity to beneficiate the low-grade phosphate ores, will force the country to depend more and more on imported high-grade rock phosphate.

The major phosphate deposits in India are of sedimentary origin, concentrated in two formations—the Precambrian Aravalli Formation and the Jurassic Lower Tal Formation. The former is of better quality, located in Rajasthan, Madhya Pradesh, and Uttar Pradesh. A significant portion of these deposits analyze over 30% P₂O₅.

Oceania

Australia

After years of staying nearly dormant, phosphate mining in Australia has revived in recent years. The original phosphate rock deposits owned by Western Mining Corporation Ltd. (WMC), which underpin the current operations, were initially discovered by Broken Hill South Pty Ltd. in 1966 in northwestern Queensland.

By 1978, after investment of over seventy million dollars in the mine, rail and port infrastructure, export of rock proved unprofitable due to a number of reasons including production difficulties, removal of the Australian superphosphate bounty and the failure to secure long term contracts. This resulted in the closure of mining operations and the collapse of Broken Hill South (Osborne 2001, p. 2).

In 1980, WMC acquired a major interest in Queensland Phosphate Limited and its phosphate rock reserves 130 km south of Mount Isa. The resource is an 11-m-thick deposit of approximately 2 billion tons of sedimentary phosphate rock. This deposit is close to the surface and easily extracted using open-cut mining. Having recognized that to achieve an acceptable return on investment the phosphate rock would have to be converted into either granulated TSP or ammonium phosphates, WMC decided to invest in a facility for manufacture of ammonium phosphates. This proved to be a profitable proposition and placed Australia back on the map of the world's major phosphate producers.

Nauru

Phosphate deposits occupy about 90% of the island of Nauru. These deposits are of the highest grade, with the run-of-mine ore analyzing to 40% P₂O₅. Nauru once possessed the highest GDP per capita in the world because of its rich phosphate deposits, which have been nearly depleted.

Europe

Russia

Once the world's largest phosphate producer, Russia is now ranked fourth, falling behind the United States, Morocco, and China. Both



Figure 7. Phosphate distribution in the former U.S.S.R.

sedimentary and igneous phosphate deposits are widespread in Russia. The most important igneous deposit is the Khibiny Complex in the Kola Peninsula, with the Kovdor Complex bordered by Finland being the only other significant igneous deposit. Mines at the Khibiny Complex have a combined capacity of 20 Mtpy. Phosphate ore averaging 17% P₂O₅ is upgraded to almost 39% P₂O₅ using flotation technology. At the Kovdor Complex bordering Finland, the igneous phosphate is a secondary product from iron ore mining. Electromagnetic processing of the iron ore results in tailings analyzing about 30% P₂O₅ and 4.5% MgO.

The largest sedimentary phosphate deposit in this region is the Kara Tau Basin with a resource of about 8,000 Mt averaging 21% P₂O₅. In early mining, phosphate ore was crushed, ball milled, and screened to obtain a product of 23% P₂O₅ for elemental phosphorus manufacture. Other major sedimentary deposits are located along the southern margins of the Moscow Basin (Figure 7).

Finland

Finland is the only European country other than Russia that is currently mining phosphate. The only economically important deposit is the Siilinjärvi igneous deposit.

TECHNOLOGY

Mining

Surface Mining—Dragline

At present, most phosphate rock is mined using large-scale surface methods. In the past, underground mining methods played a greater role, but their contribution to world production has declined. For example, in Idaho, phosphate mining has been transformed from 100% underground during the 1930s to nearly all surface mining

today. Phosphate rock surface-mining operations can vary greatly in size. Extraction may range from several thousand to more than 10 Mt of ore per year. In many cases, operations supply feed to a nearby fertilizer-processing complex for the production of downstream concentrated fertilizer products. The land area affected by the surface operations can vary widely, depending on the ore body geometry and thickness. At similar extraction rates, mining of flat-lying, thin ore bodies as found in Florida will affect a far wider area of land than the mining of thicker ore bodies as found in Brazil and Idaho. The depth of excavations may range from a few meters to more than 100 m. Currently, most phosphate rock production worldwide is extracted using opencast dragline or open-pit shovel/excavator mining methods. This method is employed widely in parts of the United States, Morocco, and Russia. Underground mining methods are currently used in Tunisia, Morocco, Mexico, and India.

Surface Mining—Drilling and Blasting

In Khouribga, Morocco, the 16- to 17-m-thick overburden is drilled, blasted, and removed by dragline to the side of the mining area for subsequent reclamation. Small draglines, electric shovels, and bulldozers recover the upper ore body. The intercalating limestone layer is then blasted and removed to expose the Bed I phosphate, which is loaded onto trucks. The process is repeated to mine the Bed II phosphate deposit.

At Vernal, Utah, mining begins with tractor removal of topsoil and temporary storage for reclamation. Overburden is drilled and blasted with ammonium nitrate and fuel oil and shoved into mined-out areas. The ore is then drilled, blasted, and loaded by shovel into trucks for transport to a feeder-breaker. The broken product at 25 cm is conveyed by belt to a 10,000-t live storage pile. Mining is conducted 5 days a week, in two 8-hour shifts per day. Overburden in mined areas is contoured, covered with topsoil, and seeded.

Dredge Mining

Consideration of mining systems for the Santo Domingo, Mexico, project included bucketwheel excavators, draglines, scrapers, shovels, and dredges. Selection of a dredge-based system was favored primarily on the basis that the other systems could not operate effectively below sea level. Low operating and maintenance costs prompted the final selection of floating hydraulic cutter suction dredges with 27-in.-diameter suction heads. Two Ellicott dredges were used, each capable of pumping about 2,000 tph of slurried solids to the floating primary beneficiation plant.

Dredge mining was also practiced at the Wingate Creek mine in central Florida, which ceased operation in 1999.

HAULAGE

The three major methods of hauling materials in phosphate mining are pumping, trucking, and transporting using conveyor belts. In the United States, pumping is the predominant means of moving ore and tailings, with the longest pipeline running 87 miles, via which J.R. Simplot transports phosphate rock slurry from its Smoky Canyon mine in Wyoming to Pocatello, Idaho.

PROCESSING/BENEFICIATION

Washing and Sizing

Florida (United States)—Washing

The coarsest portion of the disaggregated matrix (+50 μm) is removed to waste by trommel screens, because it usually represents lower phosphate grade and is likely to contain significant dolomite-cemented conglomerates. At one time this coarse material was broken in hammer mills to pebble size, but this is now avoided because of the grade and dolomite contamination problem. As the mining

moves to the south or west, the portion of phosphate rock product produced in the washer by disaggregation and simple screening is expected to diminish from the roughly 50% for the Bone Valley to about 20%. Because pebble production is relatively inexpensive, the reduction of this production has an unfavorable impact on costs.

The disaggregation, which largely takes place in the pumps and transport lines, is completed by log washing at high percent solids to scrub residual clay from the mineral surface and wash it countercurrently away from the rock. Vibrating, plastic-coated screen decks permit the final removal of the pebble (+1 mm) from the flotation feed (−1 to +50 μm), which is suspended in a dispersed clay (−50 μm) slurry.

The coarser washer pebbles still contain large amounts of dolomite, and therefore at some mines this coarse pebble (+20 mm) is scalped from the product and treated as waste. Two Florida mines installed heavy media hydrocyclone plants to reduce the dolomite contained in the pebble. The density separation is enhanced by the relatively high porosity of the dolomite compared to the francolite. These heavy media plants have not been operated since the early 1990s because the local chemical plants have learned to accept higher dolomite levels and the miners have learned to avoid high dolomite pebble areas by selective mining. Unfortunately, this does deplete the reserve base for continued mining activity.

Florida (United States)—Desliming

The slurry containing flotation feed and clays, which represents the combination of pebble screen undersize, log washer overflow, and most other slurry streams created in the washer, is pumped through two stages of hydrocyclones with recycled water added to the first hydrocyclone underflow for dilution. This removes roughly 98% of the fine suspended clay particles from the flotation feed but creates a clay slurry waste containing 4% to 6% solids, which by themselves settle very slowly in clay ponds. Because roughly 30% to 40% of the mined material weight is clay, these ponds represent a very substantial capital investment in terms of both construction and reclamation when filled. These ponds also act as reservoirs for water recovery and recirculation. Some plants installed the facilities required to accelerate the clay settling by flocculation using high-molecular-weight anionic flocculants. There is of course concern about the chemical quality of the recycled water removed by flocculation, but some companies believe the capital and operating costs for operating clay ponds and handling the large volumes of clay slurry exceed the cost for flocculants and any additional flotation reagents or loss of phosphate recovery incurred.

Florida (United States)—Sizing

Most phosphate flotation plants separate the flotation feed (−1 mm to +50 μm) into at least two size fractions with the split point at about 420 μm or 35 mesh. There is ever-increasing evidence of economic and metallurgical benefit to be gained by this practice. High-capacity hydraulic sizing units have been used in the industry since the mid-1980s; these provide sharper size separations than the previously used multiple stages of inclined profile wire screens. The hydraulic sizer overflow, when separating at 420 μm , contains roughly 80% of the flotation feed solids weight, whereas the underflow at about 50% solids is of such a volume that it can be more readily handled by high-speed vibrating screens. There are usually three or four products from the combination of hydraulic and screen sizing. The finest fraction, from 105 to 420 μm or passing 35 mesh, is termed *fine flotation feed* and represents about 80% of the flotation feed weight and would be the hydraulic sizer overflow. The next finer fraction, from 420 to 595 μm , is called *coarse feed* and represents about 10% to 15% of flotation feed weight and would be

a vibrating screen undersize. If there is a third flotation feed, it would be roughly from 595 to 1,000 μm and represent 5% to 10% of the flotation feed weight. In the past, this third fraction was treated by several flotation techniques such as using shallow belt flotation or flotation on spirals. Today, although consideration has been given to the use of column flotation to upgrade this stream, many plants combine this product with the final sizer vibrating screen oversize and treat this as a lower grade pebble product. In years past, the final sizer vibrating screen oversize would represent misplaced pebble and coarse flotation feed and would be recirculated to the washer for retreatment.

Australia

WMC Fertilizers, a subsidiary of the Melbourne-based WMC, recently put into operation their phosphate complex in Northern Queensland in Australia. This new facility includes a mine, a beneficiation plant, wet process phosphoric acid manufacture, an ammonia plant, and a DAP/MAP granulation plant. Sulfuric acid used in acidulating phosphate rock is manufactured from the off-gases generated by the M.I.M. Holdings Ltd. copper smelter plant about 150 km from the fertilizer production facility. The phosphate used at this facility is of a very low grade compared to other sedimentary deposits, with an average grade of only 23.5% P_2O_5 . The main impurity is silica, which makes up about one third of the ore. The only beneficiation of the ore is water scrubbing to remove fine clays.

Togo

In Togo operations, the phosphate ore is first scrubbed with seawater, then wet screened at between 0.8 and 3 mm, depending on the quality of the ore. The clay is then removed using hydrocyclones. The high ferrous product is further dried and upgraded using electromagnetic separation technology.

Jordan

JPMC is currently operating three open-pit mines: El-Hassa, El-Abiad, and Eshidiya. The company started production in the 1930s from the Ruseifa mine, 17 km north of Amman. In the 1960s, the mining operation moved to the south, where production started from the El-Hassa mine, 136 km south of Amman and 200 km north of Aqaba port. In the late seventies, production started from the El-Abiad mine, about 20 km north of El-Hassa mine. In early 1988, production started from the Eshidiya mine, which hosts the largest high-grade reserve in Jordan.

In most operations, phosphate ore is first crushed and screened to reject the 12.7-mm material. When the 12.7-mm fraction makes the grade of 66% to 68% BPL, it is directly fed to rotary cascading dryers to produce a final product. The lower grade ore requires beneficiation, which involves sizing and desliming at about 200 mesh using hydrocyclones.

Morocco—Yousseoufia

The Yousseoufia zone is the western part of the Gantour deposit. Only underground mining is practiced at this mine. This location has proven reserves up to 7.7 billion m^3 . Annual mining capability is 2 Mt of merchant-grade phosphate rock. Here, the high-grade “white” phosphate is simply dried and shipped, and the “brown” phosphate is calcined (at $>700^\circ\text{C}$) to eliminate organic matter.

Morocco—Benguerir

Located 70 km north of Marrakesh, Benguerir is the newest of Morocco's four phosphate mining centers operated by OCP. Beneficiation at this location is very simple, by first removing +100 mm

material, followed by crushing and sizing at 10 mm, with the +10-mm material rejected.

Morocco—Khouribga

Located 120 km southeast of Casablanca, Khouribga is the largest phosphate mining zone operated by OCP Group. The phosphate deposit is of sedimentary origin, with several phosphate-bearing layers alternating with layers of marl and limestone. Phosphate reserves are estimated at more than 35 billion m^3 . Production of phosphate rock started in March 1921 by underground mining. Open-pit mining was introduced in 1951, and was replaced by underground mining by 1994. High-grade ore is screened and stored, and low-grade ore is treated using log washers and hydrocyclones. Calcination is also used at this location to treat the lower grade ore.

Morocco—Bou Craâ

Beneficiation of this Saharan phosphate is also fairly simple. The ore is crushed and slurried with seawater. Unwanted materials are removed by sizing and desliming.

Crago Double Float Process

The Crago double float process has been practiced in Florida for more than half a century. Modified versions or part of the process are also practiced in other parts of the world. This process is particularly suitable for processing siliceous phosphates, where low-silica product is required. The desliming and sizing steps are described in details in the Washing and Sizing section in this chapter and are shown in Figure 8.

The flotation plant consists of a number of important processing steps:

1. The removal of flotation feed at a controlled rate from partially consolidated storage bins
2. High solids conditioning of the solids (60% to 65%) with a pH modulator and anionic flotation reagents, namely a vegetable-derived fatty acid as a collector, a petroleum extender, and sometimes surfactants to impart desirable selectivity or frothing characteristics
3. Dilution with clean, recirculated water to roughly 20% solids for the rougher flotation step of the bulk of the phosphate mineral from the sand
4. Collection of the froth concentrate and scrubbing of the solids with sufficient sulfuric acid to free the fatty acid and fuel oil coating, followed by rinsing and dewatering with clean, recycled water to provide a clean mineral surface for further separation
5. Dilution with either fresh or very clean recycled water, adjustment of the pH to approximately neutral, and addition of a cationic flotation reagent (an amine, a light petroleum extender, and sometimes a surfactant) into a mixing tank or the feed box of the flotation cells; this cleaning flotation step is aimed at removing any fine sand inadvertently carried into the rougher concentrate by the relatively high reagent levels required to float the phosphate mineral
6. Partial dewatering of the cleaner cell underflow concentrate and holding in bins until routed to appropriate storage pile locations when chemical assays are available
7. Combining of the cell underflow tailing product from rougher flotation and the froth tailing product from cleaner flotation to create a combined tailing that is pumped to reclamation areas for landfilling in the mine.

water and permits the return of a reasonably clean recycle to the flotation plant. The additional water required to achieve a balance is obtained from rainwater collected in the mine, plant, and pond areas that is diverted to the ponds for storage. Some groundwater is extracted for special uses such as for pump seals, but it is carefully monitored to avoid exceeding permit limitations. Overall, approximately 95% of the water used is recycled.

A recent study of the fate of the relatively large amounts of consumed flotation reagents (Patel and Ben-Poorat 1999; Patel, Powers, and Zhang 1999) indicates no reason for concern over environmental consequences.

Anionic Flotation Only

Senegal

In Senegal operations, after desliming and sizing, the phosphate is upgraded using a fatty acid tall oil. The silica and the iron and aluminum oxides are depressed and a high-grade concentrate analyzing up to 80% BPL is produced.

South Africa

Foskor of South Africa produces phosphate rock from three sources, namely pyroxenite ore, foskorite ore, and PMC tailings. The pyroxenite ore is crushed and milled to 15% +425 μm and 20% –74 μm . The mill product is pumped to conditioners from which it flows to the flotation circuit, where apatite is floated using Wemco flotation cells. Flotation is done in a four-stage flotation circuit comprising rougher, scavenger, cleaner, and re-cleaner stages, with the recirculation of middlings. The pyroxenite process with only two reagents in the system is relatively simple and hardly ever gives any trouble. A straight-chain petroleum sulphonate or sulphonic acid and a tall oil fatty acid are added to the pulp at the conditioners. From ore with a head grade of 7% P_2O_5 , a concentrate with a P_2O_5 content of 39.6% is produced with a recovery of 70% (Coetzee, Visser, and Mehrliss 1976; Lovell 1976).

In the circuit for foskorite, flotation is also done in a four-stage flotation circuit comprising rougher, scavenger, cleaner, and re-cleaner stages, with recirculation of middlings, using Wemco flotation cells. Three reagents are used: sodium silicate ($\text{Na}_2\text{O} \cdot \text{SiO}_2$) as a dispersant; nonyl phenyl tetraglycol ether as a modifier and depressant; and a tall oil fatty acid as a collector. The average head grade of the foskorite is 7.5% P_2O_5 , whereas the concentrate grade is 38.5% P_2O_5 with a recovery of 67%.

PMC mines and processes the central carbonatite plug and the surrounding foskorite ore separately. The carbonatite contains an average of 3.5% P_2O_5 . After PMC extracts the copper and the magnetite from the ore, the slurry is pumped to Foskor. The PMC tailings stream is deslimed using two-stage cyclones, which remove 85% to 90% of the –12- μm slime fraction. PMC tailings, being a foskorite ore, are treated in the same way as the normal foskorite ore. In addition to the flotation reagents used for the foskorite circuit, a polysaccharide is used mainly as a depressant. Polysaccharides that have been used successfully include gum arabic and guar gum.

Russia

In Russia, a majority of the phosphate rock is turned out from the phosphate mines at the central Kola Peninsula. The mines are about half open pit and half underground. Phosphate ore is first crushed to –20 mm before being sent to the beneficiation plant. In the beneficiation plant, the feed is ground to approximately 55% passing 74 μm . Anionic rougher flotation is followed by several stages of cleaning and scavenging flotation. The output is more than 9 Mtpy

(10 million stpy) of concentrates with a P_2O_5 grade of 39% from an ore assaying 18% P_2O_5 , 23.1% SiO_2 , and 13.3% Al_2O_3 in a bonded phase of nepheline-syenites.

Jordan

In Jordan, direct flotation is used where the phosphatic elements are floated by an ionic flotation, using an aqueous blend of tall oil and diesel oil as phosphate collector, sodium silicate as clay dispersant, and silica depressant for both fine and coarse fractions, with several roughing and cleaning stages.

Brazil

The Brazilian apatites also represent an important source of igneous phosphate ores. They are included in carbonatites (with simple carbonates as in Jacupiranga or as more complex ones with iron carbonates, phlogopite or vermiculite, titanium minerals, barytine, pyrochlore, etc.). The P_2O_5 contents are comparatively low, from 5% for Jacupiranga to 15% for Araxa. Flotation is carried out after a double desliming with, generally, a roughing operation followed by one or two scavenging operations, the froth being cleaned two or three times. The depression of carbonates and iron oxides is achieved at a pH of about 10 with causticized starch, and the flotation is carried out with fatty acids (tall oil). Concentrates of about 35% P_2O_5 with recovery ranging from 45% to 78% are obtained from different localities (Betz 1979). Lima (1993) carried out a comparative study of direct anionic flotation versus the reverse of the Jacupiranga phosphate, and demonstrated that double flotation with a reverse second step was not an adequate route. The superficial characteristics of the apatite and calcite of this deposit seem to indicate that the direct flotation process is the most adequate route (Lima 1993). At the same time, Leal Filho and Chares (1993) studied the beneficial role of starch in the separation of apatite from the Brazilian igneous low-grade phosphate/carbonate ores. They observed that cornstarch promotes the flotation of apatite, phlogopite, and dolomite; they observed no effect over calcite.

Finland

For the Finnish igneous phosphates (which contain about 10% apatite, 22% calcite and dolomite, 65% phlogopite, and 3% amphibole and other silicates), the flotation process is carried out using substituted N sarcosine (amphoteric compound). Flotation is performed at a basic pH (8 to 11). The flowsheet adopted is grinding to 38.5% –74 μm , one roughing flotation stage, and five cleaning flotation stages. Applying this flowsheet at the Siilinjärvi plant, a concentrate of 33.7% P_2O_5 with a recovery of 85.8% is obtained.

Mexico

Anionic rougher-cleaner flotation has been practiced in Mexico for many years. The flotation collector is a fatty acid emulsified with petroleum sulfonate and diesel oil.

Magnetic Separation

At the Phalaborwa Igneous Complex in South Africa, the pyroxenite zone is followed by the foskorite zone. This part of the ore body consists mainly of magnetite, serpentine, and apatite (Schmidt 1999). The P_2O_5 content in this zone varies from 6% to 11%. The magnetite must be removed using magnetic separation to upgrade the ore to commercial-grade rock. In the foskorite circuit, the crushed ore is conveyed to a 60-kt stockpile, reclaimed by three plough reclaimers, and conveyed to the milling plant. After copper flotation, Sala low-intensity magnets remove the magnetite after 750-mm and 100-mm Multotec cyclones remove

the slimes. Magnetic separation is also conducted on the PMC tailings before phosphate flotation.

At the Kapuskasing Phosphate Operations in Canada, magnetic separation is carried out on the final flotation product. The re-cleaner flotation concentrate is pumped to a reconditioned high-gradient magnetic separator (HGMS) purchased from the Iron Ore Company of Canada. The HGMS reduces the iron content from approximately 5% to less than 2%. HGMS product is pumped to a concentrate thickener.

At an Egyptian mine, the run-of-mine ore is delivered from the underground mines to a storage area where it is screened at 60 mm, the oversize of which is crushed in a rotary crusher. The crushed ore is screened again at 60 mm. The resultant oversize (+60 mm) is discarded because of its high impurities, and the fraction below 60 mm is delivered to the beneficiation plant for further treatment. In the beneficiation plant, the −60-mm fraction is scrubbed in a 3.6×10 -m drum scrubber to disintegrate the ore. The scrubbed product is then screened on 2-mm screen. The oversize fraction (+2.0 mm) is discarded because of its high dolomite content. The fraction below 2 mm is classified using a group of hydrocyclones to separate the clay fraction below 0.080 mm. The latter is discharged to the main thickener of the plant as slimes. The deslimed product (−2.0 + 0.080 mm) then goes through a second stage of washing in attrition scrubbers. A hydroseparator further classifies the product of the latter, at about 0.2 mm, into coarse and fine fractions. The coarse fraction (−2.0 + 0.2 mm) is filtrated and dried to ~1.5% moisture. This fraction represents the coarse concentrate. In the meantime, the fine fraction (−0.2 mm) from the hydroseparator is discharged to a group of hydrocyclones for further classification to separate the slimes below 0.080 mm. The underflow of the hydrocyclones (−0.2 + 0.080 mm) is then discharged to a high-intensity magnetic separator to separate the ankerite (ferrogenated dolomite) impurities as magnetic product. The nonmagnetic fraction (fine concentrate) is then filtered and dried. Both coarse and fine concentrates are blended to produce a final concentrate assaying ~30% P_2O_5 and 0.55% MgO.

Magnetic separation is also practiced in Togo and Mexico.

Calcination

Calcining is used to treat phosphate rock to achieve one or more of the following objectives:

- To remove carbonaceous materials, dolomite, or calcite
- To remove organic matters
- To improve reactivity of the rock
- To make low-grade, slow-release fertilizers

Calcination (at higher than 700°C) is widely used in Morocco to eliminate organic materials from the so-called “brown” or “black” phosphate rock.

In the last decade, calcination was studied and recommended to treat phosphate ores in Saudi Arabia, where water supply is limited and energy is inexpensive. In the study, a Saudi phosphate ore containing 40% to 50% carbonate and 16% to 25% P_2O_5 was treated by calcination at 850°C for about an hour, followed by quenching with 5% ammonium nitrate (NH_4NO_3), 5% ammonium chloride (NH_4Cl), or water. Under the best test conditions, a concentrate containing 38% P_2O_5 was obtained (Al-Fariss 1993).

Two low-grade Indian carbonaceous ores were successfully upgraded using a continuous-flow calcination process. Phosphate recoveries ranged from 63% to 84.6%, with concentrate grades of 31.3% to 38.5% P_2O_5 . The roasting temperature was 900°C (Good 1976).

Beneficiation of Sedimentary Carbonaceous Phosphates

Sedimentary carbonaceous phosphate ore is, by far, the most widely present in the world and constitutes more than two thirds of present-day reserves. Some deposits, though, are being beneficiated using calcination processes followed by elimination of CaO fines. Because of ever-increasing energy costs, more economical means are becoming increasingly attractive, including the froth flotation process. The largest difficulty, however, arises from the fact that the physicochemical properties of phosphatic minerals and carbonates are very similar (Waksmundzki, Neczaj-Bruzewica, and Planik 1971). In the last three decades, numerous studies have been carried out to separate carbonaceous gangue from sedimentary phosphate ores. These processes include direct flotation of phosphate with depression of the carbonate gangue (Awasthi et al. 1977) and reverse flotation of the carbonate gangue with depression of the phosphates (Smani, Cases, and Blazy 1975; Awasthi et al. 1977; El-Shall 1994).

China

China is quite successful in processing sedimentary carbonaceous phosphates using flotation technology, perhaps because the majority of their phosphate deposits (about 80%) belong to this category. The Chinese phosphate resources have three distinct characteristics: old geological age, high dolomite and other impurities, and being finely disseminated. Before beneficiation, fine grinding is usually required to liberate impurity minerals from phosphate. About 98% of the phosphate deposits occurred in Cambrian or Sinian formation at the age of more than 500 million years. Because of old geological age, the phosphate rocks are usually in massive and very hard structures.

The Jinping phosphate mine is located in Lianyungang of Jiangsu Province. The processing plant was put into operation in the late 1950s with the capacity of 1.2 Mtpy mining and beneficiation. At the early stage of production, the run-of-mine did not contain much MgO. A process with soda ash as pH modifier, water glass as the silica depressant, and crude tall oil as phosphate collector could produce very high quality phosphate concentrate. As the high-grade ore was depleted, the MgO impurity was gradually increasing, up to about 10%. A new process was therefore developed and implemented. The as-mined ore is subject to two-stage crushing to −50 mm, and then ground in a closed circuit of ball mills and spiral classifier to −0.3 mm (containing 40% −200 mesh) as flotation feed. The feed slurry in 42% to 45% solids is conditioned with Na_2CO_3 , L_{339} , and crude tall oil, and is transported to flotation operations consisting of one rougher, two scavengers, and three cleaners. The froth product as concentrate is gravity flowed to a thickener for first-stage dewatering. The underflow in 70% solids is further dewatered through drum filters, and the filter cake is then dried in a revolving tubular kiln to obtain dry phosphate concentrate.

The Dayukou, Hubei, phosphate ore contains 17% to 18% P_2O_5 and 4% to 5% MgO. Phosphate, dolomite, and silicate in the ore were intergrown in extremely fine particles. To achieve the desired degree of liberation phosphate from gangue minerals, the ore must be ground to a fineness of −0.1 mm (over 90% −200 mesh). For such fine particle sizes, it was once considered almost impossible to separate dolomite from phosphate by the flotation method. The Dayukou phosphate beneficiation plant was put into operation in 1996. The success of the “direct flotation” process relies on the “S” series depressants developed by Lianyungang Design and Research Institute (CLDRI) especially for effective depression of both carbonates and silicates. The “S” series depressants were derived from the by-product of petroleum industry. For beneficiating Dayukou

phosphate ore with the direct flotation process, CLDRI also developed an effective collector, PA-42, using a waste material from vegetable oil processing. PA-42 is very selective.

The flotation section of the process is in a closed circuit. The underflow of first cleaning flotation is subject to a scavenging operation, which is a key step for effective rejection of MgO impurity.

The Wengfu phosphate project, in Guizhou Province, is currently the largest integrated phosphate fertilizer complex in China, consisting of 2.5 Mtpy of beneficiation capacity, 800,000 tpy TSP, 800,000 tpy sulfuric acid, 300,000 t (P₂O₅ basis)/year phosphoric acid, and 12,000 tpy aluminum fluoride.

The run-of-mine ore containing about 30% P₂O₅ and 4% to 4.5% MgO is crushed to -15 mm. The crushed ore is then ground in an overflow ball mill. Hydrocyclones are used to control the milled product in the range of 60% to 68% -200 mesh for mineral liberation. The feed slurry of 40% solids is conditioned with H₂SO₄ as a pH modifier and PA-31 as dolomite collector, and is then subject to carbonate flotation to remove dolomite as froth product. The rougher sink is cleaned and refloated to further reject dolomite. After dolomite removal, the final sink product is dewatered using a high-capacity thickener to obtain a phosphate concentrate slurry of 70% solids.

The concentrate analyzing 36% P₂O₅ and 0.95% MgO is obtained at the overall P₂O₅ recovery of 95%. The removal rate of MgO impurity is over 80%. The minor element ratio value of the product is very low, only about 0.033.

Vernal, Utah (United States)

In Vernal, Utah, ore from the surge pile is conveyed to an 8.2-m diameter × 1.5-m semiautogenous grinding (SAG) mill, which has a 1,900-kW power capability; there it is ground at 76% solids with a 7% load of 10-cm-diameter balls (Allen 1993). The mill discharge is trommel-screened at 20 mm, with undersize pumped to vibrating screens, which return a +8-mm oversize to the SAG mill. The trommel oversize is ground at 73% solids to passing 20 mesh in a 4.1-diameter × 6.1-m ball mill, which has a power capacity of 1,500 kW. The ball mill discharge joins trommel undersize and is pumped to vibrating screens with the oversize returned to the ball mill and undersize carried to a large slurry storage tank.

This slurry is diluted from 50% to 15% solids with reclaimed water and deslimed in 66-cm-diameter hydrocyclones. The cyclone overflow at 7% solids flows by gravity to the tailings pond, and underflow at 50% solids feeds desliming hydrosizers. The hydrosizer overflow at about 7% solids flows by gravity to a scavenger dewatering circuit. The hydrosizer underflow flows by gravity to rougher conditioners, where at 70% solids the flotation reagents mix with the ore for about 8 min. Four reagents are added into the first conditioner of three in series: fatty acid, petroleum sulfonate, diesel fuel, and a frother. Conditioning is carried out at a natural pH of 7.5 to 7.9. The rougher flotation feed (240 tph) is floated at 25% solids with a retention time of about 6 min to produce a concentrate that proceeds to the cleaner cells where retention time is about 14 min with a feed at 35% solids. The cleaner concentrate has recently averaged 31.5% P₂O₅ and 0.6% MgO.

Rougher flotation tailings report to a scavenger dewatering cyclone sump together with cleaner tailings and hydrosizer overflow. The dewatering overflow reports to tailings and underflow at 72% solids flows to a scavenger section ball mill hydrocyclone grinding circuit. The grinding circuit hydrocyclone overflow reports to a circuit consisting of three-stage hydrocycloning in series, with the third-stage overflow used as dilution for the second-stage cyclone feed. The overflow from the first and second stage reports to tailings. The third-stage desliming underflow at 70% sol-

ids flows to the two scavenger conditioners in series, where the same four reagents used in rougher conditioning are added to the first conditioner and mixed for about 15 min at the natural pH of 7.5 to 7.9. The scavenger-rougher flotation at about 25% solids has a residence time of 12 min. Tailings at 9.5% P₂O₅ are recirculated to the desliming hydrocyclones before hydrosizing, and the scavenger-rougher concentrate reports to the scavenger-cleaners at 25% solids, where flotation proceeds for about 13 min more. After the addition of some sulfuric acid, the scavenger-cleaner concentrate, at 29.4% P₂O₅ and 1.1% MgO, passes through an acid-stripping hydrocyclone to remove fatty acid/diesel fuel and lower pH to depress phosphate in the carbonate flotation step. The hydrocyclone underflow at 70% solids is diluted to 55% solids and conditioned in two tanks in series for about 6 min, with additional petroleum sulfonate and frother. The carbonate flotation is done at 25% solids with a retention time of about 8 min. The concentrate (cell product) runs about 30.7% P₂O₅ and 0.75% MgO and is combined with primary cleaner concentrate as a concentrate product representing about 36% of crude ore feed weight. This combined concentrate is dewatered from 17% solids to 75% solids in the underflow and then ground in a 4.1-m-diameter × 6.1-m ball mill with 1,500 kW power, operated in closed circuit, with hydrosizers. The hydrosizer overflow at 20% solids reports to product thickeners to achieve a 60% solids underflow after addition of a small quantity of flocculant and is then pumped to mixed product storage tanks.

The CLDRI Process for Florida Dolomitic Pebbles

Under FIPR funding, IMC Phosphates conducted two major projects to develop an economically feasible process for high-dolomite phosphate pebbles in Florida. The Chinese CLDRI worked with IMC as the primary subcontractor for laboratory development and pilot-scale evaluation of flotation processes for dolomitic pebbles. As a result, the CLDRI process was developed. A typical flowsheet of the CLDRI process involves grinding, dolomite flotation, and silica flotation. It must be pointed out that, unlike most previous processes, the CLDRI process does not require the desliming step after grinding, thus reducing phosphate loss. Pilot-plant testing on two Florida samples achieved encouraging results similar to or better than those obtained in laboratory tests. An economic analysis was conducted based on the pilot testing results for a 272-tph (300-stph) battery limit plant. The estimated variable (production rate dependent) costs (including raw materials, electric power, reagents, consumables, severance tax, dam building, services, and contract maintenance) add up to \$13.80/t (\$12.52/st) of concentrate. Fixed costs (including labor, overhead, depreciation, supplies, taxes, and insurance) total an estimated \$3.42/t (\$3.10/st) of concentrate. Total operating costs, which are the sum of variable and fixed costs, are estimated at \$17.22/t (\$15.62/st) of concentrate. These numbers suggest that the CLDRI process is economically feasible under the current conditions. The battery limit plant includes silica flotation, which reduces the concentrate acid insolubles from 19% to 6%.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

The environmental issues related to phosphate mining and processing, particularly in Florida, are summarized in the following sections.

Waste Clay Ponds

As described previously, the phosphate matrix (ore) must be deslimed before flotation. A typical Florida phosphate matrix is composed of roughly one third each of phosphate, clay, and sand, resulting in the generation of approximately 1 t of clay waste (phosphatic clay) for each ton of phosphate rock product. At the current

mining rate, the industry is generating nearly 100,000 t of waste clay each day, which is pumped to the settling areas as a dilute slurry. Assuming an average solids load of 3% in the slurry, more than 3 Mt/day of slurry need to be pumped to the settling ponds. Although impounding is the most economical method for disposing of waste clay, it has several major disadvantages. Clay settling ponds occupy about 40% of mined lands and generally have limited use after reclamation, causing adverse economic impacts. The waste clay ties up a large amount of water. Clay ponds also cause a significant loss of water through evaporation because of their large size (up to 800 acres each). The impacts of clay settling ponds on the hydrological system are not yet fully understood.

Process Water

All phosphate fertilizers in Florida are produced using “wet-process” phosphoric acid. The wet acid is produced by dissolving phosphate rock in sulfuric acid solution, which generates acidic water designated as process water. This process water plays four major roles in the operation of phosphoric acid plants: (1) supplying make-up water for phosphoric acid manufacture, (2) conveying the phosphogypsum to the stack, (3) removing the heat generated during phosphoric acid manufacture, and (4) scrubbing all the exhaust gases within the chemical complex to prevent the discharge of undesirable gases to the atmosphere. Through all these functions, the process water reaches an equilibrium content of all the materials found in both the phosphate rock and the sulfuric acid. Although the plants are net water users, rainfalls often make it necessary to treat and discharge surplus water. The surplus water is first treated by neutralization with lime to remove fluoride and phosphate, followed by aeration to remove ammonia, followed by the addition of sulfuric acid to bring the pH into the range from 6 to 7. This process is expensive, and even after treatment, the water does not meet the standards for surface discharge. The industry would benefit greatly from the discovery or development of a technology that would remove any or all of the soluble salts or that would raise the pH of the process water economically.

Phosphogypsum Stacks

Phosphogypsum is a by-product of phosphoric acid manufacture. For every 1 t of phosphoric acid produced, approximately 5 t of phosphogypsum are produced. About 1 billion t of phosphogypsum have accumulated in Florida, and 30 Mt are added to the inventory each year. Many efforts have been made to turn this waste into a major asset to the state. For example, research has demonstrated that significant economic benefits can accrue from using phosphogypsum in road construction and agriculture, without creating excessive risks.

The Hydrological Systems

As Florida keeps its pace toward becoming the third most populated state in the nation, water supply—both in terms of quantity and quality—is of strategic importance. Proper water flow is necessary both to supply human needs and to maintain the ecological health of the Peace River, its tributaries, and the Charlotte Harbor estuary, among others. These issues are also of universal significance. Limited research has been conducted to investigate mined lands as water treatment and storage systems, but this topic should be studied further.

Public Health Issues

Most potential hazards associated with the phosphate industry are found in the chemical plants, where major chemical emissions include sulfur dioxide, ammonia, sulfuric acid, and silicon tetraflu-

oride. Other potential emissions are radon gas and leachate from phosphogypsum stacks, along with fugitive dusts from product storage. Although no study has shown significant health risks for either the workers or the nearby residents, efforts to minimize emissions continue. For the mining and beneficiation sites, flotation reagents are biodegradable and are further attenuated by sandy soil before reaching the surficial aquifer, except in the case of fuel oil. Research to study the spatial migration and persistence of fuel oil in the environment is ongoing.

OUTLOOK AND FUTURE TRENDS

Onsite Processing of Phosphate Rock

As energy costs increase, it is becoming increasingly less attractive economically to ship phosphate rock globally. The recent trend toward increased deep processing of phosphate rock where it is mined will continue. As the trade data in Table 3 show, trade in processed phosphate increased by more than 50% from the 1980s to the 1990s. Another reason for this trend is the historically “unfair” pricing for phosphate rock. Whenever the phosphate fertilizer market improved, significant upswing occurred for DAP prices, although rock producers did not benefit because of their being improperly recognized as a cost center rather than a profit center. In the foreseeable future, more processed phosphates in the forms of high-grade fertilizer or phosphoric acid will be produced from Morocco, China, Jordan, Australia, and Tunisia.

Industry Consolidation

Consolidation in the United States probably peaked with the Cargill–IMC merger into Mosaic in late 2004. The same cannot be said about China. China has nearly 500 independent phosphate fertilizer enterprises (Wu 1998). The production capacity of the big and middle-size enterprises is only 35% of the total capacity. Many of the small-size single superphosphate and furnace calcium and magnesium phosphate enterprises have outdated technical equipment and urgently need to be adjusted or reconstructed because of poor product quality, high energy consumption, and poor waste disposal practices. Consolidation is already happening in China and will intensify in the next decade toward more privatization and internationalization, as shown by the Cargill DAP venture in Yunnan Province.

Privatization may also take place in other major phosphate-producing countries such as Morocco, Jordan, Russia, and Tunisia. Phosphate mining companies are nearly all operated by the governments in these countries.

Sustainable Mining

The mining industry as a whole has been challenged intensively in recent years by environmental groups and local governments that try to reduce or eliminate mining, in many cases through litigation. The Florida industry, for example, is facing a tough fight in obtaining new permits. Several county governments are pooling money to challenge IMC in the courts for permit extension or new permits.

Some of the challenges can be contributed to communication gaps between the industry and numerous stakeholders. Many other cases are legitimate concerns about the sustainability of the industry. Whether being forced or voluntary, the industry will have to direct more resources at developing projects that support sustainability.

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Potash

Michel Prud'homme and Stanley T. Krukowski

INTRODUCTION

Potash is a generic term that includes potassium chloride (KCl), potassium magnesium sulfate ($K_2Mg(SO_4)_2$), potassium sulfate (K_2SO_4), potassium nitrate (KNO_3), and mixtures of sodium nitrate and potassium nitrate. The ceramics industry uses potash to refer to potassium oxide (K_2O). Potash in the form of potassium carbonate (K_2CO_3) was the first industrial mineral produced in the United States. The first patent issued in the United States was for an apparatus and process developed in 1790 for potash production (Paynter 1990). Before the 1860s, potash was sold mainly as an impure form of K_2CO_3 , produced by burning hardwood trees and leaching the potassium salts from the ashes. Primary early uses of potash included glassmaking, soapmaking, dyeing fabrics, baking, and using saltpeter for gunpowder.

In 1859, a purification process to remove sodium and magnesium chlorides was developed for carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$) found at Stassfurt, Germany; and mined potash became available. With the appearance of mined potash and the earlier (1840) discovery in Germany by Justus von Liebig that potash was a nutrient for crops, potash started to be used for high-value crops such as cotton and vegetables. The German potash companies quickly developed a manufacturing process for producing potassium sulfate for tobacco fertilization. German potash supplied nearly all U.S. consumption until it was embargoed during World War I. The United States became self-sufficient in potash when potash deposits were discovered in New Mexico in 1931. In 1962, the United States began importing potash from Canada, and 2 years later, domestic apparent consumption began to exceed domestic production.

Along with nitrogen and phosphorus, potassium is one of the three essential plant nutrients (the “K” of “NPK” terminology). As a result, 95% of potash production is used as plant fertilizer. For all plants, inadequate potassium diminishes growth and causes increased disease, stalk and stem breakage, and susceptibility to other stress conditions. Plants take up large quantities of potassium from the soil, and potash fertilization replaces this loss so that each new crop can grow with the same vigor and productivity as the previous year's crop. Potassium depletion of the soil from growing repeated cotton and tobacco crops is well known in the history of agriculture in the southern United States. For example, George Washington experimented with a lternative crops that could be grown on soil depleted by repeated tobacco harvests.

The chemical industry consumes most of the remaining 5% of potash production. Potassium hydroxide (KOH) is used to produce soaps and detergents, glass and ceramic products, dyes, explosives, alkaline batteries, and medicines. Other chemical applications are oil-field drilling mud, aluminum recycling, and electroplating. Minor uses for potassium chloride include water softener regeneration, sidewalk deicing, and salt (NaCl) substitution for human consumption. Potash is used in the food industry as potassium phosphate (monobasic, KH_2PO_4 , or dibasic, K_2HPO_4) and in production of glass products as potassium carbonate or nitrate.

GEOLOGY

Potassium is the seventh most abundant element in the Earth's crust and the sixth most abundant element in seawater. It is found in silicate minerals of igneous, metamorphic, and sedimentary rocks, and is a major constituent of many surface and subsurface brines. Most of world potash resources are found in subsurface, bedded salt deposits that yield high-grade, large tonnage ore bodies amenable to low-cost mining and beneficiation. Some potash production is from evaporation of naturally occurring brines. Because of the relatively high solubility of potassium minerals, potash from salt deposits is ideal for use as fertilizer.

Sylvite (KCl), carnallite ($KCl \cdot MgCl_2 \cdot 6H_2O$), kainite ($(4KCl \cdot MgSO_4) \cdot 3H_2O$), and langbeinite ($K_2(SO_4) \cdot 2MgSO_4$) are some of the more important potassium minerals (Table 1). Sylvite, a mixture of KCl and NaCl, is the highest-grade potash ore. Carnallite is considered a potash ore when magnesium chloride ($MgCl_2$) is removed during beneficiation, but it is considered a contaminant when mining for sylvite. Potassium sulfate and potassium nitrate typically are manufactured products. In 2004, potassium sulfate was produced from mined minerals through conversion processes in Germany and in the United States (e.g., potassium magnesium sulfate in Carlsbad, New Mexico), and from brines in Chile, China, and the United States (e.g., Great Salt Lake in Utah). Natural deposits of potassium nitrate occur only in small amounts in Chile.

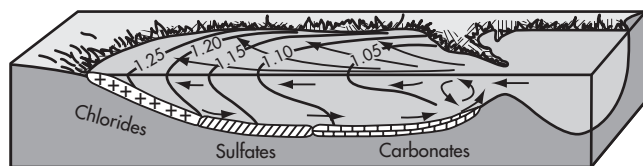
Most potash-bearing bedded salt deposits are believed to have originated from evaporation of seawater or mixtures of seawater and other brines in restricted marine basins (Schmalz 1969). Ochsnius first described the reflux depositional model for evaporite deposition in the literature in 1888. A shallow bar, or sill, across

Table 1. Some minerals, ores, and products of potash deposits

Name	Chemical Formula	K ₂ O, equivalent wt %	Remarks
Minerals			
Chlorides			
Sylvite	KCl	63.17	Principal ore mineral
Carnallite	KCl•MgCl ₂ •6H ₂ O	16.95	Ore mineral and contaminant
Kainite	4(KCl•MgSO ₄)•H ₂ O	19.26	Important ore mineral
Bischofite	2MgCl ₂ •12H ₂ O	0	Accessory contaminant
Halite	NaCl	0	Principal ore contaminant
Sulfates			
Polyhalite	K ₂ Ca ₂ Mg(SO ₄) ₄ •2H ₂ O	15.62	Ore contaminant
Langbeinite	K ₂ SO ₄ •2MgSO ₄	22.69	Important ore mineral
Leonite	K ₂ SO ₄ •MgSO ₄ •4H ₂ O	25.68	Ore contaminant
Schoenite (picromerite)	K ₂ SO ₄ •MgSO ₄ •6H ₂ O	23.39	Accessory
Glaserite (aphthalite)	3K ₂ SO ₄ •Na ₂ SO ₄	42.51	Accessory
Syngenite	K ₂ SO ₄ •CaSO ₄ •H ₂ O	28.68	Accessory
Bloedite	Na ₂ SO ₄ •MgSO ₄ •4H ₂ O	0	Accessory
Loewite	6Na ₂ SO ₄ •7MgSO ₄ •15H ₂ O	0	Accessory
Vanthoffite	3Na ₂ SO ₄ •MgSO ₄	0	Accessory
Kieserite	MgSO ₄ •H ₂ O	0	Common ore contaminant
Hexahydrate	MgSO ₄ •6H ₂ O	0	Accessory
Epsomite	MgSO ₄ •7H ₂ O	0	Accessory
Anhydrite	CaSO ₄	0	Common ore contaminant
Ores			
Sylvinites	KCl + NaCl	20–35	Canada, United States, CIS, * Brazil, Congo, Thailand
Hartsalz	KCl + NaCl + CaSO ₄ + (MgSO ₄ •H ₂ O)	10–20	Germany
Carnallite	KCl•MgCl ₂ •6H ₂ O + NaCl	10–16	Germany, Spain, Thailand
Langbeinite	K ₂ SO ₄ •2MgSO ₄ + NaCl	7–12	United States, CIS
Mischsalz	Hartsalz + carnallite	8–20	Germany
Kainite	4KCl•4MgSO ₄ •11H ₂ O + NaCl	13–18	Italy, Ethiopia, CIS
Products			
Potassium chloride	KCl	63.17	Principal potassium product
Potassium sulfate	K ₂ SO ₄	54.05	Artificial product
Potassium-magnesium-sulfate (langbeinite)	K ₂ SO ₄ •2MgSO ₄	22.69	Natural product (New Mexico)
Manure salts	KCl + NaCl	40–60	CIS and Germany
Other Sources			
Alunite	K ₂ Al ₆ (SO ₄) ₄ (OH) ₁₂	11.4	
Niter	KNO ₃ + NaNO ₃ + Na ₂ SO ₄ + NaCl	0.6–1.9	Chile
Mixed potassium nitrate and sodium nitrate	KNO ₃ + NaNO ₃	10–14	

Adapted from Adams and Hite 1983.

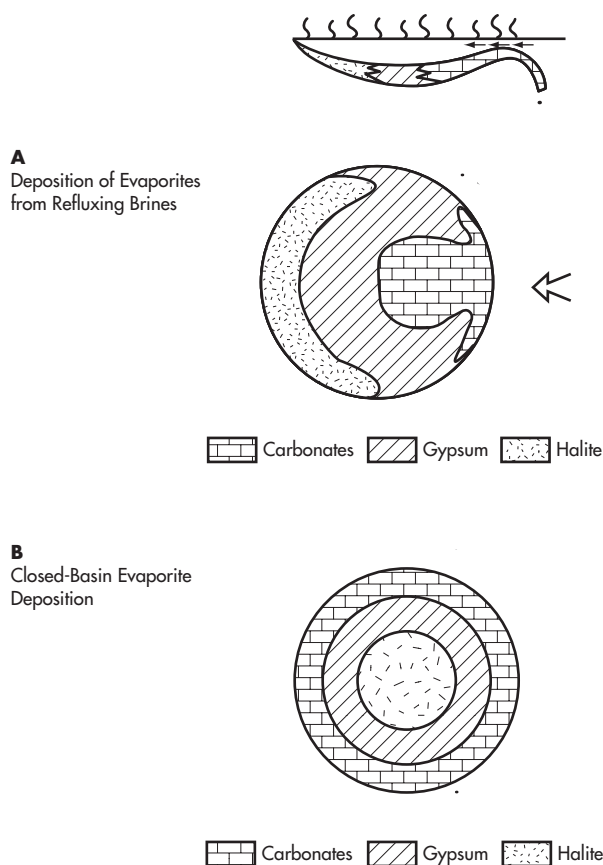
* CIS = Commonwealth of Independent States.



Adapted from Briggs 1957.

Figure 1. The reflux model of evaporite deposition. Evaporation of seawater entering the basin over a restricting sill increases in salinity at the distal end of the basin. Contours represent density of the brine. The least-soluble minerals precipitate near the inlet, and halite precipitation occurs furthest from the inlet.

the mouth of a basin restricts the inflow of seawater, which upon further evaporation becomes a salt-precipitating brine (Figure 1). At the distal end, the brine increases in density and salinity, sinks to the bottom, and creates a reflux current of higher-density brine back toward the ocean. The sill inhibits the outflow of concentrated brine back to the ocean. Least-soluble salts precipitate nearer the sill, and the most-soluble components precipitate out of solution in the deeper parts of the basin. The result is a tabular-shaped deposit with lateral facies changes resulting from salinity gradients in the brine (Figure 2A). The asymmetrical facies distribution of the Paradox Formation (Middle Pennsylvanian) in Utah (Hite 1970), the Prairie Formation (Middle Devonian) in Saskatchewan (Holter 1972), and the Salado Formation (Upper



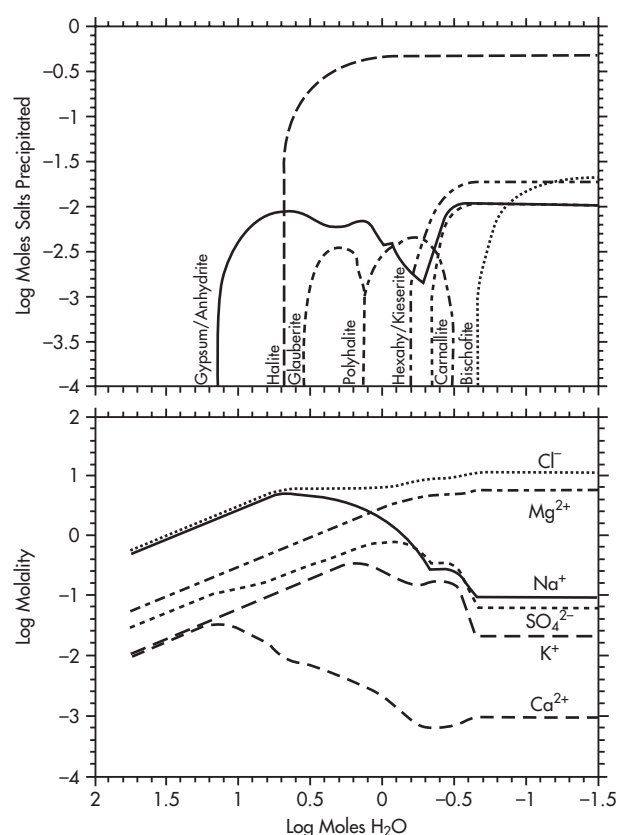
Adapted from Hsu 1972.

Figure 2. (A) Asymmetrical facies distribution of evaporite deposit formed by reflux model deposition; (B) Bull's-eye pattern of evaporite facies resulting from deposition in a basin drawdown model

Permian) in New Mexico (Lowenstein 1988) might be explained by such a model. Other deposits such as the Salina Formation (Upper Silurian) in Michigan (Matthews and Egleson 1974) show a facies distribution described as a bull's-eye pattern. Although some small sub-basins of high-grade sylvinite are found near the margins, the potash generally is located in a central part of the basin surrounded by successively less-soluble facies (Figure 2B). The sparse data available on the Miocene Mediterranean evaporite (Hsu 1972) also suggest a bull's-eye facies distribution.

Sedimentary features in marginal carbonates of some evaporite basins suggest subaerial exposure (Cercone 1988; Peterson and Hite 1969). According to Hsu (1972), subaerial exposure was the result of a basin undergoing evaporative drawdown and was responsible for deposits such as the Mediterranean Evaporite of Miocene Age, the Permian Upper Zechstein in Europe, and the Silurian Salina evaporite deposit in Michigan. Maiklem (1971) suggests the same mechanism for the Devonian Prairie Formation in Canada. Fluctuations in water depth in any ancient evaporite basin could be related to sea level changes, groundwater inflow, precipitation, and meteoric runoff, making it possible for evaporite minerals to have been deposited in either deep or shallow water and to have experienced subaerial exposure before burial.

Seawater evaporation results in precipitation of carbonate minerals first, followed by calcium sulfates, halite, magnesium sulfates, and then magnesium and potassium chlorides. The ratio of sodium



Adapted from Harvie et al. 1980.

Figure 3. Computer simulation of evaporation of modern seawater, using the program of Harvie et al. 1980. Bottom graph shows change in concentration of major ionic species with evaporation; top shows masses of minerals precipitated.

to potassium in seawater is 27:1, and, in general, minable potash beds are associated with thicker halite deposits. The potash ore zone often is located near the tops of halite beds in relatively thin layers because potash precipitates from higher-salinity brines near the end of the evaporation sequence. Carnallite rather than sylvinite is precipitated from seawater after the magnesium sulfates because of the high concentration of magnesium in seawater (Figure 3).

Evaporites of marine origin that lack magnesium sulfate and magnesium chloride minerals are the result of postdepositional dissolution processes. Carnallite may have been altered to sylvinite by reaction with magnesium-poor brines (Boorchert and Muir 1964; Garrett 1970; Braitsch 1971) or meteoric water (Hite 1982). In sylvinite deposits in Thailand, Republic of the Congo, and the Elk Point Basin of Canada, there is evidence that point-source ingress of meteoric water or seawater locally destroyed precursor carnallite, leaving sylvinite or only barren halite behind. In some instances this diagenetic process began shortly after the deposition of carnallite (e.g., the Thailand deposits), and the process may be occurring even today (Hite 1982). Recognition that nonmarine evaporite deposits are not necessarily restricted to small, terrestrial saline lake basins, however, led some workers to reassess the importance of mixing brines from seawater with other brines or with meteoric water (Hardie 1984; Williams-Stroud 1994). Some modern evaporites such as the Basque Lakes in British Columbia, Canada (Jones 1966) and those in the Qaidam Basin of Western

Table 2. Theoretical primary precipitation of stable chloride assemblages from normal seawater plus static evaporation at 25°C (without reaction at transition points)

Layer	Mineral	%	Thickness of Layer, m
A	Halite	100	100.0
B ₁	Halite	72	6.3
	Bloedite	28	
B ₂	Halite	20	4.5
	Epsomite	80	
C ₁	Halite	29	6.3
	Epsomite	30	
	Kainite	41	
C ₂	Halite	21	5.7
	Hexahydrite	3	
	Kainite	76	
C ₃	Halite	11	1.7
	Kieserite	4	
	Kainite	85	
	Kieserite	40	
D ₁	Halite	12	3.6
	Kieserite	40	
	Carnallite	48	
E	Halite	0.5	38.0
	Kieserite	1	
	Carnallite	0.5	
	Bischofite	98	

Adapted from Adams and Hite 1983.

Table 3. Calculated mineral sequence from evaporation of modern seawater and observed sequence from Zechstein 2 potash deposit[†]

Equilibrium Calculated	Observed Zechstein 2
G	G
A	A
A + H	A + H
Gl + A + H	Gl + A + H
Po + A + H	Po + A + H
Ep + Po + A + H	
Hx + Po + A + H	
Ki + Po + A + H	Ki + Po + A + H
Car + Ki + Po + A + H	Car + Ki + Po + A + H
Car + Ki + A + H	Car + Ki + A + H
Bi + Car + Ki + A + H	

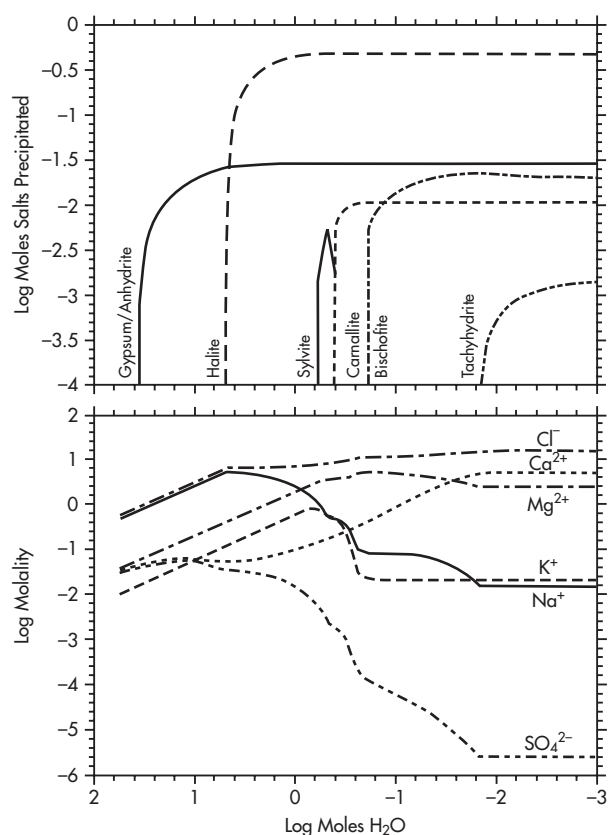
Adapted from Adams and Hite 1983.

* Equilibrium evaporation in the first column contains some minerals not found in the observed sequence from the Zechstein 2. Most of the differences can be explained by dehydration reactions.

[†] G = gypsum; A = anhydrite; H = halite; Gl = glauberite; Po = polyhalite; Ep = epsomite; Hx = hexahydrite; Ki = kieserite; Car = carnallite; Bi = bischofite.

China (Lowenstein, Spencer, and Pengxi 1989), which are clearly nonmarine in origin, precipitate a suite of minerals very similar to those precipitated from seawater.

Theoretical and experimental salt assemblages calculated by D'Ans (1933) bore close resemblance to naturally occurring assemblages. The presence or absence of some accessory minerals in naturally occurring evaporite deposits was explained by changing

**Figure 4. Computer simulation of evaporation of altered seawater where the ratio of magnesium to calcium is approximately 1:1 instead of the seawater ratio of 5:1**

temperatures in precipitating brines, mixing brines of different compositions, and reacting brines with salts precipitated previously. Table 2 gives the theoretical assemblage of primary precipitates from seawater at 25°C by Braitsch (1971). Harvie et al. (1980) show a slightly different mineral sequence (Table 3) from that calculated by Braitsch. The former predicts the occurrence of polyhalite and glauberite (CaSO_4 , Na_2SO_4), which occur in many evaporite deposits believed to be of marine or igin, although in many of these deposits polyhalite appears to be secondary after anhydrite or gypsum. For deposits such as the Stassfurt horizon of the Permian Zechstein potash in Germany, the sequence of Harvie et al. (1980) suggests that the natural mineral assemblage could be primary and does not require postdepositional alteration (Table 3). The initial brine composition is critical to the sequence of minerals that precipitate upon evaporation, but the mixing of waters during evaporation also can have a profound effect on the sequence of precipitation. Figure 4 shows that it is possible to produce widely varying mineral suites by altering relative amounts of only one or two of the initial aqueous species.

Petrographic and textural relationships as well as chemical analyses of fluid inclusions of associated halites in potash evaporites suggest that sylvite occurred in many instances as a primary mineral (Wardlaw 1972; Lowenstein and Spencer 1990; Williams-Stroud 1994). The enrichment of seawater with calcium results in early depletion of sulfate by gypsum/anhydrite precipitation and prevents the deposition of magnesium sulfates. If there exists some mechanism for magnesium removal, then carnallite may not precipitate as

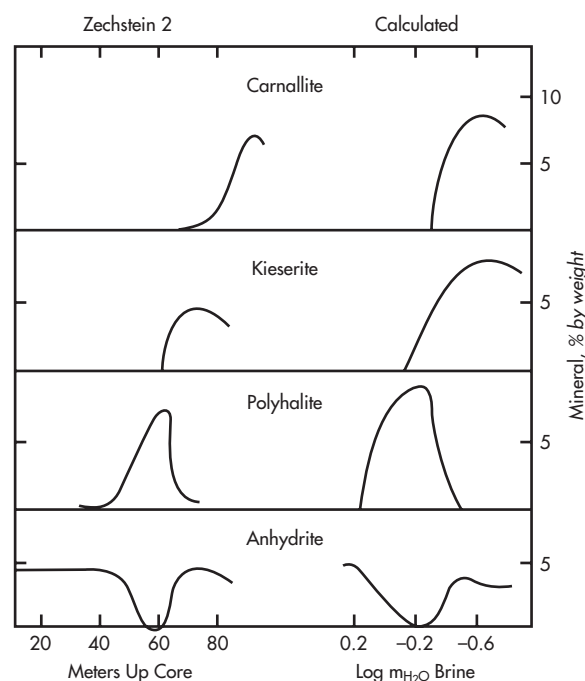
well, and sylvite will be the primary potash mineral deposited. Mechanisms for calcium enrichment or magnesium depletion include dolomitization of associated limestones or of a limestone precursor (Shearman 1966; Hite 1983), interactions with hydrothermal waters (Hardie 1990), and clay mineral cation exchange (Hite 1983). Sulfate depletion, which also may lead to nondeposition of magnesium sulfates, can occur through brine mixing (Raup 1970). When additional calcium enters into the system with other brines, sulfate may be consumed by precipitating gypsum and anhydrite before reaching saturation with respect to magnesium sulfate minerals.

Potash-bearing evaporites can be divided into two different types: magnesium sulfate-rich deposits (containing the minerals polyhalite, hexahydrate, kieserite, and epsomite) and magnesium sulfate-poor deposits (Hardie 1990). In the former, the primary potash mineral is carnallite, whereas the latter is characterized by sylvite and carnallite. The magnesium sulfate-rich evaporites (e.g., the Stassfurt horizon of the Permian Zechstein 2) exhibit the same mineralogy resulting from evaporation of modern seawater (Figure 5). The magnesium sulfate-poor potash deposits probably precipitated from brines high in calcium; these deposits constitute 60% or more of known potash basins (Hardie 1991). These two types of potash deposits display a distinctive temporal relationship (magnesium sulfate-rich types occurring only in the Permian, Miocene, and Quaternary; Figure 6), suggesting that changes in seawater composition occurred throughout Phanerozoic time or that many potash evaporite deposits did not precipitate from seawater, but were the result of the evaporation of nonmarine or mixed marine–nonmarine waters (Hardie 1991). Figure 7 shows the distribution of potash deposits that contain little or no associated magnesium sulfate salts. Many of the basins are smaller than the magnesium sulfate-rich evaporite basins, and some show an elongated shape, suggesting the formation in a graben or rift valley setting.

EXPLORATION

Evaporite deposits that are found in cratonic basins usually are associated with biogenic deposits such as shell carbonates and fringing reefs and with clastic redbed deposits. Some evaporite deposits are found at continental margins that were sites of tectonic extension during the Mesozoic and Cenozoic eras. The high solubility of evaporite minerals precludes the formation of salt outcrops in most parts of the world, and their occurrence generally is limited to the subsurface. The proximity of evaporite deposits can be inferred from saline waters in springs and wells, solution breccias, or thick outcrops of gypsum or anhydrite. Domal or collapse structures at the surface may indicate salt domes, or piercement structures, such as those found under and around the Gulf of Mexico (Halbouty 1967), under the North Sea, and in the Zechstein Basin (Trusheim 1960; Brunstrom and Walmsley 1969). Domes or anticlines that show on outcrop several periods of upward growth during a broad range of geologic time generally can be expected to have a central core of evaporites. The distribution and shape of subsurface salt structures also can be determined by geophysical techniques such as gravity and seismic methods (Sawatzky, Agarwal, and Wilson 1960).

Salt domes probably originated from the effect of gravity on layered rock where a lower-density material (e.g., salt) is overlain by higher-density material (e.g., sandstones, compacted shales, or carbonates). Compared to other geologic materials, the shear strength of halite and potash salts is very low, and the low compressibility maintains that low density even under deep burial conditions; low shear strength isabetted further by high temperatures associated with deep burial. Over geologic time, salt squeezes



Adapted from Harvie et al. 1980.

Figure 5. Mineral sequence measured in the magnesium sulfate-rich Zechstein 2 Stassfurt potash zone and the sequence calculated with computer simulation of equilibrium evaporation of modern seawater



Figure 6. Distribution of magnesium sulfate-rich evaporite deposits which occur only in the Permian, Miocene, and Quaternary



Figure 7. Distribution of magnesium sulfate-poor evaporites. Occurrences are throughout geologic time and not restricted to any particular geologic period.

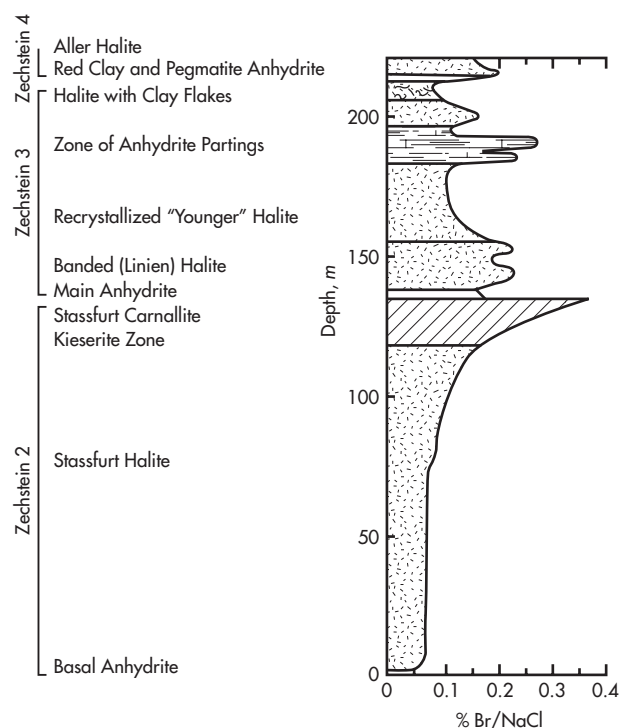


Figure 8. Bromine profile from halite in the Zechstein 2 showing regular increase in the amount of bromine that substitutes for chlorine in the halite crystal lattice

upward because of the density differential with overburden and irrespective of the presence of lateral tectonic compression. Salt flow, therefore, can be modeled as a viscous fluid (Ramberg 1981). Points of instability (i.e., intersections of fault systems or differential loading) are sites for nucleation of salt pillows, or salt hills in the subsurface. As the salt masses continue to rise, anticlines formed in the overlying layers may be pierced by this upward-moving salt, producing mushroom-shaped salt diapirs, which, in extreme cases, may detach completely from the rest of the salt deposit (Jackson and Talbot 1986). In the arid climate of northern Iran, salt diapirs pierced through the surface and flow downhill as salt glaciers. The structure of the original depositional layering in the salt inside of a diapir is highly deformed and chaotic (Talbot and Jackson 1987), and may not be suitable for conventional potash mining techniques.

Most potash deposits were discovered while drilling for petroleum. Evaluation of oil and gas exploration geophysical logs (such as gamma-ray, neutron, sonic, caliper, density, and resistance logs) is useful in interpreting evaporite lithology, stratigraphy, and mineralogy (Alger and Crain 1968). The gamma-ray log detects the gamma radiation from the natural potassium isotope K^{40} and is particularly useful as a continuous measure of the potassium content of the salt section (Adams and Hite 1983). Bromine content of salt layers has been used to evaluate potash potential and is useful as an indication of the stage of evaporation, especially in waters that were predominantly marine in origin. Bromine will substitute for chlorine in halite as the brine becomes more concentrated; that is, the bromine content of the brine increases. Because potash precipitation occurs in highly concentrated brines, the halite in and near potash beds should contain more bromide. A bromine concentration profile from seawater salt should show regularly increasing bromine

content toward the top of the halite bed (Figure 8), whereas salt precipitated from mixtures of sea water and other waters or brines, or a salt that underwent extensive postdepositional recrystallization by groundwater, may show either an irregular profile or no increase in bromine. In northeastern Thailand, economic potash deposits were discovered using bromine geochemistry (Hite and Japakasetr 1979).

Table 4 lists some general guidelines for evaluating the features of an evaporite deposit, and these may determine the success of a mining operation. The initial appraisal is based on drill cores spaced on 400–1600 m centers, depending on the depth and complexity of the deposit. Salt cores are logged, paying attention to all mappable stratigraphic, lithologic, and mineralogical features, and the potash zones are sampled as individual geological units for chemical analysis. It is generally sufficient to analyze for K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , and H_2O . The chemical analyses and the megascopic mineralogy estimated from hand specimens and thin sections are used with stratigraphic data to develop a geologic model. Factors listed in Table 4 help determine the potential for a minable deposit or the need for additional drilling or metallurgical tests.

WORLD POTASH OCCURRENCE AND RESOURCES

The U.S. Geological Survey (USGS) estimates reserves of potash that are recoverable with existing technology from known deposits at approximately 8.3 Gt K_2O equivalents. Canada and Russia have approximately 53% and 21% of the world's total reserves, respectively. The United States has only about 1% of the world's potash reserves. The resource data compiled in Table 5 are based on USGS published information. For the most part, the reserves may best be referred to as probable ore, or ore whose occurrence is reasonably assured but not absolutely certain. There is some question, for example, as to the reliability of the reserves reported for the Commonwealth of Independent States (CIS, the former U.S.S.R.), as well as that portion of Canadian solution mining reserves that are actually recoverable.

North America

Canada

Canada has most of the high-grade sylvinite ore reserves in the world. Reserves recoverable by underground mining are estimated to be 4.4 Gt (Searls 2005), based on an ore grade of 24% to 32% K_2O and a maximum minable depth of 1,100 m. The zones may be as thick as 10 m, but grade varies from approximately 3% K_2O at the top and bottom to an average 27% in the center of the zones. In 2004, potash production capacity in Canada was estimated at close to 12.3 Mt K_2O , accounting for a 35% share of global capacity.

New Brunswick. One mine produces potash from the Windsor Group of Mississippian age in New Brunswick. High-grade ore (averaging between 21% and 25% K_2O) discovered in 1970 occurs in zones located 300 to 1,000 m below the surface (Miller 1982). Windsor Group evaporites are mostly sylvinite with local minor occurrences of carnallite. Evaporites are located in a fault-bounded synclinalorium and are structurally more complex than the Prairie Formation. In some places, evaporites are diapiric in character. One underground mine was flooded in 1997. Between 1998 and 2005 its processing facilities were used for further beneficiation of potash products into higher value granular grades (the plant was permanently closed in 2005).

Saskatchewan. Ten mines currently produce potash from the Middle Devonian Prairie Formation of the Elk Point Basin in Saskatchewan (Figure 9). Three potash horizons occur in the upper part of the evaporite sequence: Esterhazy, Belle Plaine, and

Table 4. Guides to the evaluation of potash deposits

Factor to be Considered	Potential Problem	Observation to Be Made
Structure of ore horizon	Faulting, folding, or flowage of ore horizon complicating or precluding room-and-pillar mining method	(A) Correlation of stratigraphy between drill holes; (B) examination of core for evidence of deformation and recrystallization
Stratigraphy	Incorrect correlation of ore horizons; salt thickness; above ore insufficient to protect deposit from water; slabbing, and ore dilution from clay beds above ore horizon	Detailed core logging and correlation of beds between drill holes
Ore depth	Low mine extraction or excessive development and mining costs	Mining method and size of mine openings designed on basis of rock mechanics and geology
Ore thickness	Local systematic or random thinning of ore zone	(A) Isopach maps of stratigraphic units and mineralization in ore zone; (B) inspection of core for evidence of metasomatism and potash leaching, i.e., recrystallized halite, clay in intergranular clots, and horizontal mineral zoning
Ore mineralogy	Assemblages incompatible with proposed mill circuit; certain assemblages reduce stability of mine openings; high insoluble content requires extra desliming capacity	Determinative mineralogy of core
Ore grade	Grade may be too low or erratic to maintain acceptable mill feed; recoverable K ₂ O may be significantly less than total K ₂ O	Correlation and interpretation of drill hole data; comparison of chemical analyses with determinative mineralogy
Ore continuity	Erratic barren or thin areas in ore zone	Correlation of stratigraphic units and mineralization in ore zones; inspection of core for evidence of recrystallization and horizontal mineral zoning
Ore crystallinity	Inclusion of contaminants within potash minerals; fine-grained assemblages requiring finer grind	Correlation of microscopic examination of ore samples with chemical analyses of mineral separates
Ore reserves	Insufficient reserves or excessive mining and milling costs	Accurate geological description of deposit for mining and metallurgical studies

Adapted from Adams and Hite 1983.

Patience Lake members. Potash zones are 20- to 25-m thick, and are composed primarily of halite, sylvite, and carnallite (Holter 1972). Distinct layers, or finely disseminated bands, form in the potash salt and are composed of varying amounts of insolubles consisting of anhydrite and gypsum, carbonates, quartz, hematite, and clays. The entire evaporite sequence dips gently to the south at 1 to 8 m/km, with potash horizons occurring from 600 to 2,500 m below the surface. Lateral continuity and only a gentle warping of the beds permit the use of continuous mining machinery in a room-and-pillar method that minimizes rock instability and ventilation problems.

United States

In the United States, three companies operated seven mines from near-surface brines, lake brines, and under ground deposits at the beginning of 2005.

Arizona. In east-central Arizona, the Supai Formation of Pennsylvanian and Early Permian age includes thick halite deposits that also host potash. Several companies extensively explored this area, known as the Supai Salt Basin, for potash from 1963 through 1966. Drilling outlined a northeast-trending sylvinite deposit underlying about 800 km² (Peirce 1969). The deposit proved highly discontinuous with high clay content. Depths to the deposit range from 200 to 600 m, and the deposit apparently is relatively undeformed.

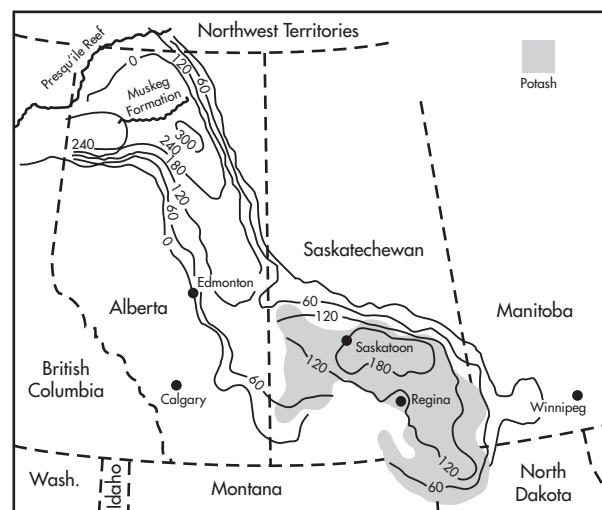
California. Potash production in California was by mechanical evaporation of subsurface brines. This mining operation is currently not operating.

Michigan. The Salina Formation of Late Silurian age hosts a large potash resource. These resources consist of a sylvinite deposit in the A-1 Salt that underlies about 33,800 km² in the Michigan Basin (Matthews and Egleson 1974). The zone of mineralization is more than 30 m thick in the central part of the basin. The vertical concentration of sylvinite is somewhat erratic in this thick deposit, but some intervals show K₂O values up to 40%. Depths to the deposit in the basin center are as much as 2,550 m, and although these depths decrease toward the basin margins, the deposit can only

Table 5. World potash reserves for 2004, kt K₂O

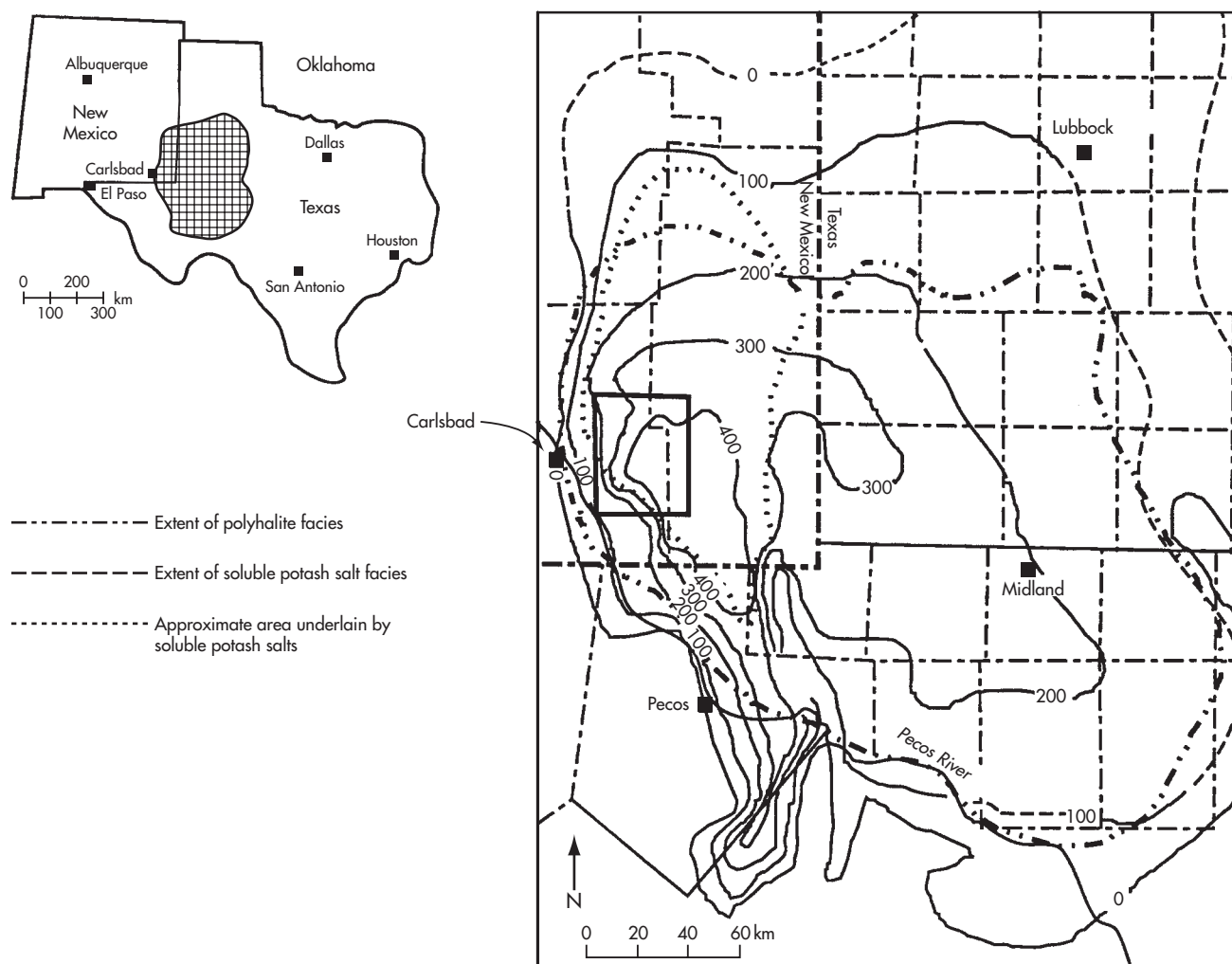
Country	Reserves	Country	Reserves
Belarus	750,000	Jordan	40,000
Brazil	300,000	Russia	1,800,000
Canada	4,400,000	Spain	20,000
Chile	10,000	Ukraine	25,000
China	8,000	United Kingdom	22,000
Germany	710,000	United States	90,000
Israel	40,000	Other countries	50,000

Adapted from Searls 2005.



Adapted from Zharkov 1984.

Figure 9. Middle Devonian Prairie Formation in Canada. Shaded area represents the areal distribution of potash. Isopach contours are in meters.



Adapted from Lowenstein 1988.

Figure 10. Salado Formation (Upper Permian) in the Permian Basin of New Mexico and Texas. Isopach contours are in meters.

be mined by solution mining. Currently, the Mosaic Company (mine formerly owned by IMC Global Inc.) is using deep-well solution mining and mechanical evaporation for crystallization on muriate of potash (MOP) and by-product sodium chloride (Searls 2005).

New Mexico. Since 1931, most potash production in this state has come from the Carlsbad mining district in the Permian Delaware Basin of southeast New Mexico (Figure 10). In this district, the Salado Formation contains sylvinite, langbeinitite, and lesser amounts of sulfate minerals in 12 potash horizons that occur over approximately 5,000 km² (Jones 1972; Lowenstein 1988). Two companies were operating three New Mexico mines at the beginning of 2005: The Mosaic Company mine, formerly owned by IMC USA Inc., and the two Intrepid Mining LLC mines (formerly owned by Mississippi Potash Inc.). These mines extract potash ore from 5 of the 10 horizons (Searls 1985). The potash ore is confined to a relatively small interval of the Salado called the McNutt Zone, in which local barren patches of almost pure halite (called salt horses) complicate mining operations. Barker and Austin (1999) give an overview of the Carlsbad potash district.

Texas. The Palangana salt dome in southeastern Texas is the only salt dome in the Gulf Coast region that hosts a significant con-

centration of potash. The Palangana, which consists of sylvinite, was explored with 25 drill holes in the early 1960s (Hofrichter 1968). The internal structure of this salt diapir is very complex and caused the abandonment of the project.

Utah. The Middle Pennsylvanian Paradox Formation has large reserves of potash in the Paradox Basin of southeastern Utah and southwestern Colorado. These deposits are found in a thick sequence of evaporite cycles. Thirty-one cycles have been identified in this sequence and 18 are known to contain potash, although only 11 cycles contain potentially valuable deposits (Hite 1964). Potash deposits are found at depths suitable for conventional shaft mining only along a series of northwest-trending salt anticlines. In 1964, Texas Gulf Company sank a shaft on the Cane Creek anticline to a depth of about 850 m to mine a high-grade sylvinite deposit that occurs in the upper part of the evaporite sequence. After about 4 years, the company ceased mining by room-and-pillar methods and converted the underground openings to a solution mine.

Potash also is produced in Utah by solar evaporation of the brines of the north arm of the Great Salt Lake, and from shallow brines in the Great Salt Lake Desert at Wendover. At the beginning of 2005, two companies operated three Utah mines: Compass Mineral

operates one mine in Ogden and Intrepid Mining LLC operates two mines (formerly owned by Reilly-Wendover and Moab Salt).

South America

The South American continent has only a few potash evaporite deposits and, so far, no extensive, high-grade, continental craton-type evaporite such as that found in North America and Europe has been discovered.

Argentina

Potash reserves occur in the Argentinean Andes provinces of Neuquén and Mendoza in evaporites of Middle Cretaceous age. These reserves are nearly 1,000 m deep. Very high formation temperatures ($>50^{\circ}\text{C}$) may preclude underground mining, so solution mining methods were investigated. The ore is sylvinitic, which is divided into two zones. The upper zone averages about 3 m thick and the lower is about 11 m thick. The grade of the potash ore averages between 20% and 25% K_2O . Development of these deposits was tentatively pursued in the late 1990s. In 2004, Potasio Rio Colorado S.A., a subsidiary of Rio Tinto's Industrial Minerals Group, carried out a series of feasibility, marketing, and technical studies to develop a large solution mine in the Neuquén Basin. Also in 2004, Companhia Vale do Rio Doce SA of Brazil acquired the exploration license for a potash deposit in Neuquén to evaluate potash reserves and study the feasibility of solution mining.

Brazil

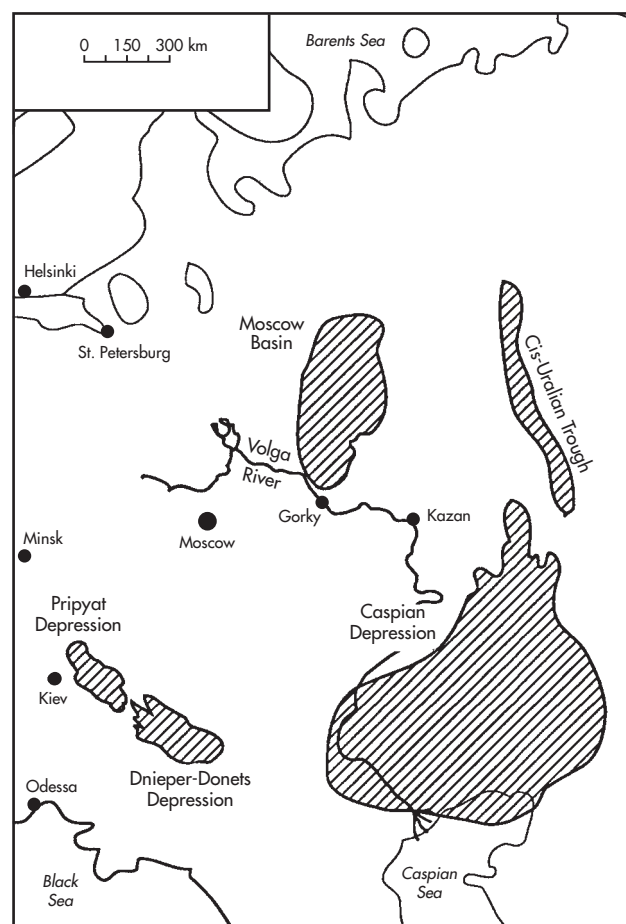
The large Amazonas Basin of Brazil contains sylvite-bearing evaporite deposits of Permian age (Szatmari, Carvalho, and Simões 1979). Two potential deposits near Manaus in the Amazon Basin are about 1,000 m deep with an average thickness of 2.7 m and average 16.5% K_2O .

A minor proven potash reserve in South America occurs in the Ibura Member of the Muribeca Formation of Middle Cretaceous age in the state of Sergipe. The deposits probably formed as a rift valley evaporite sequence that resulted from alteration of seawater brines by the addition of calcium-rich hydrothermal fluids during the separation of the African and South American plates in Jurassic to Cretaceous times (Wardlaw 1972). The mineralogy of the deposit includes halite, carnallite, sylvite, and tachyhydrite ($\text{CaCl}_2 \cdot 2\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$). The tachyhydrite is very thick (up to 90 m) and nearly pure; it occurs in a bedded sequence displaying primary depositional growth fabrics of carnallite crystals in halite, but containing no bischofite and no magnesium sulfate minerals.

In 2004, production of potash came from only one underground operation mining the Ibura Member. The ore deposit is a complex structure with rapid and frequent lateral variation of sylvite and a thick underlying deposit of metastable tachyhydrite. The sylvinitic deposit is divided into two seams by a thin halite layer, which sometimes is missing. Because the ore directly overlies tachyhydrite, 3 m of sylvinitic must be left in the floor to prevent floor heave. Extreme variations in ore grade required the mining of large tonnages of barren salt.

Chile

Significant reserves occur in several salars surrounding the area where the borders of Chile, Bolivia, and Argentina meet. Potash production from the Salar de Atacama in Chile was expanded from about 50 ktpy KCl in the early 1990s to more than 800 kt KCl in 2004. Sylvinitic is recovered as a by-product of lithium production, mainly from the Sociedad Química y Minera de Chile (SQM). The bulk of potash production is used in manufacturing high-grade potassium nitrate. Potassium sulfate also is extracted as an associated



Adapted from Zharkov 1984.

Figure 11. Distribution of Permian potash-bearing salt deposits in the East European Basin

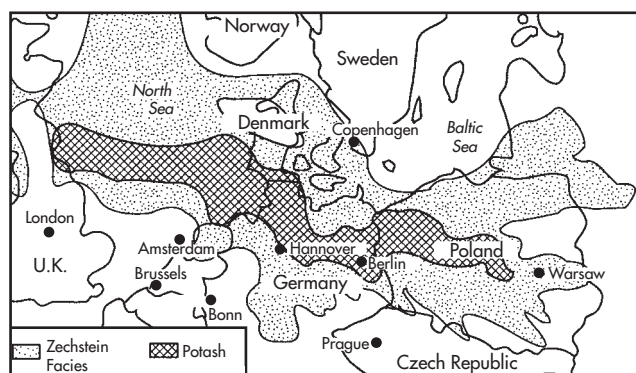
ated mineral. A part of the caliche deposits in Chile have minor amounts of potassium nitrate in the ore.

Europe

Commonwealth of Independent States

The CIS has an estimated 3.5 Gt K_2O (32% of the world's potash reserves), which occur in several sedimentary basins (Figure 11). In the Pripjat Depression and the Dnieper-Donets Depression, potash occurs in Devonian age salt. Several potash-bearing salt deposits of Permian age occur in the East European Basin (Zharkov 1984). The Dnieper-Donets Depression also contains Lower Permian Asselian and Sakmarian deposits (Figure 11). Sakmarian salt also is found northeast of Moscow in the Moscow Basin. The Caspian Depression contains Kungurian deposits that also occur in the Belsk and Solikamsk depressions of the Cis-Uralian trough. The thickest salt strata with potash salt horizons occur in the Kungurian deposits. In the late 1980s, one mine was lost to flooding in the Berezniki Area of Perm, but sylvinitic ore from another mine kept the beneficiation plant operating.

Belarus. In the Pripjat Depression, four potash horizons were identified in the lower salt sequence of the Liven horizon of Devonian (Frasnian) Age (Zharkov 1984). Potash horizons range from about 130 to 1,500 km^2 . They contain beds of sylvite with minor



Adapted from Zharkov 1984.

Figure 12. Lithologic map of Permian Zechstein 3 evaporite deposit

carnallite in beds 4 cm to 1.5 m thick interbedded with muddy halite. Above the salt of the Liven horizon, 60 potash occurrences were identified in the upper salt sequence in the Elets horizon (Famennian). Potash occurs in an area of about 5,000 km² at depths varying from 200 to 3,000 m on local uplifts. Potash-bearing halite occurs in the upper part of the sequence in zones of sylvite as thick as 70 m, interbedded with halite. Major potash production is from the Elets horizon at an average depth of 480 m; potash ore grade is about 18% K₂O.

Kazakhstan. Kungurian (Lower Permian) salt in the Precaspian Depression contains polyhalite–halite, bischofite–carnallite, carnallite–halite, and sylvite–halite rocks. The salt sequence was studied in more detail on the flanks of the Precaspian Depression. In the center of the depression where the salt is strongly deformed, drill holes in several salt domes explored for potash salts or other mineral resources.

Russia. The Permian salt in the Solikamsk Depression is found in the Iren horizon of the Kungurian stage. The potash member is divided into two intervals: the lower sylvinite and upper sylvinite–carnallite. Average thickness of the lower interval is about 21 m; the upper interval averages 60 m. Deposits are generally medium grade (16% to 23% K₂O), occurring at depths between 200 and 500 m.

Siberia. Cambrian salt covers an extensive area in eastern Siberia. Potassium salts occur in the Chara horizon (Lower Cambrian), where three sections are distinguished: carnallite, sylvite–carnallite, and sylvinite. The potash horizon lies at depths of 600 to 900 m and contains some sylvite ore grades that are more than 30% K₂O. Currently, there is no production in Siberia.

Ukraine. In western Ukraine, low-grade potash deposits were mined from Lower and Middle Miocene rocks near the Stebnik and Kalush-Golyn regions (Kopin 1963). The first three of four evaporite cycles contain individual beds of langbeinite, kainite, and langbeinite–kainite with minor chlorides, and also beds that contain sylvinite, carnallite, kainite, langbeinite, schoenite, and polyhalite. The percentage of insoluble residues is high, averaging between 9% and 14% K₂O in the langbeinite–kainite ores to as much as 33% in the sylvinite ores. The fourth evaporite cycle contains polyhalite, but it has no soluble potassium salts.

Low-grade potash ore also was recovered from the Kramatorsk Formation of probable Sakmarian age in the Dnieper–Donets Basin. Interbeds of sylvinite, carnallite, carnallite–halite, and sylvite–carnallite occur in the upper part of the formation. Potash salts form two horizons: the Privolno sylvinite horizon and the upper Chasov-Yar sylvinite–carnallite horizon.

England

The Boulby mine in England has produced potash from sylvinite beds in the English Zechstein Basin since 1973. Two sylvinite beds averaging 6 to 8 m in thickness occur at depths between 1,000 and 2,700 m. Underground facilities suffered from water inflow, affecting production in the late 1990s. Potash production capacity in 2004 was estimated at 600 kt K₂O.

France

Potash was mined in France until 2002, when the economically viable potash ore was depleted. The principal potash reserves of France were in evaporates, deposited in the Oligocene Rhine graben. Potash salts occur in the subsurface at depths from 420 to 1,100 m in two laterally continuous zones in the upper third of the evaporite section. The lower potash interval, which contains sylvite with some carnallite, is up to 5 m thick. It is separated from the upper sylvite zone, which ranges up to 2 m thick. The ore contains several bands of claystone that impart a high content of insolubles. Dips of more than 10° are common, and mining was by longwall rather than room-and-pillar method.

Germany

The largest production comes from the Permian Zechstein, where the world's first subsurface potash occurrences were discovered (Figure 12). The Zechstein contains four evaporite cycles with the lower three containing five potash horizons: Thuringen, Hessen, Stassfurt, Ronnenberg, and Riadel. The Hessen and Thuringen horizons are mined for carnallite and hartsalz. The latter is potash ore containing sylvite and kieserite, a relatively hard mineral. In the Werra-Fulda District, these deposits are mined at depths of 400 to 1,000 m. Beds are flat-lying and relatively undeformed; the potash is of uniform grade and distribution, permitting room-and-pillar mining. Potash deposits in the Hannover District are on steeply dipping flanks of both conformable and piercement salt structures. Mining is by stoping and backfilling, and is concentrated between depths of 300 and 800 m. The ore is irregular and discontinuous, and requires underground exploration drilling.

Mining in the Stassfurt District also exploited potash reserves of the Zechstein salt until 1972. During a restructuring of the German potash industry in the early 1990s (following reunification of East Germany and West Germany) five mines were closed because of low ore grade or problems of mine waste disposal. By 2004 the total production capacity of potash operations in Germany was estimated at close to 4.3 Mt K₂O.

Italy

Potash mines on the island of Sicily extracted kainite from the Solfifera Series of Miocene age. The only other known kainite reserves are found in Ethiopia and Ukraine. Kainite from Sicily was used in the manufacture of potassium sulfate. The potash operations shut down during the mid-1990s. Other minerals present in the Solfifera were carnallite with some sylvite, kieserite, and bischofite in beds 2 to 30 m thick with dips up to 60°.

Poland

In Poland, potash deposits are known to occur in the Zechstein in three separate areas (Orska and Werner 1978). In the late 1960s, polyhalite deposits were found in the Puck Gulf region along the Baltic Sea. According to Werner (1975), one drill hole intersected 6.5 m of nearly pure polyhalite at a depth of 788 m. At present, there is no development of this deposit. Another potash deposit in the Zechstein consists of carnallite and occurs in the Nowa Sol Area, 60 km east of the German border (Orska and Werner 1990).

Spain

Potash mines in northern Spain produce potash from evaporites of Late Eocene to Early Oligocene age. In the Navarra mining district, potash occurs at depths of 120 to 600 m in two beds: a lower sylvinite bed and an upper bed, which is principally carnallite. Carnallite and sylvinite deposits in the Catalonia mining district occur in four folded and deformed beds. Mining beds that dip at 30° are common.

Africa and the Middle East

Egypt

The Red Sea rift zone contains thick Miocene evaporites that extend northwest into the Gulf of Suez region. Potash minerals, including sylvite, polyhalite, and langbeinite, were identified in side wall cores from petroleum exploration wells in the Gulf of Suez (Hite and Wassef 1983). Correlations in the thick sequence of evaporites in the Zeit and South Garib formations show that millions of tons of polyhalite occur in the Suez Area (R.J. Hite, unpublished data).

Ethiopia

Potash deposits in the Danakil Depression of Ethiopia are young (Quaternary) and contain extensive kainite beds. Potash occurs in three members in the Houston Formation: the uppermost sylvinite member, up to 10 m thick; the intermediate member, 3 to 24 m thick containing carnallite throughout with sylvite at the top and kainite at the base; and the Lower Kainite Member, 4 to 13 m thick. The deposit is in a salt pan in a rift valley depression characterized by recent volcanism and high heat flow (Holwerda and Hutchinson 1968). Several hot springs and brine pools are found in the salt pan; groundwater in sedimentary units interbedded with the evaporites is a potential hazard for underground mines. Several companies explored the deposit in the 1960s and 1970s. In 1973, exploratory drilling and mining ended after an overlying water-bearing alluvial fan caused flooding in the mine.

Israel and Jordan

Israel and Jordan are the only major producers of potash in the Middle East. Potash is produced from brines of the Dead Sea, which contains 980 Mt K₂O (Neev and Emery 1967). Both countries use solar evaporation ponds along the margins of the Dead Sea to recover carnallite, which then is converted into potassium chloride. In 2004, their combined potash production capacity was estimated at 3.4 Mt K₂O.

The Dead Sea rift zone also hosts several salt beds beneath the floor of the Dead Sea. These contain potash deposits originally discovered by petroleum exploration wells.

Morocco

The Moroccan Meseta basins contain Late Triassic sylvite–carnallite deposits with bischofite and rinneite (FeCl₂•NaCl•3KCl). Potash salt deposits, interbedded with basalt flows (Tortochaux 1968), occur at depths between 490 and 790 m. The sylvinite bodies are low grade and erratic.

Republic of the Congo

Potash production started in 1969 at Holle, 40 km northeast of Point Noire. Cretaceous potash beds contain sylvite and carnallite. Irregularities in the potash beds initially caused difficulties for boring machines. When a mining machine opened a brecciated collapse column connected to an aquifer in 1977, the Holle potash mine was lost after it abruptly flooded. Since then, a few studies evaluated the feasibility of renewing mining operations in the district. In 2004, MagMinerals Inc., a subsidiary of Canada-based MagIndustries Corp., announced its plan for the construction of a

solution mining operation and a magnesium plant complex that would use potassium brines from the Kouilou salt deposits.

Saudi Arabia

In the Red Sea rift zone, thick (up to 3,000 m in cores) and extensive Miocene evaporites occur near the surface in a group of salt domes in the Farasan Islands along the west coast of Saudi Arabia. Minerals include bischofite and only minor carnallite.

Asia

China

Although China has been mining and exploring evaporite deposits for nearly 2,000 years, only minor amounts of potash have been discovered. The most extensively explored basin is in Sichuan where brines from Triassic evaporites produced potash for many centuries. The brines produce sodium chloride primarily, but small amounts of other by-products, including potash, also are recovered. The Triassic halite deposits in this basin locally have bromine values as high as 300 ppm, and so the Ministry of Geology and Mineral Resources (MGMR) concentrated most of its exploration efforts in this basin. No economic concentrations of potash were discovered other than minor amounts of polyhalite. Sylvite deposits are found in rock salt mines in the Simao Basin in Yunnan Province. The evaporites occur in rocks of Middle Jurassic, Late Cretaceous, and Paleocene ages. Although their precise age is unknown, it seems likely that the Simao Basin evaporites are the same age (Cretaceous) and occur as a northern extension of the potash-bearing evaporites of the Khorat Plateau of Thailand and Laos. The Yunnan sylvite deposits are lenticular and have a high degree of deformation. Ore grade seldom exceeds 15% K₂O. Because of the lenticular nature and deformation, low grade, and extremely remote location of the sylvite, the government does not consider this area worthy of further exploration.

Currently, most potash production in China comes from a large salt lake in the Qaidam Basin in Qinghai Province. In 2004, potash production occurred at more than 30 operations; production was estimated to exceed 1.2 Mt K₂O from the solar evaporation of carnallitic brine.

China's need for potash is acute. Over the centuries, soils in China's principal farming areas were depleted in potash because of continued agricultural use. Potash consumption was 0.5 Mt K₂O in 1986; it reached 4.9 Mt K₂O in 2004. The global ratio of N:P:K applied to agricultural lands is 1.0:0.45:0.36, but in China the nutrient ratio in 2004 was 1.00:0.39:0.19, compared with 1.00:0.19:0.03 in 1986.

Pakistan

The Salt Range in West Pakistan has a thick sequence of Lower Cambrian evaporites that include some potash. The evaporites are near the surface at several localities along where they are mined for their halite content. At Khowra and elsewhere, the potash occurs and is exposed in rock-salt mines in 10 discrete zones or deposits (Jones 1970). The potash minerals include langbeinite, kainite, sylvite, and polyhalite.

Thailand

Potash deposits are present in the Maha Sarakham Formation (Cretaceous) on the Khorat Plateau of northeast Thailand and eastern Laos. They occur in the lowermost of three thick halite deposits. A northwest-trending uplift (Pu Phan) divides the deposits into a southern basin (Khorat) and a northern basin (Sakhon Nakhon). Because the evaporite stratigraphy is identical in either basin, the uplift probably formed after deposition of the evaporites. The base

of each evaporite sequence in both basins is undeformed, but the tops are folded into numerous salt anticlines and domes. Most of the potash consists of carnallite, as much as 95 m thick (Hite and Japakasetr 1979). This is carnallite deposit, thought to be primary, also contains the highly soluble mineral tachyhydrite. Locally around the anticlines and domes, meteoric waters altered the carnallite deposit into lenticular bodies of high-grade sylvinite (Hite 1982). The Thailand Department of Mineral Resources did most of the exploration, although concessionaires also performed some drilling in recent years. The government of Thailand planned to exploit the carnallite deposit near Bamnet Narong; in 2004, however, the Ministry of Industry announced that the Thai government had withdrawn its financial support for the ASEAN Potash Mining Co.'s potash mining project in Bamnet Narong. Since 1990, Asia Pacific Potash Company (APPC), a subsidiary of Asia Pacific Resources, has carried out an extensive exploration program and completed feasibility studies for the development of an underground potash mine and the construction of beneficiation facilities. APPC holds prospecting licenses for two large sylvinite-bearing potash deposits in the Sakon Nakhon basin. In May 2003, APPC filed a mining lease application for its Udon South potash deposit (the "Somboon" deposit) near Udon Thani in northeast Thailand. The company is hopeful that it will obtain the mining license in 2006 and start potash production by 2009.

Oceania

Australia has several large salt basins, but no economic occurrences of potash have been discovered. In the Carnarvon Basin, minor occurrences of sylvite have been observed in petroleum test holes in a Silurian halite deposit. In addition, three petroleum tests drilled in the Adavale Basin found potassium minerals, mainly sylvite, in the Etonvale Formation (Devonian).

PRODUCTION TECHNOLOGY

Mining

For underground mining of sylvinite, ore grade should be 14% K_2O or higher, and bed thickness should be 1.2 m with about an 8-m-thick salt back (or roof). The USGS established the 14% K_2O rule in Carlsbad, New Mexico, in the early 1930s; East Germany and Russia however, mined potash ore as low as 11% K_2O while operating under centrally planned economics. Carlsbad potash (sylvite) producers have operated with 80% to 85% recovery in the mill (some producers operate at 92% recovery by pulling pillars). French and British operators installed crystallizers to the back ends of the mills to capture potash from waste liquor before sending the liquor to the tailings piles with waste salt. This is an additional step raised recovery at their plants to as high as 92%.

The proved amount of ore for a new mine should confirm a minimum of 20 years of production given mill size, mill recovery, and the underground recovery factor for ore depth. Plant or mill size should be at least 300,000 t K_2O to compete in a market that has many plants in the 1-Mt K_2O size. This is the economies-of-scale concept expressed by economists. The existence of "salt horses" in the ore zone is another factor to consider (Jones and Prugger 1982). In Saskatchewan, these barren patches of almost pure halite can constitute as much as 10% of the ore and require additional monitoring of the mining operation.

Conventional North American mining methods illustrate two extremes for percentage of underground recovery. Carlsbad mines operate at a depth of about 270 m, with one mine sloping down to 430 m. These mines recover about 75% of the ore on the first pass, and attain 90%, sometimes with surface subsidence, on the retreating pass. In contrast, the mines in Saskatchewan normally are oper-

ated between 1,000 and 1,100 m with a 35% to 45% recovery. Mines in the Patience Lake Member recover about 35% to 40% of the ore whereas mines in the Esterhazy Member, which has at least 18 m of competent salt back above the ore zone, recover about 45%. The Canadian operations do not have a retreating pass. After the original pillars collapse enough for waste heaps to take up the weight of the back (roof), miners return and mine the pillars. This provides a higher underground recovery. Another example of a mine operating at a lower recovery rate is the Boulby mine near Whitby, England. This mine is at a depth of about 1,100 m and achieves around 35% underground recovery.

Much sylvinite mining is now mechanized, using boring machines, drum miners, or longwall miners and occasionally road headers. Boring machines in Canadian mines can continuously produce 12 t/min, occasionally producing up to 17 t/min for as long as 8 hr. Mining machines take the central 3 m of high-grade ore. Mine depths of more than 1,000 m in a sedimentary sequence require sophisticated techniques that sometime involve controlled collapse of panels. All borers feed directly onto conveyor belts connected to main haulage ways or over-bridge conveyors that are connected directly to the conveyor belt system (Jones and Prugger 1982). Drum miners are converted to continuous miners with the addition of bridge conveyors for direct connection to main conveyor belts. In France and Belarus, longwall mining has been used for higher underground recovery and continuous mining. The longwall conveyor belt discharges to a ladder-chain conveyor on the floor of a development roadway at one end of the longwall panel. The ladder-chain conveyor discharges onto the conveyor belt leading to the skips of the ore hoist. Road headers typically use shuttle cars to connect to the conveyor belts but can be connected directly. The Carlsbad mines that recover langbeinite still must use jumbo drills, undercutters, blasting, mucking, and shuttle cars because of the hardness of the ore.

Borers mine ore in very long galleries to take advantage of their cutting method, rather than room-and-pillar, which is the method used with drum mining. Some Canadian mines produce 1,200-m-long galleries with longwalls in between. Other Canadian mines use panels having five entries per panel, with the outer two entries collapsing in 1 or 2 days. Sylvinite and langbeinite mining in Carlsbad is room-and-pillar. The Boulby mine on the eastern coast of England drives five panels with crossovers in a V shape to redistribute the stress.

Where ore zones are not flat-lying, other methods of underground mining are used. PotashCorp at its underground operation at Penobscis, near Sussex in New Brunswick, Canada, mines with road headers in a cut-and-fill technique up one side of an anticline. Provincial environmental regulations require that no tailings pile remain on the surface, so all tailings are backfilled into the mine using a second conveyor belt system. Some German potash mines use block-caving (bench-mining and funnel-stoping) methods because potash ore is on the flanks of salt domes.

Solution mining can substitute for conventional shaft mining in potash deposits that occur below approximately 1,100 m, but it is not an alternative for some potash zones too deep for conventional mining methods. Thickness, mineralogy, and structure of the deposit, as well as technical considerations of the mining operation, must be evaluated to determine the suitability of solution mining. Two forms of solution mining are practiced today. A site that was mined initially by conventional underground methods can be converted to solution mining to recover ore that remains in the pillars. Pipes are drilled down to meet the former underground galleries providing communication between an inlet pipe that supplies undersaturated brine to the ore zone and a return pipe that brings

saturated brine to the surface. This method is effective in relatively thin ore zones, for example, those slightly thicker than 1 m. The Intrepid mine at Moab, Utah, was the first to employ this type of solution mining in 1971. Boreholes were drilled to the lowest point in the mine and to all the highest points in the branch galleries. Boreholes in the branch galleries supplied fresh water, and the lowest point in the main gallery became the return pipe for the dense brine. The lower elevation of the return pipe allows only saturated brine to come up from the ore zone, whereas in a flat-lying ore zone it would be difficult to prevent the less dense, undersaturated brine from returning to the surface. PotashCorp converted the Patience Lake mine to a solution mine in 1988 after it was flooded by water coming from a breccia that occurred downdip from the ore zone. Heated brine, which was nearly saturated with respect to NaCl, was then introduced into the mine. The brine dissolved only potash for return to the surface ponds. The imposed hydrologic head prevented most of the less-concentrated brine from the intruding aquifer from entering the mine. Mosaic Company (formerly IMC Canada) operates the largest solution mine in the world at Belle Plaine in Saskatchewan, Canada. In 2004, the facility had a production capacity of more than 1.7 Mt K₂O.

Solution mining with concentric pipes solves the problem of establishing communication between the inlet and the return pipe. Three concentric pipes are required: the innermost and the deepest for the return flow, and the middle for the inlet flow of hot NaCl-saturated brine. The outermost concentric pipe injects oil, which floats above the brine, to force the injected water to mine outward instead of upward around the pipe. A large diameter for the cavity must be established, and it is critical that the potash zone or sequence of zones be sufficiently thick. Development of mine production by this technique generally requires that the cavity have enough potash to pay for drilling the well, for the equipment in the well field, for the pipes leading to the crystallizers, and for all recovery plant costs.

Solution mining also is used in shallow, high-grade deposits where structural complexity precludes successful underground mining by conventional methods. Conversion to solution technology at the mine in Moab was dictated by the high degree of structural deformation of the ore layer, a problem that was not indicated by the original exploration drilling (Evans and Linn 1970). Solution mining initially was quite successful because of the large surface area of potash ore in the original room-and-pillar structure. The K₂O content of the brine pumped to the surface has diminished continuously with removal of the mine pillars, and there is little indication of active dissolution of ore beyond the original mine workings.

Processing and Beneficiation

In operations where potash reserves are surface or subsurface brines, or where ore is extracted by solution mining, potash must be recovered with technologies specific to brines. Three processes currently used for performing this recovery are crystallization of potash by solar evaporation, by reduction of brine temperature, and by artificial processing through crystallization–evaporation cycles. Each process uses selective dissolution and precipitation of sylvite from brine. Where brine is saturated mutually with KCl and NaCl, the solubility of NaCl decreases slightly with increasing temperature up to 90°C, above which the solubility of NaCl then increases with temperature. Because the solubility of KCl increases dramatically up to 90°C, a warm brine would dissolve much less NaCl if there were sufficient sylvite available to saturate the solution with respect to KCl. When the brine is cooled, sylvite precipitates more rapidly than halite, and, at certain temperatures, a solution saturated

with respect to both KCl and NaCl precipitates only sylvite; the NaCl remains in solution.

Climate is extremely critical for effective solar evaporation from surface ponds. Brine brought to the surface at the Moab mine evaporates completely in single ponds to precipitate a mixture of sylvite and halite. Dyes added to pond brines increase solar energy adsorption and so increase brine temperature and rates of evaporation. The operations at Ogden and Wendover, Utah, use lake water or near-surface brines and multiple ponds. Multiple ponds are used to establish brine densities for crystallization of various minerals at different stages. Efficient solar evaporation occurs during only 3 months of the year (June, July, and August), with more than half the total evaporation occurring in July. During this 3-month period low rainfall must combine with sufficient wind to keep the brine mixed and to enhance evaporation. At Moab and Wendover, both sylvite and halite precipitate out of solution in the potash-harvesting ponds. The harvest then is sent to a standard flotation-type beneficiation plant to separate the two salts.

Two potash operations at the south end of the Dead Sea benefit from a climate that promotes evaporation throughout the year. During evaporation of the Dead Sea brine, carnallite and halite precipitate out of solution in harvesting ponds. MgCl₂ is washed away with freshwater, leaving a mixture of sylvite and halite. On the Israeli side, sylvite is separated from halite in three different processing plants. The oldest plant uses flotation technology. A capacity expansion added a process that uses dissolution–recrystallization. The newest plant uses a proprietary cold-crystallization process that uses a low-heat crystallizer to produce KCl.

The solution mine of PotashCorp in Patience Lake, Saskatchewan, uses a selective precipitation process that takes advantage of natural cooling. One large pond operates from September through May. As warm brine from the mine flows into the pond, only sylvite crystallizes on exposure to the cold winter air. Then the pond is dredged and the precipitated sylvite is dried for marketing. The process is predicated on the temperature dependence of NaCl and KCl solubilities.

Another method of recovery is used by the Mosaic Company in Belle Plaine, Saskatchewan. The brine is processed using two trains of evaporators and crystallizers. Evaporators remove NaCl from the brine and KCl precipitates in the crystallizers.

Ore beneficiation methods also differ according to the type of ore. For less-soluble ores such as the langbeinite mined in the Carlsbad area, leaching is an effective beneficiation method for ore grades at about 9% K₂O. One of the two processes involves preferential dissolution of associated salts (mostly halite with a little sylvite) from the ore. The other process uses heavy media separation and flotation in addition to leaching. Gundiler (1999) reviews processing technology at the Carlsbad potash district.

The potash industry began using flotation technology for sylvite in the early 1930s in Carlsbad. The use of flotation gradually spread to France, England, Germany, the CIS, and Israel. After the slimes (clay and hematite) are washed away, the pulp (the suspension of crushed sylvite in saturated brine) is treated with a long-chain amine (C-18 to C-22) and a frother (such as pine oil). It is then passed to an agitation cell where compressed air is introduced from the bottom. A froth of amine and entrained air bubbles carries the potash to the surface, where it is mechanically swept over the side of the cell into a trough. Carnallite is avoided during mining because it has a detrimental effect on flotation cell recovery (Jones and Prugger 1982).

The Mosaic Company uses heavy-media technology in its plants in Saskatchewan. Sylvite and halite crystals of the Esterhazy zone are crushed to 1 cm and separated by heavy media using the

Table 6. Product specifications

Grade	Minimum K ₂ O Equivalent, %	Approximate Particle Size Range*		Type of Potash
		Mesh†	mm	
Granular	60, 50, 22	6–30	3.34–0.85	Muriates, sulfates, and magnesium sulfates
Coarse	60	8–28	2.4–0.6	Muriate
Standard	60, 50, 22	14–65	1.2–0.21	Muriates, sulfates, and magnesium sulfates
Special standard	60	35–150	0.4–0.11	Muriate
Soluble	62	35–150	0.4–0.11	Muriate
Chemical	63	NA‡	NA	Muriate

* From approximately 2% to 98% by weight percent cumulative.

† Tyler standard.

‡ NA = not applicable.

small-density difference between halite and sylvite. In Carlsbad, one heavy media circuit separates sylvinites and langbeinite, then a second heavy-media circuit separates sylvite and halite.

In the early 1910s, the French developed dissolution–recrystallization technology at their former operations for processing potash ore with high insoluble content. The first Carlsbad potash mill also used this technology but converted to flotation when it became obvious that the latter would clean sylvinites ore (<3.5% slimes). One Carlsbad mine continues to use the dissolution–recrystallization technology for ores with >5% slimes content.

Electrostatic separation of potash was first investigated in Carlsbad after World War II, but it was not implemented. It was resurrected in Germany and, after years of development, proved to be a low-cost, high-volume process (Singerwald and Neitzel 1983). The waste product is dry, there are no waste brine disposal problems, and little heat input is required of the operation. The process involves moderate heat, reagent coating, a source of electric power, and careful control of relative humidity in the separation chamber. Separations can be serialized in a multistage process line.

Potash Products

The fertilizer trade refers to potassium chloride as muriate of potash (MOP), potassium sulfate as sulfate of potash (SOP), and potassium magnesium sulfate as sulfate of potash-magnesia (SOPM). About 96% of potash used for fertilizer is in the form of MOP; the remainder in the forms of sulfates and nitrates (Searls 1985). Lixivation is used for production of potassium sulfate. The process starts with kainite, either mined or crystallized from lake brines. Kainite is converted to schoenite ($\text{MgSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot \text{H}_2\text{O}$), and potassium sulfate is crystallized from the schoenite. An other method of beneficiation of potassium sulfate is through ion exchange.

SOP does not occur naturally. Most commercially produced SOP is synthesized by heating MOP and H_2SO_4 to approximately 650°C in large furnaces. Some German potash mines produced SOP by combining kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) and sylvite (Singerwald and Neitzel 1983). A potash operation plant in Carlsbad produced SOP by mining sylvinites and langbeinites and performing a base exchange (Anon. 1968). Great Salt Lake Minerals & Chemicals Corp. uses solar evaporation to produce kainite ($4(\text{KCl} \cdot \text{MgSO}_4) \cdot \text{H}_2\text{O}$) from Great Salt Lake brines, and beneficiation follows with the lixivation process.

MOP, which constitutes close to 96% of the world's production of potash, has a minimum requirement of 60% K₂O content. SOP has a minimum requirement of 50% K₂O content, and SOPM has a minimum requirement of 19% K₂O content. Table 6 lists product specifications, including various grain sizes of different grades of

potash. Coarse MOP is the most popular size sold in the United States, but granular MOP for use in machine-spread fertilization and bulk blending is a close second. Standard MOP is preferred in countries where fertilizers are still hand cast. Particle sizes listed in Table 6 do not describe fully the current expectations of farmers. Current potash producers claim to match the current particle-size distribution of monoammonium phosphate (MAP) or diammonium phosphate (DAP) particles.

By-products and Coproducts

Typical potash beneficiation is based on flotation technology and generates NaCl as waste. Some waste salt has clay, hematite, and other impurities such as shale. Some potash sources and beneficiation techniques produce a variety of by-products. German mines using electrostatic separation produce magnesium sulfate (kieserite) and rock salt pure enough for road deicing. German mills that use dissolution–recrystallization produce magnesium chloride, salt, and bromine. The Israelis also produce bromine as a by-product. Potash produced from the brines of Searles Lake in California has soda ash and salt cake coproducts. The surface brine at Wendover, Utah, produces salt and magnesium chloride as by-products. Great Salt Lake Minerals & Chemicals Co. produces salt for road deicing, Glauber's salt ($\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$), and magnesium chloride. The solution mine at Belle Plaine, Saskatchewan, produces large amounts of clean salt brine, which is sold to a nearby salt producer. The dissolution–recrystallization mill in Carlsbad, New Mexico, occasionally processes ore that contains some sulfate. The sulfate plugs up the circuit as glaserite (K_3NaSO_4), which is recovered and sold in small amounts as a low-priced substitute for SOP if the crop can tolerate the slight amount of sodium.

ECONOMIC FACTORS

U.S. Historical Consumption

The United States passed through an S-shaped potash consumption curve between 1920 and 1990 (Figure 13) as it learned to feed an ever-growing population. U.S. consumption of potassium fertilizer peaked at about 5.7 Mt K₂O in 1981 and gradually declined afterward to stabilize at about 4.5 Mt annually. In 2004, the overall consumption in fertilizers was estimated at about 4.6 Mt K₂O (Heffer 2004). The decline in potash consumption reflects more efficient use of fertilizers and a decline in crop exports as other countries began their own green revolutions. Generally, the need for fertilizer increases as the population increases, but populations do not buy fertilizer until they can afford it (Figure 14). Many developing countries need fertilizers (in addition to good weather and modern farming practices) but are not able to purchase them until the

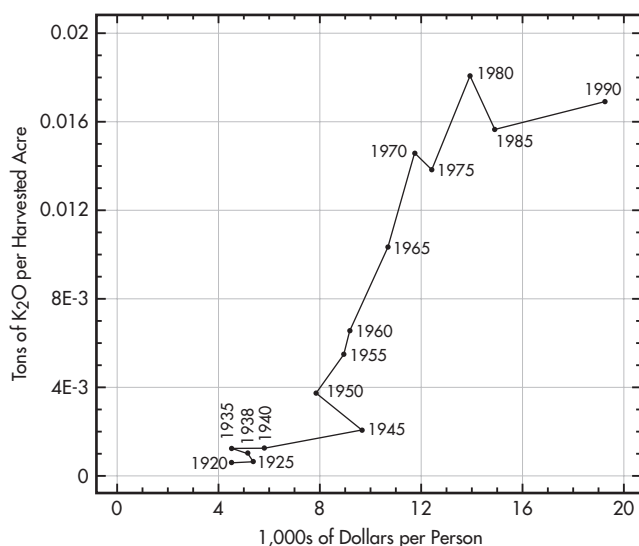


Figure 13. History of U.S. potash consumption and growth of wealth

wealth (gross domestic product [GDP] per capita) of the population increases. By grouping countries and taking averages of these groups, one can clearly see in Figure 14 the progression of potash consumption as a function of wealth.

A worldwide overcapacity of potash has forced several potash producers to operate below capacity since 1990. For example, Potash Corporation of Saskatchewan produced well below nameplate capacity during much of this period. U.S. potash companies could not meet current demand in the United States (Figure 15). Potash mines in Canada currently provide more than 90% of the U.S. apparent consumption. U.S. potash producers exported about 23% of their total sales to the Caribbean and the Pacific Basin. Transportation costs govern much of this export routing. Table 7 shows world potash mine production for 2004.

U.S. Prices

Prices for commodities are hard to define because many firms sell at slightly lower prices to large-volume buyers. Large-volume buyers also may receive extended terms, the period allowed for the buyer to pay without interest penalties. Terms may be 30, 90, or even (rarely) 180 days. Prices reported by the USGS represent the average annual prices received by U.S. potash producers, free on board (f.o.b.) at the plant; annual prices are computed by dividing total dollars received by tonnage sold (Searls 2005). The average for U.S. producers includes all types of potash (MOP, SOP, and SOPM) for all grades (sizes). Large-size particles command a premium price in the United States.

Other

Prices can be quoted for standard MOP, f.o.b. Vancouver, British Columbia, Canada. Prices around the world tend to be set by firms or countries by summing the Vancouver price and the transportation cost from Vancouver to a port of competition, then backing out their own transportation cost to that port of competition.

Transportation

Deepwater transportation prices rise and fall with the overall supply and demand for all types of ocean shipping. As an example,

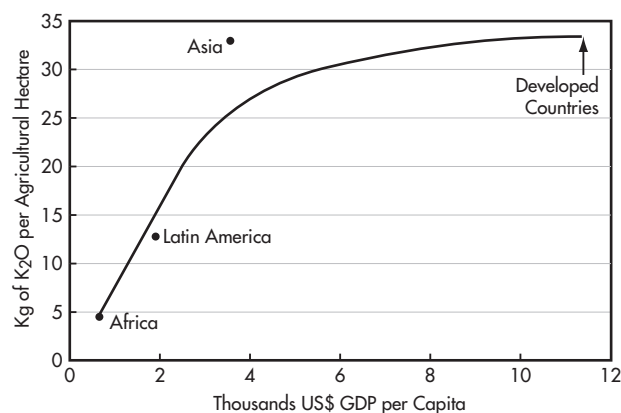


Figure 14. Relationship of wealth to consumption of potash

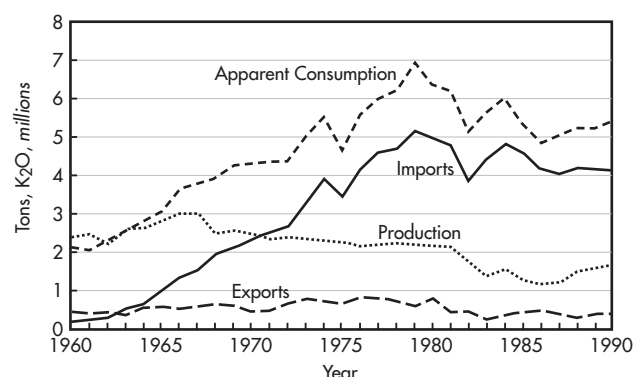


Figure 15. Components of U.S. supply and demand for potash

Table 7. World potash production for 2004, kt K₂O equivalent

Country	Production	Country	Production
Belarus	4,610	Israel	2,140
Brazil	370	Jordan	1,160
Canada	10,100	Russia	5,600
Chile	520	Spain	550
China	1,050	United Kingdom	540
Germany	3,630	United States	1,200

Adapted from IFA (Potash Statistics 2004) and Searls 2005.

between April 2002 and April 2005 international maritime freight rates increased fivefold. Certain potash shipments move at lower costs because they are backhauls. A backhaul is made when a ship or railcar returns to its origination point with another cargo.

Substitutes

Potassium (K⁺ ion) is essential to plant and animal life, and Li⁺, Na⁺, Rb⁺, and Cs⁺ are not substitutes. Potassium is essential to protein synthesis in plants, and it specifically activates the enzyme responsible for starch formation. In humans, K⁺ ions and Na⁺ ions in nerve sheaths are the essential sodium pump that allows signals to travel along nerve pathways. Potash is the low-priced, water-soluble form of K⁺ ions available at this time. For plants, green manure is a

substitute but only near farms that fatten beef and raise pigs, chicken, sheep, and dairy cattle. Green manure does not contain enough potash to transport over distances >80 km. MOP is concentrated enough to ship a few thousand kilometers. Greensand (glauconite) is used by organic farmers if it is available. Greensand contains up to 7% K_2O , but it is shipped long distances because it contains some phosphorus and because it meets the requirement of organic farmers for natural fertilizer, for which they are willing to pay extra.

For industrial uses, NaOH (caustic soda) substitutes for KOH (caustic potash) because of its wide availability and lower cost. Potassium nitrate or potassium carbonate impart different optical, density, and luster qualities to certain glasses, making them desirable to glass manufacturers. Potassium carbonate is used in chocolate and cocoa manufacture, liquid soaps, welding rods, vat dyeing, photographic chemicals, electroplating compounds, fire extinguishers, and rubber antioxidant applications. In smaller amounts, it is used in many consumer end products.

GOVERNMENTAL CONSIDERATIONS

Environmental Regulations

Activities of the potash mining industry may result in a wide variety of environmental effects. Typically these are quite localized and confined to the mine site in most cases. At any specific site the type and extent of environmental effects depend on factors such as mining methods, beneficiation processes, waste disposal methods, and proximity to existing population centers and infrastructure.

Underground mining methods tend to create fewer environmental problems. A major issue is possible surface subsidence induced by the removal of extensive flat-lying ore deposits. Water quality also may be affected by release or leakage of slurry brines and contaminants into process water. The land surface and subsurface are disturbed by mining extraction methods, deposition of overburden, disposal of beneficiation wastes, or surface subsidence. Environmental impacts caused by handling, such as dust and exhaust emissions, tend to be local. Dust may be generated from traffic on unsealed roadways, from loading and unloading operations, from conveyor transfer points and stacking stockpiles, and from reclamation operations. In Carlsbad, New Mexico, dust emissions were once an issue; in recent years, however, a variety of baghouse and wet scrubber emission-control equipment was installed throughout ore-handling and processing facilities.

Large volumes of waste tailings generated from beneficiating potash potentially may generate harmful environmental effects. Wastes can comprise impure salt, slimes, clay, dolomite, anhydrite, and other salts such as magnesium chloride. The potash industry uses a wide variety of waste disposal methods such as discharge of wastes into rivers and oceans, pile stacking, backfilling of solid and liquid wastes into mined-out underground openings, or deep-well injection of brines.

In Germany, potash mining generates 0.78 t of waste per ton of beneficiated ore; these wastes consist of salt and magnesium chloride brines. Brines are disposed by either deep-well injection or discharge into the Werra and Ulster river system. A computer system monitors and controls the discharge to ensure that the maximum permitted salt concentration of 2.5 g/L of river water is not exceeded as river conditions and flow rate vary. This system prevents adverse environmental effects in the riparian and aquatic ecosystems downstream.

Tailings are designed as integrated systems comprising engineered impoundments, walls, containment dykes, liners, drains, ditches, and capture wells. In Saskatchewan, salt wastes typically are disposed of as slurry on the tailings pile. Insolubles and brines drain into the settling ponds at the base of the pile. The brine is then

either recirculated into the process or disposed of through deep-well reinjection. In Germany, dry separation processes allow dry disposal on a salt tailings pile.

Backfilling of mine and process wastes into underground openings is conducted at a few operations. The technical feasibility of backfilling mines in flat-lying ore bodies was studied in large-scale trials, but it was hindered by the difficulty of placement, safety concerns, and cost. Currently, the cost of backfilling these spaces may be 10 times greater than the cost of surface disposal methods. Deep-well injection is used to dispose of brines at some operations. PotashCorp's New Brunswick Division operation uses effective and environmentally sound waste management by returning all waste to underground workings using a closed-loop system. This system returns all waste slimes and brines underground through a slurry pipeline into the excavated salt rooms. Clarified brine is recovered from the salt rooms and returned as input to the crystallization circuit for recovery of residual potassium chloride. The water balance of the operation essentially is a closed system.

Surface- and groundwater contamination can occur through the release or seepage of tailings effluent and brines from dams, ponds, and stacks. Leakage of liquid wastes such as brines from storage and disposal ponds is controlled to a large extent by containment techniques such as plastic or clay liners, ditches, drains, and containment pumping wells.

A number of companies have conducted trials to determine the feasibility of sealing the surface of potash salt tailings piles to isolate the salt from the environment, to allow the establishment of vegetation, and to leave a stable landform. In Germany, rehabilitation of a small tailings pile of less than 11 Mt of waste salt began in 1997 by capping it with demolition rubble from the City of Hannover. Then the salt tailings pile was covered with soil (as a growing medium) for revegetation. In France, the closure of the potash operations led to a vast rehabilitation program of the salt tailings. One method consisted of capping the piles with plastic, clay, or bituminous liners; covering them with a growing medium; and revegetating with grasses. The other method involved dissolving the salt component in the pile using fresh water and discharging the resulting brines in a controlled manner into the adjacent Rhine River.

For a comprehensive discussion on environmental aspects of potash mining, see UNEP/IFA (2001).

SAFETY AND HEALTH CONSIDERATIONS

Because potash mines are in sedimentary deposits along with oil and gas, and most potash mines were discovered through oil and gas exploration, some potash mines contain high amounts of methane gas. Recovery in these mines requires special precautions and expensive equipment, but these deposits are minable and have good safety records. Scaling the mine roof is a constant concern in some potash mines. Mud seams often are associated with, or are directly above, potash zones; often the level of the cut is gauged by these mud seams. In the Esterhazy ore zone in Canada the mud is present as a thin band in the middle of the highest quality ore. This band of mud can be seen only by holding a miner's lamp to the face of the ore and watching for the disappearance of the halo around the lamp. In other potash ore zones, mud bands are too few or too thin to be recognized during mining and are insufficient to provide additional support to the potash beds. There is little adhesion between sylvinite and clay, and roof falls may take place causing potential injuries. In some mines in Carlsbad, New Mexico, relief holes are drilled at intersections to bleed off any nitrogen that may lie about 1 m above the potash zone. Roof bolts are installed at the intersections for support. Health effects of potash dust were studied at the University of

Saskatchewan (Markham and Tan 1981); investigators noted that chronic phlegm production, mild shortness of breath, and chronic cough were more common in high-exposure groups such as mining crews and screening operators, but that severe respiratory symptoms were rare.

PROBLEMS AND FUTURE TRENDS

Supply

Since the mid-1980s the worldwide market for potash has been in a situation of oversupply. Because of sustained potash demand and increased production and transportation costs, however, the market became tight in 2004, leading to a series of capacity expansions by established producers and exporters.

According to the International Fertilizer Industry Association (IFA), world potash production in 2004 reached 31 Mt K₂O. The world's potash producers reached an average operating rate in 2004 of 83% of capacity, the highest level in the past 10 years. Excluding Belarus, Canada, Germany, the United Kingdom, and Russia, the rest of the industry operated at close to capacity. In the next few years, potash capacity will increase in almost all producing countries. The major projects include expansions at existing mine sites in Brazil, Canada, Germany, Israel, Jordan, and Russia. Future potash prospects include developments in Argentina, Laos, and Thailand. In 2004, the IFA estimated that world potash capacity would reach close to 40 Mt K₂O in 2008. Between 2003 and 2008, additional capacity will exceed 3 Mt K₂O, of which 70% will be located in exporting countries, 25% in China, and 5% in Brazil.

Demand

In the 1980s and 1990s, the world potash market underwent some significant changes, including the break up of the former Soviet Union and the Eastern Bloc; changes in the agricultural policy of the European Union; the expansion of agricultural production in developing countries; and the consolidation of the potash industry in key producing countries. World fertilizer consumption increased steadily during the 1990s but declined in 2000. Global fertilizer demand recovered thereafter and increased at an average annual rate of 2.4% between 2000 and 2004.

In 2004, the FAO forecast world fertilizer demand in 2008–2009 at 160 Mt, which equates to an average annual growth rate of 1.7% between 2004 and 2008; world potassium nutrient consumption was expected to reach 27.2 Mt K₂O, which equates to an annual growth rate of 1.8% over that of 2004.

There are three different regional trends in fertilizer consumption: decline in demand in developed markets such as North America and Western Europe, transitional markets in the CIS and Central Europe, and increased consumption in developing markets such as Asia and Latin America, driven by urbanization and a growing population.

In 2004, the FAO projected a relative tightening of the global potash market from 2004 to 2008. The prevailing global surplus will gradually decline as demand exceeds supply. Regionally, the total requirement for potassium shows a growing deficit in major importing regions. According to the IFA (Heffer 2004), the regional supply/demand imbalance was projected to increase by more than 14% in Latin America, 16% in East Asia, and 21% in the rest of Asia. The total potassium deficit in all importing regions will exceed 17 Mt K₂O in 2008, an increase of 2 Mt K₂O over that of 2004. In the major producing/exporting regions, the surplus is projected to increase in the CIS and West Asia, and to increase slightly in both Western Europe and North America.

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Pumice, Pumicite, and Volcanic Cinder

Gordon C. Presley

INTRODUCTION

Pumice, pumicite, and volcanic cinder are volcanic rocks characterized by a cellular structure. They form as gases (primarily water) dissolved in molten rock (magma), generating a froth that cools and solidifies into rigid foam. The cells or bubbles are referred to as vesicles and range in size from a few thousandths of a millimeter to several centimeters. Because of their vesicular character, both pumice and cinder have lower density and higher porosity than most other rock types. As their vesicle walls are broken, sharp cutting edges are continually generated. These properties are the basis for their commercial value as lightweight aggregates, insulators, absorbents, and abrasives.

The terminology applied to volcanic products is imprecise, reflecting to varying degrees the diversity of volcanic rocks, the relative youth of volcanology as a distinct field of study, and customs and practices of commercial trade. In general terms, pumice is light colored (white, gray, pink, pale yellow, or brown) and highly vesicular and usually has vesicle walls that are visibly glassy. Many pumice fragments are light enough to float on water. Pumice is readily cut by steel tools, and some can be crushed by hand. Individual pumice fragments may range from 1 or 2 mm to <1 mm in one dimension. Commercially, finer fragments are called pumicite or volcanic ash. In volcanology, the term *ash* refers to any fragment <2 mm regardless of its composition. Cinder, or scoria, is dark (black, red, brown) with thick vesicle walls that appear dull or stony and that may exhibit iridescence. Cinder typically is heavier than pumice and has a higher crushing strength. In volcanology, the term *scoria* refers to dark vesicular material throughout a wide size range. Common commercial practice is to use the term *scoria* for larger fragments (usually >2.5 cm) and *cinder* for smaller fragments.

GEOLOGY

Composition and Physical Characteristics

Most pumice is silicic ranging from 60% to 70% SiO₂ or dacitic to rhyolitic in composition. Pumice of less silicic composition, including basaltic, is less common, and does not have extensive commercial use. Scoria and cinder are typically basaltic to andesitic with a composition of approximately 50% to 60% SiO₂.

Pumice and cinder may contain phenocrysts of feldspars and various ferromagnesian minerals that crystallized in magma before eruption. Fragments of rock through which the magma has passed

may be entrained in the melt and wall rock may be fragmented and admixed during an explosive eruption. Some scoria fragments have lithic fragment cores. Phenocrysts and lithic fragments can be detrimental in certain pumice products.

Pumice typically has vesicles of <1 mm separated by thin walls. Vesicle shapes include irregular, spherical, elliptical, and elongate to the point of being tubular with a silky appearance (Figure 1). In some pumices the vesicles are interconnected, making the fragments permeable and highly absorbent. In others the vesicles are isolated, forming a highly porous but very impermeable pumice. Floating masses of pumice fragments from the eruption of Krakatoa in 1883 were reported in the Indian Ocean for up to 2 years after the eruption. Vesicles in cinder are larger and range from spherical to highly irregular in shape with much thicker walls and abundant interconnections. Scoria and cinder are typically porous, but heavier, and do not float.

Density and hardness of pumice must be expressed precisely to avoid confusion. Density can refer to the glass itself, the apparent density of the vesicular pumice particle, or the bulk density of pumice in a deposit or in a pumice product. Pumice glass has a specific gravity of 2.5 or more, depending on its composition. Pumice fragments typically have a specific gravity of <1.0. Expressed as density, pumice fragments typically weigh <1 g/cm³. Depending on moisture content, particle density, and particle-size distribution, the bulk density of pumice typically ranges from 500 to 700 kg/m³. Typical bulk densities of cinder range from 700 to 900 kg/m³ for material used as lightweight aggregate. The bulk density of cinder used for highways and railroad ballast can be considerably higher.

Hardness in pumice can refer to the glass vesicle walls, possibly including crystals or lithic fragments, or to the apparent hardness of the particle as a whole, which is more a measure of the strength of the vesicle structure. Pumice glass typically has a Mohs hardness of 5 to 5.5. A pumice particle may have a much lower apparent hardness and be easily cut with a knife or steel saw because the vesicle walls break readily.

Pumice and cinder are primarily pyroclastic (fragmental) products of volcanic eruptions. Several classification systems differing in various details have been proposed for pyroclasts and pyroclastic deposits based on particle size (Fisher 1961; Schmid 1981; Cas and Wright 1988). Generally, particles >64 mm are referred to as blocks or bombs, depending on their shapes. Particles between 64 mm and 2 mm (4 mm in some schemes) are called

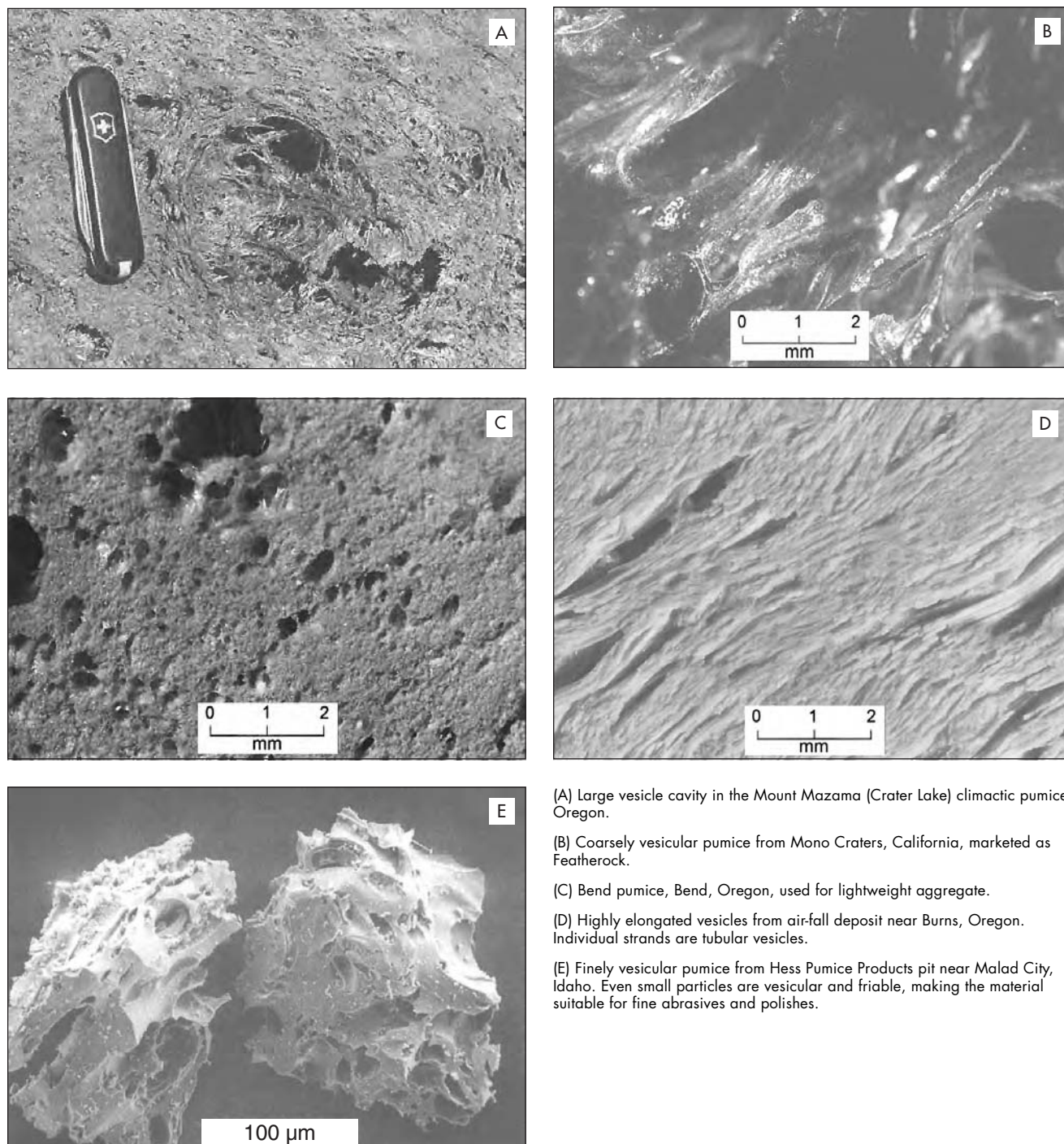


Figure 1. Variations in vesicle shape and size.

lapilli, and smaller particles are called ash. These names may be modified by compositional terms, for example, pumice lapilli or scoria lapilli. Most commercial deposits are composed of fragments in the lapilli size range. In the United States, pumice fragments having one dimension of 5 cm or more are legally defined as block pumice. The procedures for acquiring pumice from federal land are determined in part by this definition and are described in a later section.

(A) Large vesicle cavity in the Mount Mazama (Crater Lake) climactic pumice, Oregon.

(B) Coarsely vesicular pumice from Mono Craters, California, marketed as Featherrock.

(C) Bend pumice, Bend, Oregon, used for lightweight aggregate.

(D) Highly elongated vesicles from air-fall deposit near Burns, Oregon. Individual strands are tubular vesicles.

(E) Finely vesicular pumice from Hess Pumice Products pit near Malad City, Idaho. Even small particles are vesicular and friable, making the material suitable for fine abrasives and polishes.

Origin

The science of volcanology has grown rapidly, particularly in the last 50 years. Both field and laboratory studies have greatly expanded the understanding of eruptive rocks and eruptive processes. Cas and Wright (1988) and their extensive list of references detail much of this work.

The formation and preservation of highly vesicular rocks involve the interplay of a large number of variables, including

temperature, viscosity, gas pressure, and diffusion rates within the erupting magma and external conditions such as wall rock permeability, water influx, vent blockage, wind conditions, and whether the eruption is subaerial or subaqueous. None of these is constant and may change significantly, even during a single eruptive event.

Basaltic magmas tend to be more fluid than more silicic magma and, as they near the surface, degas quickly without generating a stable vesicular structure. Even after vesicle formation, scoria particles may be fluid enough to collapse on impact or to adhere to each other, forming a dense mass rather than a friable, porous deposit.

Silicic magmas are less fluid and offer less opportunity for gas escape and the collapse of vesicle walls. Conditions that reduce gas escape—such as high magma viscosity, impermeable wall rock, or a blocked vent—may lead to eruptions explosive enough to shatter the vesicle walls, generating a fine ash rather than a vesicular particle. Pumice particles entrained in a pyroclastic flow may be reheated enough to soften and collapse into nonvesicular glass.

The unconsolidated nature and low density of pumice and scoria deposits make them readily susceptible to erosion, and the extremely large surface area of the irregular vesicular particles promotes rapid chemical weathering. As a result, most deposits of pumice and scoria are geologically young, rarely more than a few million years old and often only a few thousand years old.

Types of Pumice Deposits

Pumice deposits can be broadly classified into four major types: flows and domes, air-fall deposits, pyroclastic flows, and epiclastic (reworked) deposits. There are gradations between types and deposits and there may be a mixture of types reflecting variations in eruption conditions. Changes in wind direction, blocking and clearing of the vent, increase in vent diameter, influx of water into the magma chamber, influx of a different magma, and rapid gas exsolution by unloading and depressurization may contribute to the character of the resulting ash and pumice deposits.

Flows and Domes

Viscous magmas can extrude with little explosive activity, forming lava flows and domal mounds. A vesicular rind, or carapace, can develop on their rapidly cooled outer surfaces, often forming a surface of blocky pumice rubble (Figure 2) underlain by obsidian or by nonvesicular lava. Continued cooling and crystallization of the flow increase the volatile content of the remaining liquid, which can then cause more vesiculation within the flow, often interlayered with nonvesicular rock. Buoyant masses of this pumice can forcibly pierce the overlying flow to the surface as pumice diapirs. Increased volatile content and resultant increased internal gas pressures can also form explosive craters on the surface of the flow and generate pyroclastic flows long after eruption has ceased. Pumice flows and domes typically are only a few square kilometers in aerial extent. Rock Mesa, a pumice flow in the central Cascade Range of Oregon, is about 6.5 km² (Fink and Manley 1987); and Mono Craters, a multiple dome and flow complex in east-central California, covers about 30 km² (Chesterman 1956). Pumices associated with domes and lava flows often have larger vesicles than other pumice types and can form blocks up to about 1 m in dimension. The erratic nature of vesiculation can make exploration and development difficult.

Air-Fall Deposits

Explosive eruptions eject fragments of dense magma, vesiculated magma (pumice), and country rock in various proportions and with various velocities and degrees of fragmentation. These fragments, and in many cases the deposits formed by them, are broadly referred to as pyroclastic.



Figure 2. Undisturbed surface of a pumice flow with rubble blocks up to 1.2 m in size on Rock Mesa, in the Cascade Mountains of Oregon. The flow lies within a wilderness area and is unavailable for commercial development.

In a Plinian-type eruption (named after Pliny the Younger's description of the AD 79 eruption of Mount Vesuvius), pyroclastic material is explosively ejected upward from the volcanic vent. The pyroclasts are boosted into the atmosphere by the explosion and maintained in suspension by convection, giving the appearance of a vertical column that flattens and spreads out at its top. Pliny the Younger compared its shape to that of a pine tree with a tall trunk (Bullard 1976). Based on grain size and dispersal characteristics, Walker (1980) concluded that some Plinian columns, or eruptive columns, may exceed 50 km in height.

Dense or large fragments leave the vent ballistically and fall at distances dependent on their exit velocity. Smaller or less-dense particles such as pumice lapilli and ash may be removed from the Plinian column by winds and cooled and deposited over wide areas, depending on column height, wind velocity and direction, and the particle size and density.

Air-fall deposits typically decrease in thickness and particle size with increasing distance from the vent and commonly contain pumice particles up to several centimeters. Air-fall deposits can blanket the existing topography over very large areas. Thicknesses range from tens of meters (those near the vent) to only millimeters (those several hundred kilometers away from the vent). Most commercial pumice operations use air-fall deposits.

Pyroclastic Flows

Decreases in eruption activity or overloading by continued eruption can cause the eruptive column to collapse either continuously or sporadically. The hot pyroclastic material falls from the column and flows outward from the vent following topography, and may flow more than tens or hundreds of square kilometers. Such pyroclastic flows can retain enough heat to fuse or weld the particles together after movement stops. The names applied to these rocks historically have included tuffs, welded tuffs, ash flows, and ignimbrites. Pumice fragments may survive intact on upper and lower surfaces that cool before welding occurs, but pumice fragments in the flow interior soften and collapse. Pumice deposits associated with pyroclastic flows tend to be thinner than air-fall deposits, and because unwelded portions are either easily eroded flow tops or are overlain by welded portions, pyroclastic-flow pumices are less frequently exploited commercially than air-fall pumice deposits.

Table 1. Uses of pumice

Use	Product Form and Processing	Essential Properties
Lightweight aggregate		
Decorative and structural concrete blocks; cast concrete; lightweight structural members, wall panels, floor decking; stucco and plaster mixes; pozzolan in cement; civil engineering, lightweight fill	Granular: crushing, screening, blending	Low density; good crushing strength; thermal insulator; acoustical insulator; fire resistance; moisture resistance
Abrasives		
Grill cleaners; scouring sticks for porcelain, tile, swimming pools; buffing wheel cleaners; cosmetic skin removal	Blocks: sawing, irregular lumps as mined	Broken vesicle (bubble) walls form sharp-edged particles; wear continues to generate fresh cutting edges
Stonewashing: water, pumice, and garments tumbled together in laundry machine; pumice must float; abrades and softens textile fibers	Coarse granular, ± 1.9 cm: crushing, screening	Broken vesicle (bubble) walls form sharp-edged particles; wear continues to generate fresh cutting edges
Hand soaps; scouring compounds; rubber erasers; polishing compounds for glass, metal, plastics; dental cleaners; wood finishing; nonskid paints; cleaning printed circuit boards; tumble polishing; leather finishing; matches and striking surfaces	Granular: drying, milling, screening, air flotation, blending	Broken vesicle (bubble) walls form sharp-edged particles; wear continues to generate fresh cutting edges
Absorbents		
Potting soils; hydroponic media; pet litter; floor sweep; turf aeration	Granular: crushing, screening	High porosity; large surface area; low chemical reactivity
Acid washing: impregnated with bleaching agents, tumbled dry with garments; requires high absorption rate; gas "charcoal" grills, absorbs fat and grease drippings	Coarse granular, ± 1.9 cm: crushing, screening	
Catalyst carriers; carriers for pesticides, herbicides, fungicides; screening; blending	Granular: drying, crushing, milling	High porosity; large surface area; low chemical reactivity
Architectural		
Loose-fill insulation; roofing granules; textured coatings; ground-cover resistance	Granular: crushing, screening	Low density; thermal insulator; acoustical insulator; fire resistance; moisture
Landscaping; decorative interior and exterior veneer	Blocks: boulders as mined; sawn slabs	Low density; easily shaped; low maintenance
Fillers		
In rubber, paints, and plastics; mold-release compounds; hot asphalt mixes; brake linings; screening; blending	Granular: crushing, drying, milling	Particle shape; cost
Filter media		
Both expanded and unexpanded forms used to filter animal, vegetable, and mineral oils; screening; firing; air flotation	Granular: crushing, drying, milling	Particle shape; expandability
Other uses include diluents; engineered fill; geotechnical uses; pottery clays	Granular: crushing, drying, milling	Absorbency; particle shape; expandability; sealing qualities

Epiclastic Deposits

Epiclastic processes include erosion, transportation, and redeposition by such mechanisms as water, wind, and mass movement. From a commercial standpoint, these processes can either degrade or enhance a pumice deposit. All could reduce pumice particle size and possibly intermix with nonpumice material, but wind and water can also sort by size and density and benefit the deposit by separating pumice from crystals and rock fragments. Movable thicknesses of pumice were produced in the central United States when surface drainage washed thin blankets of airborne ash into lake basins.

Scoria and Cinder Deposits

Scoria and cinder may be associated with many eruptive styles, but deposits exploited commercially are nearly all cinder cones. Cinder cones are unconsolidated piles of scoria and cinder formed by subaerial eruptions. Fresh cinder cones are typically conical, steep-sided, and often have a central crater. They are rather small volcanic landforms with diameters ranging from 100 m to about 2.5 km and heights from 30 to 500 m with slopes to about 30° (Wood 1980a, 1980b; Osburn 1982). Heights and slope angles are degraded with age and erosion, and composite cones of cinder and lava flows may have lower angles than cones of only cinders.

Cinder cones formed from a single vent can be nearly circular, but elongate forms can develop under strong prevailing wind condi-

tions or from fissure eruptions or multiple vent eruptions. Variations in color from red to black are often concentric around the vent. Cinders are black initially, but those deposited near the vent are subject to heating after deposition, causing oxidation of iron to shades of brown and red.

USES AND TECHNOLOGY OF PUMICE AND CINDER

Pumice and cinder at first appear to be interchangeable in many applications. In fact, each has distinct qualities that preclude direct substitution without some change in performance. Both are used extensively as lightweight aggregates in concrete products, but pumice produces lighter weight and lighter color whereas cinder produces greater strength. Pumice is used in abrasives ranging from screened material for stone washing to highly processed abrasives for polishing optical glass. The abrasive action of cinder is much too harsh for such applications. Cinder is used for road and highway aggregate and surfacing, but pumice of ten lacks sufficient mechanical strength to be similarly useful. Both are used as landscaping material but with obvious differences in color, weight, and texture.

Pumice

Table 1 summarizes the uses, processing, and essential properties of pumice. The largest volume end use in the United States is by far lightweight aggregate in concrete, followed by abrasives and

stonewashing. Because of the method used to collect production data, the lesser volume uses cannot be accurately ranked.

Lightweight Aggregate

Pumice is used as a lightweight aggregate in both cast concrete and concrete block units. Lightweight concrete reduces the total weight of the structure and reduces bearing strength requirements of the supporting members while contributing thermal and acoustical insulating qualities. Similar advantages are realized in plaster and stucco applications.

Decorative and structural concrete block units with pumice aggregate are easily handled, reducing construction time and worker fatigue. A typical $0.2 \times 0.2 \times 0.4$ m structural block with sand and gravel aggregate weighs about 17 kg (Figure 3). Commonly, a mixture of the two aggregate types is used to produce a block that retains the advantages of lightweight aggregate with an increased strength while sacrificing some of the weight advantage. A block unit with a 50/50 mix of pumice aggregate and sand and gravel aggregate weighs about 13 kg.

The light color of pumice is also advantageous in producing decorative blocks using mineral pigments. Blocks produced with broken surfaces, or split faces, exhibit a color contrast between the pumice particles and the pigmented cement matrix (Figure 4).

Pumice for lightweight aggregate is typically sold in sizes of <8 mm. American Society for Testing and Materials (ASTM) Standard C331 gives grading requirements (particle-size distribution) for concrete masonry units, but these may be waived for special applications that require particular texture, strength, weight, acoustical, or thermal properties. Grading is critical to the shrinkage characteristics of masonry units and is controlled in processing by crushing and dry screening.

ASTM Standard C331 also specifies unit weights of oven-dry material from 880 kg/m^3 for fine aggregate to $1,120 \text{ kg/m}^3$ for coarse aggregate. Lithic fragments must be limited to control weight, but obsidian fragments are deleterious because they may hydrate to silica gel, which expands and weakens the concrete. Organic debris and particle coatings of clay, iron oxide, or fine ash are also detrimental.

Suitable crushing strength of pumice particles is often tested qualitatively by hand or under foot, whereas quantitative measurements are made on masonry units. Schmidt (1956) reports ranges of compressive strengths and various other properties of concrete with pumice aggregate.

Pumicite and finely ground pumice are also added to concrete mixtures as pozzolanic material, an application distinct from lightweight aggregate. Pozzolans form cementitious compounds by reacting with calcium hydroxide, which forms as Portland cement hardens. Without the addition of pozzolanic material, calcium hydroxide can be leached from the concrete, causing it to deteriorate.

Abrasives

Pumice abrasive products are sawn and shaped blocks, granules, and powders, and bonded and reconstituted forms. The glassy vesicle walls are brittle; exhibit conchoidal fracture forming thin, sharp cutting edges; and have a Mohs hardness of 5.0 to 5.5. Fresh cutting edges are continuously generated as the friable pumice particles wear down during use.

Sawn and shaped blocks and irregular lumps of pumice are used in applications requiring handheld abrasives for scouring various surfaces. The United States Pumice Co. produces sawn blocks from its block pumice deposits on Mono Craters near Lee Vining, California. Large lumps and blocks of uniformly vesicular pumice,

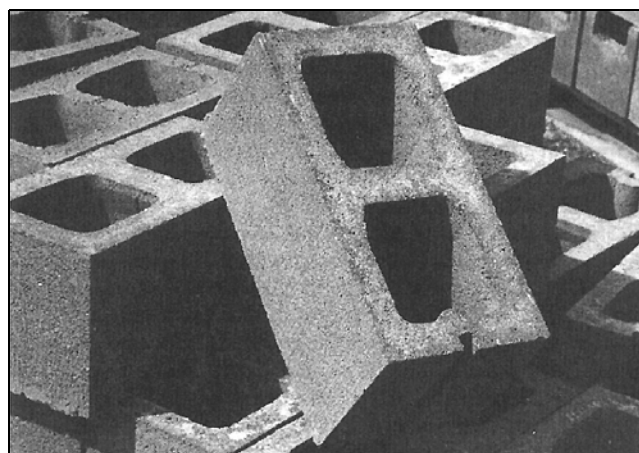


Figure 3. Structural concrete block unit, $0.2 \times 0.2 \times 0.4$ m



Figure 4. An installation of pumice aggregate concrete blocks used as both structural and decorative elements. The smaller blocks are 0.1×0.4 m and molded with smooth faces. The larger blocks are 0.2×0.4 m with split faces formed by breaking apart a double block unit before the concrete has completely cured.

free of lithic fragments, crystals, and obsidian stringers, are sawn into rectangular blocks of various sizes. The $7.6 \times 7.6 \times 15.2$ cm blocks are sold under the brand name of Grillmaster for cleaning restaurant grills (Figure 5). The pumice gently scours the grill while neither scratching the metal surface nor removing the thin, seasoned layer that prevents food from adhering. Smaller blocks are sold for home use to clean porcelain and tile surfaces and for cosmetic skin removal. Pumice blocks and lumps are still used to clean buffing wheels, but demand has dropped with the decreasing use of chrome plating by the automotive industry.

Stonewashing of fabric—once the most rapidly growing segment of the pumice industry—is declining in favor of chemical or enzyme systems. Stone washing involves two distinct processes: abrasion, in which coarse granular pumice abrades the garment surface, and absorption, in which pumice acts as a carrier for bleaching chemicals. The term *stonewashing* is applied both to laundry use in general and to the abrasive process specifically in which finished garments, water, and pumice are tumbled together in large washing machines. The term *acid washing* refers specifically to the treatment

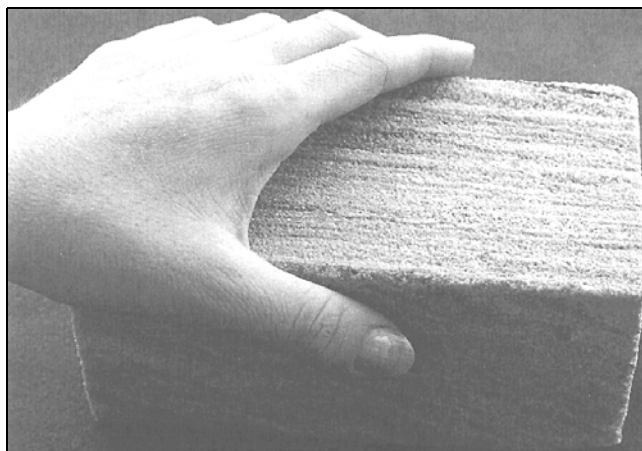


Figure 5. Scouring block produced by United States Pumice Co. from its Mono Craters deposit near Lee Vining, California.

process using pumice as a chemical carrier. Both processes use pumice particles of 2 cm to more than 8 cm. Smaller particles produce a more uniformly worn effect whereas larger particles impart a more irregular effect (Hoffer 1991). Each process requires pumice of different characteristics; acid washing is discussed in the section on absorbents in this chapter.

The abrasive process of stonewashing uses pumice particles with a low enough density and a low enough permeability to float in the laundry machine. The pumice must be hard enough to survive at least one wash cycle, but not so hard that it unduly damages the cloth fibers. Clean, light-colored pumice with few lithic fragments is preferred. The industry has a few standardized specifications. Often a new source of pumice is tested simply by using it—a potentially wasteful approach. Hoffer (1991, 1994) developed testing procedures to evaluate pumice for laundry use that measure particle density, absorption, surface fines, impregnation rate, and abrasion loss. Particle density and abrasion loss are the most important properties for stonewashing pumice.

The popularity of stone washed garments led to the development of many new pumice deposits, particularly in Turkey, Indonesia, and several Latin American countries. Traditional producers of aggregate pumice supply some laundry pumice, but many were unable to expand quickly enough to meet demand, some do not have pumice with appropriate particle sizes or other characteristics, and some are reluctant to make extensive modifications to their current operation and product mix to serve what is an ephemeral market driven by clothing fashions.

Pumicite and ground pumice are used in many abrasive products as loose granules and compounded in such products as hand soaps, rubber erasers, and polishing compounds for metal, plastics, and glass. Particle sizes for fine polishing compounds range from a few millimeters for non skid coatings to <100 μm . Consumer perception determines the particle size in some applications. Pumice is used in bar soaps, soft soaps, and liquid soaps, but products marketed for heavy-duty hand cleaning are more acceptable if they contain coarser pumice, giving a rougher texture in use. There may be differences between producers and particle-size distributions of respective grades, but abrasive pumice is still described by the system reported by Hatmaker (1932). Letters F through FFFF describe progressively finer particles from about 150 μm downward, and whole and fractional numbers from 0 through 10 are used for progressively coarser particles up to about 5 mm.

Most granular abrasives require uniformly finely vesicular pumice. Typically, the vesicle diameters are several times smaller than the finished product particle size (Figure 1E). Crystal, obsidian, and lithic fragment content must be very low to produce an abrasive with uniform hardness and wear characteristics. For example, pumice is used as an intermediate abrasive in polishing television tubes, optical components, and certain types of flat glass. It is used following grinding by coarser abrasives and is followed by final polishing with metal oxides. In a recirculating slurry system, any harder or tougher particles will accumulate to intolerable levels and produce scratches. Less than 1.0% nonpumice particles is required and less than 0.5% is preferred. Beneficiation to remove crystals, obsidian, and lithics is difficult, especially in fine particles, and few deposits have the low nonpumice content required.

Processing pumice and pumicite for abrasives involves drying, crushing, milling, air flotation, screening, and blending. Sizing is often done with wire or cloth screens and equipment designed for flour mills. Screening can be a difficult and time-consuming operation because the density, shape, and surface texture of pumice particles often cause clogging, or blinding, of the screens. Blending further controls product particle-size distribution. Abrasive pumice prices of up to 100 times aggregate pumice prices reflect the rarity of suitable deposits, the higher capital and operating costs of processing plants, and the higher product tolerances required for pumice abrasives.

Absorbents

The high porosity, large surface area, and low chemical reactivity of pumice make it suitable for many absorbent applications ranging from floor-sweep products to catalyst carriers. Processing ranges from simple screening to the same sophisticated techniques used to produce fine pumice abrasives.

Coarse granular pumice, +1.9 cm in size, is used to acid-wash garments. The pumice is impregnated with bleaching chemicals by various immersion and vacuum techniques and then tumbled dry with finished garments. The chemicals are released as the pumice touches the fabric. Unlike pumice for abrasive stonewashing, acid-washing pumice does not have to float and it must have sufficient porosity and permeability to absorb and release the chemicals. Surface coatings of fine ash or clays reduce the absorption rate, and the clays release the chemicals at a more rapid rate than pumice, causing uneven bleaching. Surface fines should be less than 5% by weight (Hoffer 1991). Iron oxides are also detrimental because they can be deposited on the fabric, producing a yellow or brown stain.

Lumps of pumice about 5 cm in diameter are used in gas grills to absorb grease drippings and reduce flaming. The pumice is marketed both as the manufacturer's original equipment in the grill and as a replacement product through retail outlets. These markets are shared with scoria, but both have declined in favor of steel plates.

Finer granular pumice is used in potting soils and as a hydroponic growth medium. Both the absorption and abrasive nonskid characteristics of pumice are valuable in its use as a floor-sweep material on machine shop or meat-packing plant floors. Finely ground pumice is also used as a catalyst support and carrier, and it is compounded with pesticides, herbicides, and fungicides to permit uniform application of small amounts of chemicals.

Architectural Applications

Pumice has architectural applications in addition to its use as lightweight concrete aggregate. Its low density, fire and moisture resistance, and thermal and acoustical insulating qualities make it useful in textured plasters and coatings, as loose-fill insulation, and as roofing granules. The high reflectivity of white pumice is also

advantageous in roofing applications. Coarse granules and pebbles as groundcover reduce the water otherwise required to maintain plant groundcovers, and pumice is distinctively colored and easily handled.

Large blocks and boulders of pumice are used in decorative landscaping. They are easily handled and can be readily fitted together or sculpted to specific shapes such as planters and lanterns. Pumice can be bored and hollowed for electrical and plumbing systems for fountains and waterfalls (Figure 6).

Pumice blocks are sawn on one surface and used as decorative veneer (cantera stone) on both interior and exterior walls, producing a highly textured, fire-resistant surface. The slabs can be shaped easily with hand tools for rapid and precise installation (Figure 7).

Density, pattern, and color are important for both landscaping and veneer products, but the most specific requirement is large block size. Few pumice deposits, primarily flows and domes, contain blocks of 1 m or more, and only one is currently in production in North America, by United States Pumice Co., a subsidiary of Featherrock, at Lee Vining, California.

Fillers

Mineral fillers are rock and mineral materials added to formulations to give products specific characteristics such as tensile strength in plastics, gloss (or lack of gloss) in paints, or weight and surface finish in paper. Typically, fillers are added as very fine powders, and many factors affect the choice of materials used.

The important attributes of pumice and pumicite as fillers are low cost, hardness, particle shape, particle size, absorbency, vesicularity, density, and low chemical reactivity. Permeable vesicular pumice particles are absorbent and can be used to vary viscosity, impermeable vesicular pumice can be used to decrease the density of the product, and platy vesicle wall fragments can increase tensile strength. The hardness of pumice can increase the abrasion resistance of the finished product, but it also increases wear on processing equipment. Very finely vesicular pumicite from Kern County, California, has been tested successfully as an opacifying agent to partially replace titanium dioxide in paints. Grading, or particle-size distribution, is critical to the performance of asphalt, and pumicite can be used to achieve the proper ratio of fines in asphalt mixes.

Filter Media

Liquids ranging from water, juices, and beverages to oils and fuels are clarified by filtration, which mechanically removes suspended particles. Filters can be beds of granular material (filter media) or granular material supported by porous membranes. Filter media can also be mixed into the liquid to remove more efficiently particles and to maintain porosity of the filter. Finer filter-media particles are required to remove finer particles from the liquid.

Pumice is useful as a filter aid because of its fine particle size, particle shape, low chemical reactivity, and, in some applications, expandability by pyroprocessing. Pumicite in Kansas and adjoining states is composed of broken vesicle walls, which are used to form a filter bed of overlapping plates to remove fine particulates (Figure 8A). Some of the pumicites can be fired and expanded into hollow spheres similar to those formed by expanding perlite (Figure 8B). The expanded pumicite is then milled to produce filter-media particles of specific sizes and flow characteristics.

Volcanic Cinder

The uses of volcanic cinder and pumice overlap in some applications, but cinder is not processed into as wide a variety of products as pumice. Volcanic cinder usually has thicker vesicle walls than pumice and produces a heavier but stronger lightweight concrete

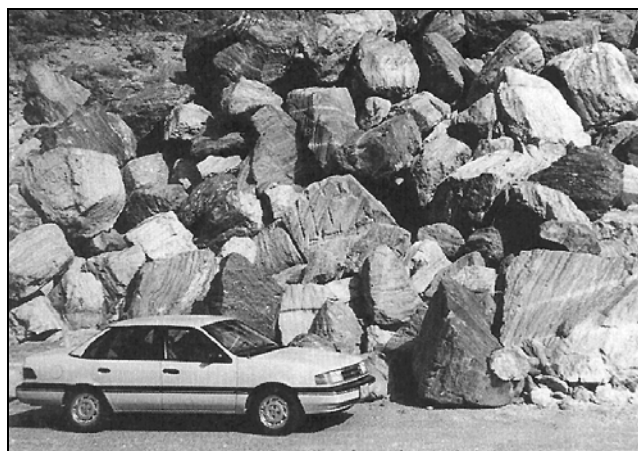


Figure 6. Pumice landscaping boulders quarried from the Mono Craters deposit near Lee Vining, California, by United States Pumice Co., a wholly owned subsidiary of Featherrock, Inc.

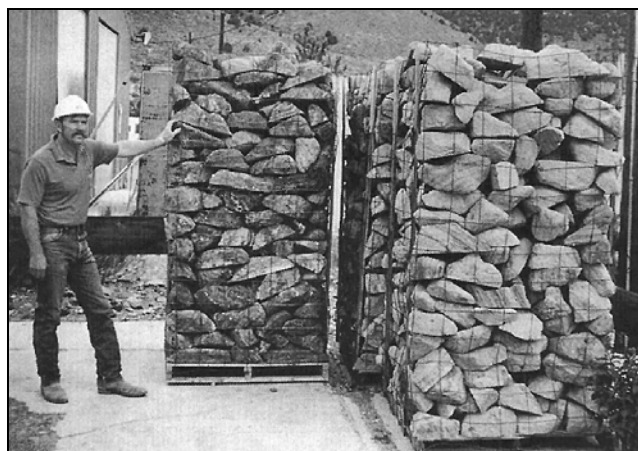


Figure 7. Pumice veneer slabbed and palletized for delivery, Lee Vining, California

with insulating qualities less than those of pumice concrete of comparable strength and weight. Block units are gray or red depending on the cinder color.

Cinder and scoria are also used in the same construction applications as sand and gravel and crushed rock: base courses, road surfacing, asphalt aggregate, and railroad ballast. Cinder for these purposes must meet the same specifications as any other aggregate material, including abrasion resistance, immersion disintegration, and aggregate degradation. Cinders that qualify have a higher density than those used for lightweight concrete. The friable, fragmental nature of cinder deposits results in much lower production costs than from nonvesicular rock that must be crushed.

Cinders are also used to sand highways to improve traction on icy surfaces. Cinders are typically crushed and screened to sizes from about -16 to +4 mm. Coarser particles can damage vehicle windshields, and finer particles can retain moisture and freeze in stockpiles or during transit.

Cinders and scoria are used in landscaping as both placed boulders and coarse granular ground cover. Scoria blocks are also

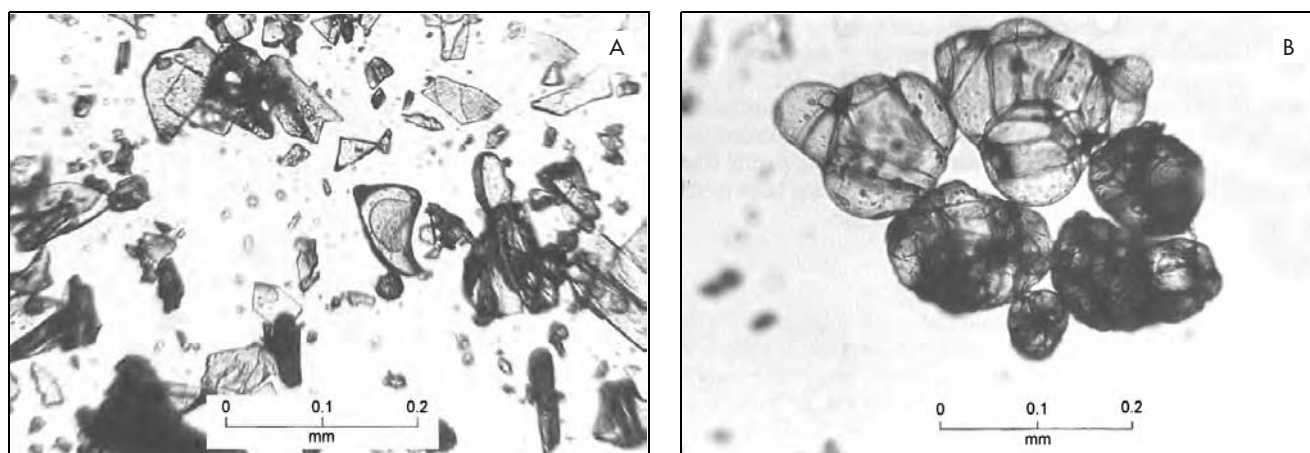


Figure 8. Pumicite from deposit near Mankato, Kansas: (A) Pit-run material composed of vesicle wall fragments; (B) Pumicite expanded by pyroprocessing for use in filtering

Table 2. Sources of information on pumice and pumicite deposits

World	Anon. 1977
	Harben and Bates 1984
	McMichael 1990
	Robbins 1984
	USBM (now USGS) yearbooks, published annually
United States	
Arizona	Hoffer 1991
California	Chesterman 1956
Colorado	Williamson and Burgin 1960
Idaho	Asher 1965
Kansas	Bauleke 1962
	Hardy et al. 1965
Nebraska	Burchett 1990
Nevada	Horton 1964
New Mexico	Clippinger and Gay 1947
Oklahoma	Burwell 1949
Oregon	Moore 1937
	Geitgey 1992
Utah	Van Horn 1964
Washington	Carithers 1946
Wyoming	Harris and King 1986

used as building stones. Uniformity of color is of importance in landscaping and decorative uses. Scoria lapilli is used as an absorbent bed in gas cooking grills.

DISTRIBUTION OF DEPOSITS

The ephemeral nature of pumice and cinder deposits limits their occurrence to areas of geologically recent volcanism such as the Circum-Pacific belt, the Mediterranean region, and oceanic ridges. Table 2 lists sources of information on pumice and pumicite. Most of those tabulated have extensive lists of references to specific deposits and to more detailed descriptions.

Pumice lapilli deposits in the United States are largely confined to the area west of the Rocky Mountains, and airborne ash from this area has formed pumicite deposits throughout the Great Plains states. Pumice has been produced in the past for various pur-

Table 3. Pumice and pumicite mines active in 2004 in the United States

Company	Deposit Location	
	County	State
Aimcor Precast	Bonneville	Idaho
California Lightweight Pumice Inc.	Madera	California
Calvert Corporation	Norton	Kansas
Cascade Pumice Co.	Deschutes	Oregon
Copar Pumice Co.	Santa Fe	New Mexico
C.R. Minerals Co.	Santa Fe	New Mexico
Glass Mountain Pumice Co.	Siskiyou	California
Hess Pumice Products	Oneida	Idaho
Kansas Minerals Inc.	Jewell	Kansas
Pacific Custom Materials Inc.	Inyo	California
Producers Pumice	Bonneville	Idaho
Sierra Cascade LLC	Deschutes	Oregon
Super-Lite Block Inc.	Coconino	Arizona
Tufflite Inc.	Coconino	Arizona
United States Pumice Co.	Mono	California
Utility Block Co.	Bernalillo	New Mexico

Courtesy of USBM.

poses from nearly every western state, including Hawaii, but currently mines in only six states are active. Table 3 lists pumice mines active in 2004 in the United States.

The principal pumice deposits are in north-central Arizona in the San Francisco volcanic field near Flagstaff in Coconino County. Several air-fall pumice lapilli and ash units occur in the area, and these have been mined for lightweight aggregate, horticultural, and laundry uses. In several other counties, epiclastic deposits of pumice and pumicite have been mined for lightweight aggregate and pozzolanic material (Hoffer 1991).

Chesterman (1956) listed and described more than 60 deposits of pumice and pumicite in California. All types of occurrences are represented, including flows, domes, air-fall, pyroclastic flow, and epiclastic lacustrine and fluvial deposits. Since the first recorded production in 1883, numerous companies have been

active throughout the state, producing pumice and pumicite for nearly every end use. Production from currently active areas illustrates this wide range of markets.

Pumice in the Glass Mountain Area of Siskiyou County in Northern California occurs as air-fall deposits and block pumice flows. Glass Mountain Pumice produces stonewashing pumice and lightweight aggregate from an air-fall deposit. Pumice for scouring blocks has been mined from Glass Mountain in the past, but the block pumice deposits are not being mined at present.

The Mono Craters deposit near Lee Vining in Mono County is a multiple dome and flow complex. The surface of the domes is a jumbled mass of pumice rubble at least 45 m thick through which spires and pinnacles of pumice protrude (Loney 1968). The flow surfaces are covered with loose angular blocks and exhibit complex movement patterns, and the flows terminate in steep talus slopes. Blocks of up to 2 m are mined by United States Pumice Co. for landscaping and decorative veneers. The company produces large blocks of coarsely vesicular pumice in a variety of colors and textures (Figure 1B; Figure 6). Smaller blocks are sawed into thin slabs for decorative veneer (Figure 7). United States Pumice Co. uses pumice of finer texture from the same deposit to produce abrasive blocks of several sizes for cleaning grills and ceramic surfaces and for cosmetic purposes. Small trimmings are sold for use in gas cooking grills, so there is very little waste in the processing operation.

California Lightweight Pumice Inc. mines water-laid pumicite in Madera County, in central California, and processes it for filler applications. Most of the pumicite particles in the deposit are <325 mesh (Chesterman 1956).

Pumice and cinder occurrences in Idaho are associated with volcanics of the Snake River region in the southern part of Idaho (Asher 1965). The active pumice mines are Producers Pumice near Idaho Falls and Hess Pumice Products north of Malad City in Oneida County, both of which supply graded material for lightweight aggregate. The Hess deposit is partially indurated, and the pumice is finely vesicular with a very low lithic and crystal content. From it, Hess produces high-quality abrasives for a wide range of markets, including glass polishing, metal finishing, soaps, and erasers.

Numerous beds of Pliocene and Pleistocene volcanic ash occur throughout the Great Plains states. The Valles Caldera, in the Jemez Mountains of northern New Mexico, has been identified as the source for much of the airborne material. The ash occurs as thin air-fall blankets and as reworked fluvial and lacustrine deposits with varying amounts of admixed detrital minerals. Some beds are altered to clays and others are composed of clean, unaltered glass fragments, nearly all of which are less than 100 μm .

Deposits in several states have been mined for abrasives, polishes, asphalt filler, absorbents, and ceramics. Some of the pumicites bloat into hollow spheres under proper heating conditions, and extensive testing has been done to produce filter aids and cellular glass blocks (Ham 1949; Bauleke 1962; Hardy et al. 1965). Currently, two companies are mining two different beds of expandable pumicite in north-central Kansas. Kansas Minerals, near Mankato, produces filter aids by drying, air classifying, and expanding the pumicite and milling the expanded fragments to the desired size ranges. Calvert Corporation, near the village of Calvert, sells a dried and screened product that its customers use in both expanded and unexpanded forms to filter vegetable oils.

Pumice occurs in several areas in New Mexico, but those deposits currently being mined are air-fall units associated with the Valles Caldera volcanics. Copar Pumice, C.R. Minerals, and others have produced lightweight aggregate, stone washing pumice, and material processed into granular abrasives. Several other areas of

the state produced pumice in the past, including East Grants Ridge near Grants in Cibola County.

Pumice production in Oregon is limited primarily to the Bend pumice, an air-fall lapilli unit around the city of Bend in Deschutes County. Cascade Pumice and Sierra Cascade produce lightweight aggregate, horticultural pumice, and landscaping material. Less than 5% of the fragments in the Bend pumice are greater than 2.5 cm in diameter, but Cascade Pumice screens this coarse fraction for stonewashing material.

A limited amount of pumice has also been produced from an extensive air-fall and pyroclastic flow unit formed when Mount Mazama collapsed, forming Crater Lake (Bacon 1983). The climactic air-fall lapilli unit now blankets an area of more than 5,200 km^2 with a thickness >1 m and an area of more than 900 km^2 at a thickness >3 m, with little or no overburden. To date, the Mazama pumice has not proven as satisfactory as the Bend pumice for lightweight aggregate, but some of it has been sold for stone washing material (Geitgey 1992).

Pumice deposits are distributed in other volcanic areas throughout the world. Historically, the relatively low value of lightweight aggregate has limited large-scale production to deposits such as those in Germany, Greece, and Italy that are near markets or near bulk transportation facilities. Increased industrialization has created greater markets for lightweight aggregates, and the higher value of stone washing pumice has led to the development of formerly uneconomic deposits. The following summary of international pumice occurrences is based on articles published in *Industrial Minerals* (Anon. 1977; Robbins 1984; McMichaels 1990), Harben and Bates (1984), various editions of the *USBM Minerals Yearbook*, and U.S. Geological Survey (USGS) Mineral Commodity data (Bolen 2004; Founie 2005).

The Italian peninsula is well endowed with volcanic rocks, but the country's most important commercial pumice deposit is on the island of Lipari, about 35 km off the northern coast of Sicily. An unconsolidated deposit of high-quality pumice has been the source of aggregate and industrial pumice for Europe and North America for many decades. Pumex SpA (Italy's largest producer) supplies lightweight aggregate, powders, and granular material for various industrial uses, and cosmetic stones. Italpomice SpA produces aggregate and stone washing pumice. Both companies can load directly from their operations onto ocean-going vessels.

Many of the islands of Greece, particularly the Cyclades and Dodecanese groups in the southern Aegean Sea, have pumice deposits. Several have been mined in the past, including Thera (Santorini), but production is now only on the island of Yali, where Lava Mining and Quarrying mines aggregate grade pumice for markets throughout Europe, North America, North Africa, and the Middle East. Yali is the principal source for lightweight aggregate pumice for markets on the U.S. East Coast.

Pumice exports from Turkey have increased over the last 10 to 20 years from almost none to an average of 832,000 tpy for the period from 2001 to 2004. Nearly all the production is stonewashing pumice, primarily for European markets. The deposits are located in relatively remote areas of central and eastern Turkey, and the pumice must be transported long distances by truck to ports on the Mediterranean Sea. Small amounts are used domestically for construction, and some companies are now producing granular and powdered material. Pumice mines are operated by about a dozen companies.

Many other countries produce pumice for both export and domestic use. Spain has active mines in the province of Ciudad Real and on Tenerife in the Canary Islands. Both Iceland and New Zealand are mining beyond local needs and are now supplying

various export markets. Several countries, including Ecuador, Guatemala, and Indonesia, are shipping stonewashing pumice.

Statistics

The United States had 16 domestic producers with 17 active operations in 2004, up 1 from 2003 (Bolen 2004; Founie 2005). The 16 producers operated in six states. There were 21 producers in 1985, 19 in 1986 and 1987, 20 in 1988, 11 in 1990, 14 in 1991, and 12 in 1992. Just more than 76% of production came from Arizona, New Mexico, and Oregon. The remaining production came from California, Idaho, Kansas, and Nevada.

During the period from 2000 to 2003, imports were mainly to markets on the East Coast and the Gulf Coast. Imports came from Greece, 80%; Italy, 14%; Turkey, 5%; and other sources, 1%.

According to the USGS, in 2003 world production was, by country: Algeria (500,000 t); Chile (850,000 t); Ecuador (90,000 t); France (450,000 t); Germany (500,000 t); Greece (1,700,000 t); Guadeloupe (210,000 t); Guatemala (260,000 t); Italy (4,500,000 t); Iran (1,100,000 t); Spain (600,000 t); Turkey (800,000 t); and 1,800,000 t were in other market economy countries. This is a total estimated world production of 14,400,000 t in 2003.

Both domestic and import sales of pumice and pumicite were affected by the 1991–1992 recession. Demand for lightweight concrete products decreased because of the decline of construction activity. A rebound in construction activity in the period from 1993 to 2004 increased domestic production of pumice and pumicite.

The most important markets for pumice and pumicite are building blocks, horticulture and landscaping, stonewashing, laundries, abrasives, concrete aggregate, absorbents, diluents, filter aids, roofing granules, water treatment, pet litter, engineered fill, geotechnical uses, pottery clays, and other unspecified uses (Table 1).

In 2004, about 76% of pumice was used by the building block industry. The remaining 24% was used in abrasives, millstones, abrasive wheels, laundries, aggregates, insulation, pesticide and herbicide carriers, roofing granules, and landscaping. Micronized pumice is used in toothpaste, polishes, soaps, and other applications where a high-gloss finish is required. Micronized pumice has individual particles with sharp cutting edges, even though the mineral itself is relatively soft.

The USGS estimates that identified domestic reserves of pumice and pumicite in the western United States exceed 25 Mt. The estimated total pumice and pumicite resources, identified and undiscovered, in the western and Great Plains states are at least 250 Mt, and may total more than 1 billion t.

All domestic mining was by open-pit methods and generally occurred in remote areas where land-use conflicts were not severe or were nonexistent. Mining and milling of pumice and pumicite generates reject fines that must be disposed of, but the environmental impact is restricted to small, remote geographical areas.

ALTERNATIVE MATERIALS

Nearly every end use of pumice and cinder has natural or manufactured alternative materials that have similar performance characteristics. Lightweight concrete is produced with blast furnace slag, expanded perlite, expanded clays, and air-entraining agents. Numerous minerals are used as granular abrasives. Clays, diatomite, and zeolites function as various types of absorbents and carriers. Other rocks and various manufactured materials serve for landscaping and veneer uses. Hollow microspheres of glass and plastic are used as low-density fillers, and diatomite and expanded perlite are used extensively as filter media.

The choice of pumice and cinder is often a function of costs—both production costs and transportation costs. Pumice and cinder

deposits typically are not indurated and relatively inexpensive to mine. Unlike perlite, expandable clays, and diatomite, many pumice uses do not require expensive pyroprocessing.

Pumice of various unique characteristics in some applications such as lightweight landscaping boulders and stonewashing that are not precisely matched by either manufactured materials or other natural rocks. Similarly, block and granular pumice occupy unique niches in the abrasive field because of their texture and friability.

PROBLEMS AND FUTURE TRENDS

Caution should be exercised in interpreting pumice and cinder statistics. Clear distinctions are not always made among various volcanic materials or their end uses, either currently or historically. Some reports cite only volcanic materials without specifying pumice, pumicite, cinder or scoria, pozzolans, or other volcanic rocks. Volcanics produced for construction materials can include pumice or cinder for lightweight aggregate, pumice or pumicite ground for pozzolan, and pozzolanic materials other than pumice. Uniform methods of data collection are impossible, particularly when production is sporadic, mines are in remote areas, or production is only for local use.

In the United States, mineral production statistics are reported to the USGS only on a voluntary basis. Through 1980, the USBM reported combined statistics of pumice, pumicite, and volcanic cinder. Since 1981, volcanic cinder statistics have been reported instead with crushed stone, a more accurate reflection of the principal market of cinder. The apparent abrupt decrease in production and number of producers in volcanic materials reflects a change in reporting procedures rather than a decline of the industry. The USGS has modified its pumice questionnaire to obtain more detailed data on specific products and markets.

Problems have arisen in the United States concerning acquisition of mineral rights to pumice on federal land. Many pumice deposits occur on federal land administered by the U.S. Bureau of Land Management for the U.S. Forest Service. Access to minerals is obtained by leasing, by staking mining claims, or by purchase, depending on the mineral. Leases and mining claims grant exclusive development right whereas saleable commodities are available to any purchaser. Leases require royalty payments; mining claims do not. Federal law has been modified over the years to specify which minerals are acquired by which methods.

Before 1955, pumice on federal land could be acquired by mining claims; and if the staking claims have been maintained, they remain valid. The Surface Resources Act of 1955 (U.S. Code, Title 30, Section 611) names sand, stone, gravel, pumice, pumicite, and cinders as common variety materials. As such, they can only be purchased; they cannot be acquired by staking mining claims. But the act also expressly excludes block pumice from the list of common variety materials, defining block pumice as pumice “which occurs in nature in pieces having one dimension of two inches or more.” Also excluded are “deposits of such minerals which are valuable because the deposit has some property giving it distinct and special value.” Many pumice deposits have some particles larger than 5.1 cm, but that may not necessarily qualify the deposit as block pumice. Stone washing pumice has a much higher value than aggregate pumice, but particles as small as 2 cm may be suitable. The courts and boards of appeal have given various, and sometimes conflicting, interpretations, and it is still unclear under what conditions, if any, exclusive mineral rights can be obtained for pumice found on federal land. Continued litigation is probable.

Future trends in pumice production will depend principally on building construction and fashion. Aggregate pumice remains the largest volume market, and sales fluctuate with construction activity,

which in turn is a reflection of general economic conditions. The appearance and softness of stonewashed garments remain in high demand, and as yet no satisfactory alternative to pumice has been developed. The higher value of laundry pumice has led to the development of new sources throughout the world, which may in turn lead to a more diversified pumice industry in those areas.

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Pyrophyllite

Tadataka Hida and Ryuji Kitagawa

OVERVIEW

Pyrophyllite is a hydrous aluminum silicate that is generally described by the molecular formula $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$. This alteration mineral is light green or white with a waxy texture. In nature, pyrophyllite rarely exists in its pure form and is normally associated with accessory minerals such as quartz, kaolin, diaspore, corundum, andalusite, boehmite, sericite, chlorite, and alunite. Pyrophyllite ores can also include iron-containing impurities such as pyrite, hematite, and limonite; therefore, different mineral samples that are classified as pyrophyllite can contain various combinations of accessory minerals and have different chemical compositions. It is important to understand the origins and distributions of pyrophyllite deposits in order to extend pyrophyllite applications. This chapter therefore describes basic methods for the mineral's identification and analysis.

In Japan, pyrophyllite mined in the Mitsuishi District of the Okayama Prefecture was used in engraving from around 1800 until the early 1900s. With the introduction of primary school education in 1886, pyrophyllite ores began to be processed and used for slate pencils. During the 20th century, the demand for pyrophyllite ores as raw materials for ceramics—particularly refractory materials—grew in response to the increasing needs of industry. Quality checks during mining and strict quality control during the crushing and grinding processes are essential because the major, accessory, and trace ingredients of the raw ores determine the properties of the products, including refractory characteristics, coefficients of thermal expansion and contraction, melting point, hardness, and color.

Pyrophyllite ores have been used for many years in a range of applications. The quality requirements, however, have recently become much stricter as a result of competition from several minerals with similar properties. Consumption is also decreasing for a number of reasons, including advances in paper-manufacturing techniques, in which pyrophyllite is used as a filler; decreases in the number of dustings with insecticides because of improvements in agrochemicals; and the trend toward the use of longer-lasting bricks in the refractory industry.

Research is needed to expand the potential applications and, therefore, the demand for pyrophyllite ores. Low-quality ores might be used after removing impurities and by developing energy-saving furnaces that can operate at lower temperatures. In addition, advances in powder technologies are likely to increase the uses of

pyrophyllite ores in fine ceramics. Efficient usage remains important, however, because these ores have limited distributions and worldwide reserves.

CLASSIFICATION OF PYROPHYLLITE ORES

The name *pyrophyllite* derives from the Greek words *pyro* meaning *fire*, *phyllon* meaning *leaf*, and *lithos* meaning *stone*; it refers to the flaking or exfoliation that occurs on the surface of the mineral when it is fired. It is known as *roseki* in Japan, *nab-suk* in South Korea, *yelashi* in China, *agalmatolite* in North and South America, and *wonderstone* in special grades in South Africa. In Japan, pyrophyllite ores are divided into three main types on the basis of their mineral constituents: pyrophyllite, kaolin, and sericite (Table 1). This division is also applied to the ores in other parts of Asia.

PRODUCTION, CONSUMPTION, AND TRADE

Pyrophyllite is similar to talc in appearance, properties, and applications, and is generally grouped with talc in published statistics. Figures for pyrophyllite production alone are therefore often unavailable. Because it does not have an independent product classification from the World Trade Organization, there are no independent international trade statistics for pyrophyllite. It has been necessary to rely on the efforts of individual researchers and on limited regional figures. Furthermore, the figures for ore reserves, production, and consumption in China have many gaps, and China is passed over by current research despite its large share of global production. This chapter provides previously unavailable information on East Asia and Russia and covers pyrophyllite as a separate mineral clearly distinguished from talc.

Statistics

Global production of pyrophyllite ores in 2002 was an estimated 3 Mt, assuming a 1-Mt output for China and the United States, with Japan, the Republic of Korea, and China accounting for more than 70% of the total (Table 2). Japanese production fell slightly in 2002, to an estimated 600,000 t. This production was for use in refractories, ceramics, tiles, agricultural chemicals, cement, and glass fiber. Korea produced approximately 890,000 t that year, destined for use in cement (56.3%), tiles (7%), refractories (4.4%), ceramics (0.5%), and other applications (glass fiber, resin, etc., 17.9%), and 13.9% was exported for similar purposes (MOCIE 2003). Korean pyrophyllite ore exports were in the form of crude

Table 1. Classification and use of pyrophyllite ores in Japan

Large Grouping	Classification		Mineral Composition*		Usage
	Main Division	Subdivision	Main Constituents	Minor Constituents	
Pyrophyllite ores	Siliceous pyrophyllite	Siliceous P ore	Q, P	K, D, S	R, T, Cl, G
	Pyrophyllite	Pyrophyllite ore	P	Q, K, D, S	R, T, Cl, G
	High Al ₂ O ₃ pyrophyllite	D bearing P ore	P, D	K, S, Q	R
		C bearing P ore	P, C	K, S, Q	R
		A bearing P ore	P, A	K, Q	R
Kaolin ores	Siliceous kaolin	Siliceous K ore	Q, K	D, P	T, G
	High Al ₂ O ₃ kaolin	Dickite	K	D, Q, P	T, Cl, G
		Diaspore	D, K	P, Q	R
Sericite ores	None	Pottery stone	Q, S	P	T, Cl, R
		Sericite	S	K, P, Q	R, T

Modified from Matsumoto and Yano 1995.

* A = andalusite; C = corundum; Cl = clay powder; D = diaspore; G = glass fiber; K = kaolin minerals; P = pyrophyllite; Q = quartz; R = refractory; S = sericite; T = tile and other ceramics.

Table 2. Production of pyrophyllite ores in the world, 1999 to 2003, t

Country	1999	2000	2001	2002	2003*
Argentina	3,400	3,877	2,754	2,341	2,500
Australia	347	1,727	1,500*	868	1,000
Brazil	160,000	150,000	189,500	200,000	200,000
China	W†	W	W	W	W
India*	85,000	85,000	86,000	85,000	85,000
Japan	694,317	692,998	623,097	600,000*	600,000
Pakistan	67,670	54,365	55,000	57,500	55,000
Peru*	8,000	8,000	8,000	8,000	8,000
South Africa	13,277	11,989	14,386	15,587	13,968
South Korea	754,657	917,973	1,101,825	889,961	900,000
Thailand	38,053	46,011	59,602	103,496	103,000
United States	S W	W	W	W	W

Source: Virta 2004.

* Estimated.

† Withheld to avoid disclosing company proprietary data.

ore, shipped to Japan, Taiwan, and other countries in Southeast Asia. For reference, Chinese production was reported to be 623,000 t in 1991, for application in building materials, refractories, ceramics, agricultural chemicals, glass fiber, cosmetics, and other products (Zhu 1995). Other major producers are Brazil, India, the United States, Pakistan, Thailand, South Africa, and Peru.

Production Sites

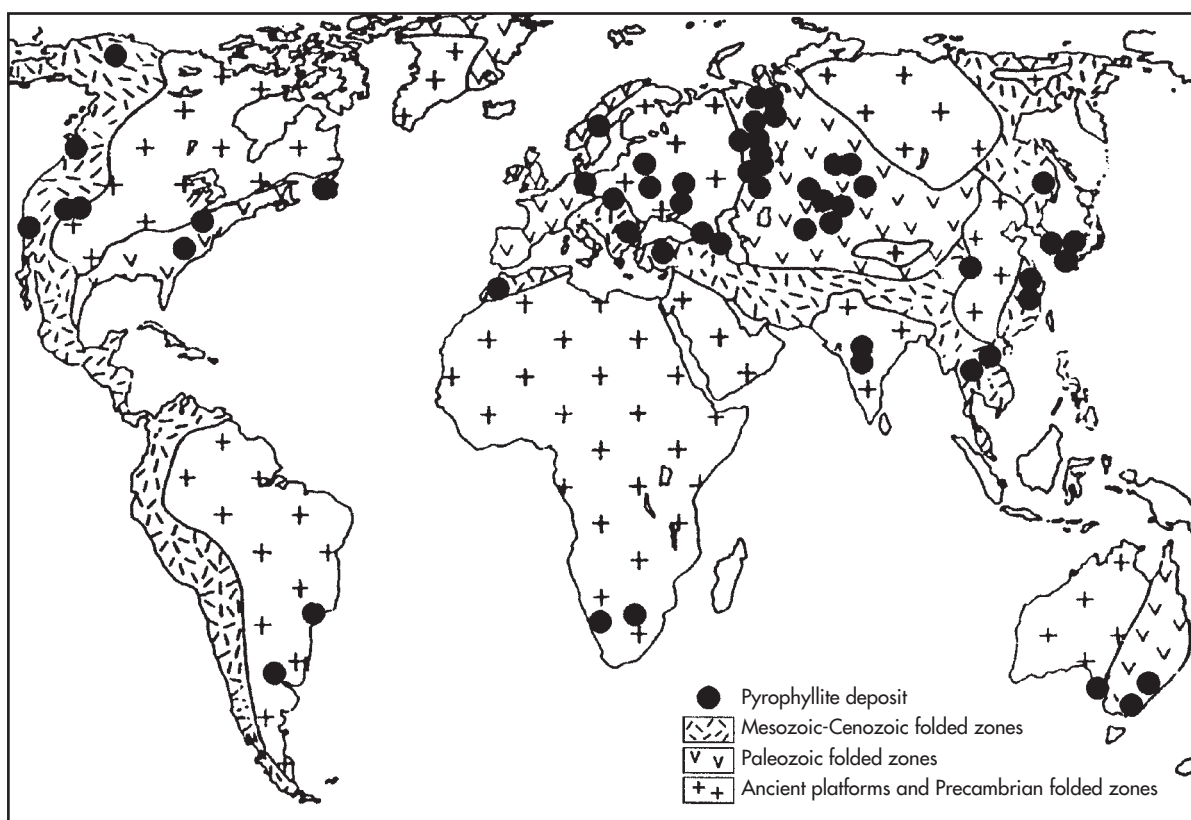
Most pyrophyllite deposits are found in subduction zones, related to plate movement, or in the region of old volcanoes formed at the site of collisions between tectonic plates. Global deposits are concentrated primarily in East Asia (Figure 1). These deposits originate from rhyolite and dacite formed in the Late Mesozoic and are relatively large and of high quality. Because of its natural properties, pyrophyllite ore is used principally in refractories. High-quality ore is used in making long glass fibers in East Asia; kaolin and silica sand are used for this purpose in the United States and Europe. Pyrophyllite ore is extracted mainly in low-cost open-pit mining, although some large-scale sites in both Japan and South Korea use trackless underground mining.

Japan

The main pyrophyllite mines in Japan are located in the prefectures of Okayama, Hiroshima, Nagasaki, and Hyogo. These deposits occur in rhyolite, dacite, and granite that is Cretaceous to Paleogene in age. In the Mitsuishi and Wake districts of the Okayama Prefecture, pyrophyllite ore is extracted by both open-pit and trackless underground operations. The ore is chiefly composed of pyrophyllite, quartz, sericite, and kaolinite. The Yano-Shokozan mine in Hiroshima Prefecture uses stepped-level open-pit extraction. The extracted ore consists of pyrophyllite, quartz, and kaolinite accompanied by diaspore, corundum, sericite, alunite, and other minor constituents (Matsumoto and Yano 1995; Hida et al. 1996). Reserves in this mine were approximately 18 Mt in 2004, with a production rate of 70,000 tpy for use in glass fibers, agricultural chemicals, cement, refractories, and pharmaceuticals.

South Korea

Hydrothermal alteration in the Late Cretaceous period formed the Korean pyrophyllite deposits, which are found in rhyolitic rocks. The main production sites are in the provinces of Chollanam-Do,



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Figure 1. The distribution of main pyrophyllite deposits in the world

Chungchongbuk-Do, Gyeongsangnam-Do, and Gyeongsangbuk-Do. Proven reserves have been calculated to contain 1.96 Mt, and probable reserves contain 49.68 Mt, for a total of 51.64 Mt (Table 3). The main pyrophyllite mines in Chollanam-Do are in the districts of Nohwado (Wando mine) and Haenam (Bakam, Bugok). At the Wando mine, stepped-level open-pit mining and trackless underground excavation are used. The deposits generally contain pyrophyllite and quartz, accompanied by diaspore, corundum, kaolinite, and sericite (Naito et al. 1999). The Bakam and Bugok mines extract rock containing kaolinite, dickite, and quartz. Production showed a continuous upward trend until 2001 but has declined since 2002 (Table 2). Exports accounted for 13.9% of production in 2002; the principal destinations were Japan, Taiwan, Sri Lanka, Indonesia, and Malaysia for use in cement, glass fibers, refractories, and other applications (MOCIE 2003).

China

Acidic igneous rock of Mesozoic age is found throughout the coastal regions of China, where pyrophyllite deposits have formed in rhyolite and dacite. The main production sites are in the provinces of Zhejiang, Fujian, and Inner Mongolia. Chinese figures for 1985 show proven reserves of 16.09 Mt, probable reserves of 22.79 Mt, and possible reserves of 47.46 Mt, for a total of 86.35 Mt (Table 4). Fujian Province has open-pit mines at Emei, Shoushan, Luoyuan, Pingxi, and elsewhere. The Emei and Shoushan mines have seen the greatest development in recent years. In 1984, reserves in these districts were set at 4.81 Mt and 4.36 Mt, respectively. The extracted ore consists of

Table 3. Reserves of pyrophyllite ores in South Korea (2002), kt

Province	Proven Reserves	Probable Reserves	Total
Chungchongbuk-Do	na*	8,915.0	8,915.0
Chollanam-Do	1,601.4	32,079.4	33,680.8
Gyeongsangbuk-Do	19.3	3,912.6	3,931.9
Gyeongsangnam-Do	343.0	4,772.2	5,115.2
Total	1,963.7	49,679.2	51,642.9

Source: MOCIE 2003.

* na = not available.

Table 4. Reserves of pyrophyllite ores in China (1985), kt

Province	Proven Reserves	Probable Reserves	Possible Reserves	Total
Fujian	8,970	7,430	14,820	31,220
Zhejiang	5,040	6,540	9,420	20,990
Hebei	na*	2,340	3,300	5,640
Beijing	2,090	na	2,500	4,590
Inner Mongolia	na	6,150	11,250	17,400
Others	na	350	6,150	6,500
Total	16,090	22,790	47,460	86,350

Source: China National Metals and Minerals Import and Export Corporation 1989.

* na = not available.

pyrophyllite and quartz, together with diaspore and kaolinite. Principal uses are in glass fibers, refractories, and handicrafts. In Fujian Province, production figures for 2002 were reported to be 150,000 t; the majority of this was used for manufacturing glass fibers, both domestically and through exports to Japan and South Korea. Zhejiang Province has mining operations at Taishun, Qingtian, and Shangyu, among others. At the first two sites, corundum is mined along with pyrophyllite. Taishun is an open-pit mine, with reserves of some 50 Mt and an extraction rate of some 300,000 tpy, according to the author's survey in 2003, used principally in glass fiber production, refractories, and tiles. Known sites in Qingtian include Shankou, Lingtou, and Beishan, where underground mining is employed. At Shankou and Lingtou, the ore consists chiefly of pyrophyllite and quartz, whereas at Beishan, it also contains a relatively large amount of kaolinite. The production rate in the Qingtian District is approximately 120,000 tpy, and the main uses of this pyrophyllite are in glass fibers, ceramics, tiles, and crucibles. The data in this paragraph were obtained from a survey conducted by the authors in 2003.

Brazil

Known pyrophyllite mines in Brazil include those in the states of Minas Gerais, São Paulo, and Paraná. In Minas Gerais, deposits are scattered along a 64-km stretch and are in the form of lenses or podiform masses in sericite and sericite-chlorite schists. Demonstrated reserves of 5.7 Mt have been calculated (Ciullo and Thompson 1994). The agalmatolite contains pyrophyllite, sericite, diaspore, kyanite, and quartz; uses include refractories, ceramics, paints, and soaps.

India

Pyrophyllite mining is principally concentrated in the states of Madhya Pradesh, Uttar Pradesh, Rajasthan, Orissa, and Maharashtra. This pyrophyllite formed through hydrothermal alteration of Paleozoic clastic rock (Zaykov, Udachin, and Sinyakovskaya 1988). The main production sites are in Madhya Pradesh and Uttar Pradesh, with mineral reserves of 4.33 Mt and 3.05 Mt, respectively (Harpavat 1995).

Russia

Large deposits of pyrophyllite have been identified in the alteration zones adjacent to sulfide deposits in the Urals. Although these pyrophyllite deposits have not yet been developed, they have the potential for significant output. Recent testing and research to investigate how these deposits can be economically exploited indicate suitability for refractories and ceramics in particular.

Other Countries

Commercial pyrophyllite deposits in the United States are located in volcanic metasedimentary rocks of Precambrian age in the Piedmont plateau of North Carolina. The pyrophyllite is found with kaolinite, sericite, andalusite, topaz, and diaspore and with lesser minerals (Harben and Kuzvart 1997). The ore, which is extracted in open-pit mines, is used in the production of ceramics, refractories, pottery, and insulators.

South Africa has three reported pyrophyllite mines: the Witpoort and Wonderstone sites in Ottosdal, North West Province, and the G and W Base mine in Mpumalanga. The pyrophyllite ore is found in the form of lenses or strata contained in rhyolite. Wonderstone is black or gray and consists of pyrophyllite combined with kaolinite, diaspore, sericite, and rutile. The ores are used in the diamond industry and in ceramics and paper manufacturing (pitch control).

The only pyrophyllite mine in Vietnam is located in Tan Mai in Quang Ninh Province. Geological surveys from 1980 to 1985

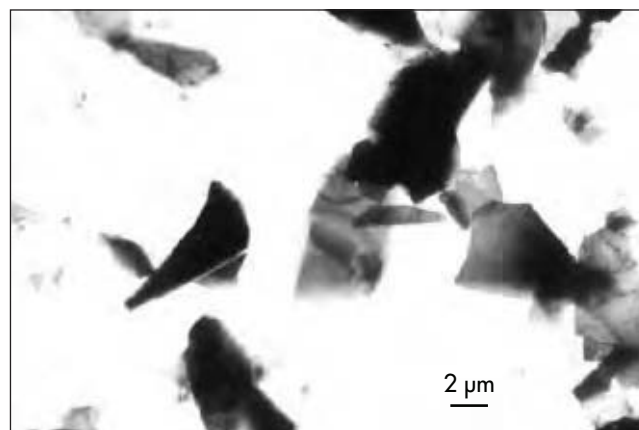


Figure 2. Transmission electron micrograph of pyrophyllite crystals from Chistogor deposit in the Urals, Russia

estimated 28.81 Mt of proven reserves and 16.33 Mt of probable reserves, for a total of 45.14 Mt (Taran 1990). Production was 19,200 t in 1999. The ore contains pyrophyllite, kaolin, and quartz and small quantities of chlorite, alunite, and diaspore. Principal applications are for refractories and pottery, and some ore is exported to Japan for use in glass fiber and resin manufacture.

MINERALOGY AND CHEMICAL PROPERTIES

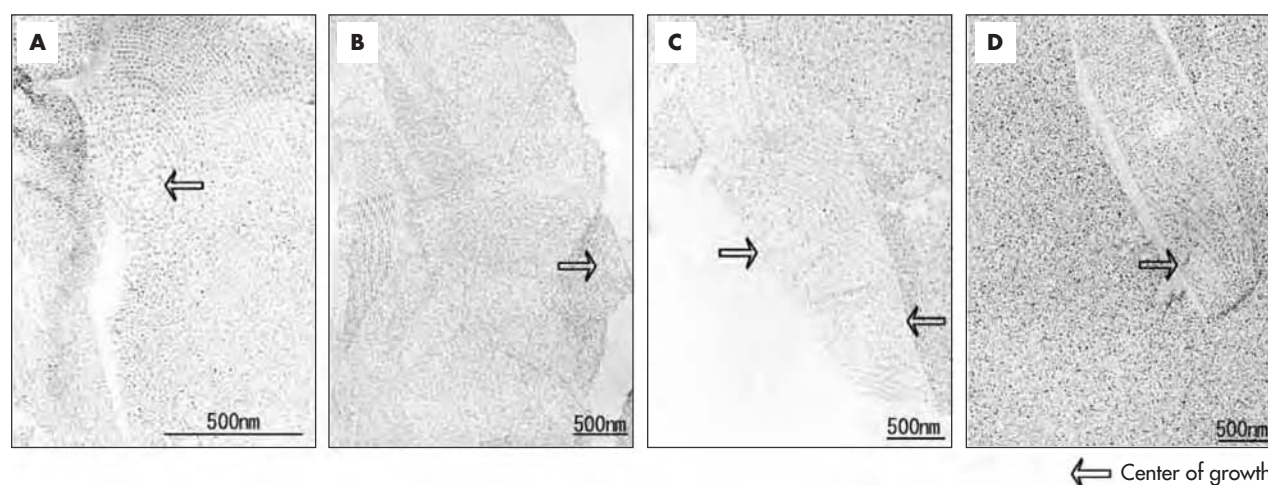
Mineralogy

Pyrophyllite is a soft mineral with a hardness of 1–2 on the Mohs scale, and its ores are easily processed into fine-grained powders. It is generally characterized as smooth and white, although it can range from white to yellowish, pale green, or light gray; this variation is thought to be due to differences in the trace elements present.

Pyrophyllite is a 2:1 phyllosilicate mineral that consists of an octahedral alumina sheet sandwiched between two silica tetrahedral sheets. The basal oxygen atoms are adjacent at the interlayer of the sheets, and the interlayer bonding forces are believed to be weak Van der Waals forces, although electrostatic attraction and hydrogen bonding are also indicated. The weak interlayer bonding forces account for the soft nature and smooth feel of pyrophyllite. Cleavage pieces bend easily and the material is only slightly elastic.

The ideal chemical formula of pyrophyllite is $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$. Each layer is electrically neutral and interlayer cations are not generally present. In nature, the replacement of Si^{4+} in the tetrahedral sheet with Al^{3+} is common; in addition, the replacement of Al^{3+} in the octahedral sheet with magnesium (Mg), Fe^{2+} , ferric iron, and titanium (Ti) has sometimes been observed. The basal spacing of pyrophyllite is approximately 9.3 Å, and it has triclinic and monoclinic polytypes with interlayer spacing of 4.3 and 4.0 Å, respectively (Brindley and Wardle 1970). Hydrothermal synthesis revealed that the triclinic polytype forms at higher temperatures than the monoclinic polytype (Eberl 1979). The pure triclinic polytype is rare in nature, however, and the monoclinic polytype or complexes of the two are more frequently observed. Pyrophyllite also occurs in association with clay minerals such as kaolin, mica, and mixed layer minerals.

The three most common forms of pyrophyllite ore are massive aggregates with or without a transparency, schistose structures, and radial aggregates of needle-like crystals. Irregular platiform crystals are commonly observed under electron microscopy, whereas fixed platiform crystals are relatively rare (Figure 2). The gold (Au)



Source: Jige and Kitagawa 2003.

Figure 3. Surface microtopographies showing malformed circular parallel growth patterns on pyrophyllite crystals by Au decoration method (A, B: Gay, South Urals; C, D: Kul-Yurt-Tau, South Urals)

Table 5. Chemical composition of pure pyrophyllite in selected deposits in Russia and South Korea

Chemical, %	Russia					South Korea		
	Gay	Kul-Yurt-Tau	Chistogor	Berezousk	Polar Ural	Gussi	Heanam	Nohwado
SiO ₂	67.6	66.5	67.0	67.2	66.9	66.2	66.0	67.6
TiO ₂	0.4	na*	na	na	na	na	na	na
Al ₂ O ₃	28.3	28.6	28.2	27.9	27.7	28.7	28.6	28.9
FeO	0.1	na	na	0.1	0.3	0.1	0.2	0.3
MnO	na	na	0.1	na	na	na	na	na
Cr ₂ O ₃	0.2	na	na	0.1	na	na	na	na
MgO	na	0.1	na	na	na	na	na	na
CaO	0.1	na	na	na	na	na	na	na
Na ₂ O	0.1	0.2	na	na	na	0.2	0.2	0.2
K ₂ O	na	0.1	0.1	na	na	na	0.3	0.1
Total	96.7	95.5	95.4	95.3	95.0	95.2	95.3	97.0

* na = not available.

Table 6. Chemical composition of selected pyrophyllite ores (by country and area)

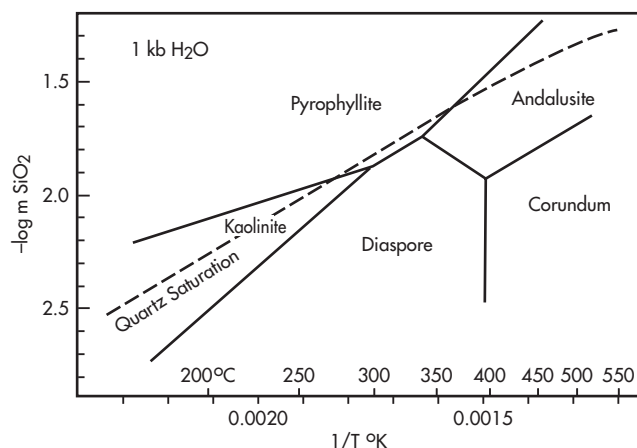
Chemical, %	Japan		South Korea		China		Brazil	India	United States	South Africa	Russia
	Mitsubishi	Shokoan	Wando	Hyeonsan	Qingtian	Taishun	Matheus Leme	Madhya Pradesh	North Carolina	Klerksdorp	Ural
SiO ₂	80.12	75.23	73.88	79.80	65.75	74.90	63.64	64.50	76.32	59.20	78.59
Al ₂ O ₃	15.79	19.90	21.31	15.69	27.04	20.25	25.59	28.75	19.80	30.51	16.16
Fe ₂ O ₃	0.07	0.20	0.06	0.13	0.18	0.15		0.22	0.18	0.77	0.82
TiO ₂	0.26	0.37	0.60	0.24	0.20	0.21		0.57		1.77	0.22
Na ₂ O	0.10	0.07	0.09	0.08	0.11	0.11	0.29	0.09	0.07	0.22	0.19
K ₂ O	0.09	0.04	0.12	0.16	0.69	0.16	2.48	0.61	0.27	0.78	0.20
LOI	3.11	4.01	3.92	3.37	5.68	3.85	4.81	5.19	3.44	6.77	3.50
Total	99.54	99.82	99.98	99.47	99.65	99.63	96.81	99.93	100.08	100.02	99.68
Reference	Benbow 1988	Shokoan Research Laboratory*	Shokoan Research Laboratory*	Shokoan Research Laboratory*	Shokoan Research Laboratory*	Shokoan Research Laboratory*	Benbow 1988	Shokoan Research Laboratory*	Cornish 1983	Shokoan Research Laboratory*	Zaykov and Udachin 1994

* Unpublished author data.

decoration method has revealed the growth pattern of the different pyrophyllite crystal structures through microtopography (Figure 3). In this growth pattern, massive aggregates and schistose structures are formed by an elliptic two-dimensional crystal nucleus growth mechanism; by contrast, radial aggregates are formed by a polygonal spiral growth mechanism. The exact form of pyrophyllite might depend on the environmental conditions present during growth.

Chemical Properties

Pyrophyllite consists of 66.60% SiO₂ (silicon dioxide), 28.30% Al₂O₃ (aluminum oxide), and 5.00% H₂O⁺. High-purity pyrophyllite, however, is rare both in natural and synthetic forms. Tables 5 and 6 show the results of chemical analyses of pyrophyllite from deposits in different countries. Slight differences in chemical composition are thought to influence the color of pyrophyllite ores; for example, the



Source: Hemley et al. 1980.

Figure 4. Phase diagram for the system $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ at $P_{\text{H}_2\text{O}} = 1$ kbar

pale blue green coloration of the ore from the Russian Gay deposit indicates that chromium (Cr) might be a coloring factor (Table 5).

A number of researchers have investigated the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system. According to Hemley et al. (1980), the temperature of the equilibrium boundary between kaolinite and pyrophyllite at a pressure of 1 kbar varies as a function of the concentration of SiO_2 ; as the SiO_2 concentration increases, kaolinite becomes stable at higher temperatures (Figure 4).

Pyrophyllite is inert and electrically neutral and therefore highly resistant to most strong alkalis and acids. It can, however, be decomposed to gelatinous aluminosilica with sulfuric acid.

Physical Properties

Pyrophyllite shows high fire resistance, thermal resistance, and thermal conductivity. On heating, pyrophyllite dehydroxylates at 700°C and changes to a metastable phase. This dehydration is accomplished by the loss of an OH^- group between the octahedral and tetrahedral sheets. On further heating up to $1,200^\circ\text{C}$, pyrophyllite decomposes to cristobalite and mullite; the latter has a hardness of 7–8 on the Mohs scale. Thermal characteristics vary between pyrophyllite ores, however, because of differences in their mineralogy and chemical composition. This variation contributes to the wide range of applications of pyrophyllite ores.

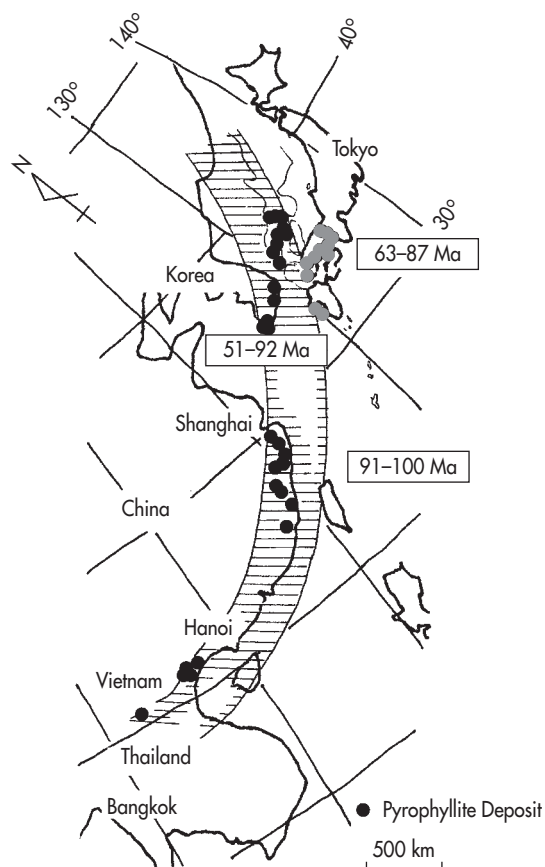
Because the water content of pyrophyllite is lower than that of other clay minerals such as kaolin, calcining is unnecessary. In addition, the coefficient of thermal expansion of fired pyrophyllite is lower than that of clay, resulting in more durable refractory products (Harben 2002).

GEOLOGY

Distribution and Formation Age of Pyrophyllite Deposits

Pyrophyllite deposits are mainly found in East Asia and the Ural District of Russia. Many of the East Asian deposits are distributed in the Japan–South Korea–China–Vietnam belt, which extends for more than 4,000 km; these deposits are largely concentrated in Japan, South Korea, and China (Figures 1 and 5).

No single report collates the dates of formation of pyrophyllite deposits worldwide. Several published studies describe the formation age of deposits in Japan on the basis of potassium–argon (K–Ar) radiometric dating of associated illite (Shibata and Fujii



Source: Kitagawa, Nishido, and Takeno 1988; Kitagawa et al. 1999.

Figure 5. Distribution of main pyrophyllite deposits in East Asia

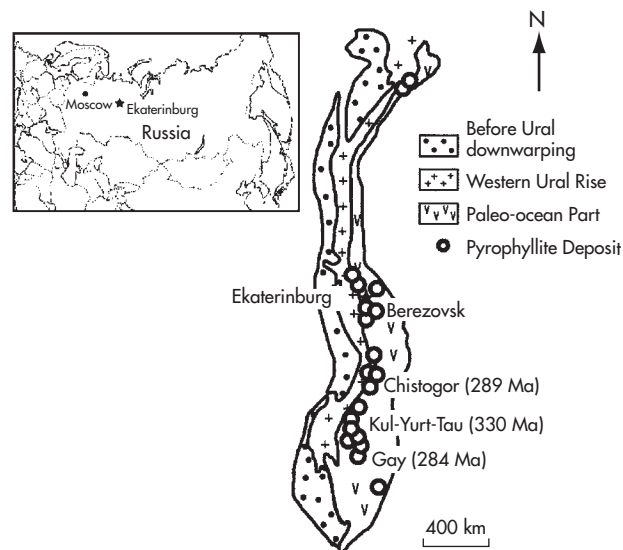














Figure 6. Distribution of pyrophyllite deposits in the Urals with K–Ar ages of illite

Country	Japan		South Korea		China	
Area	Mitsuishi	Shokozan	Wando	Haenam	Qingtian	Shoushan-Emei
Geologic Time ^{*1}	Late Cretaceous	Late Cretaceous	Late Cretaceous	Late Cretaceous	Late Jurassic	Late Jurassic
Caldera/ Basin Structure ^{*2}						
	Wake Caldera	Kawakita Basin	Nohwado Island	Haenam Caldera	Caldera	Furongshan Caldera
Scale of structure ^{*2}	23 × 15 km	15 × 10 km	?	35 × 25 km	30 × 25 km	10 × 10 km
Stratigraphy ^{*3} (Late Mesozoic) ★ Deposits						
	Rhyolite (Dacite)	Rhyolite Shale & sandstone Dacite (Rhyolite) Andesite	Acidic rocks Shale & sandstone Lacustrine sediments Andesite	Acidic rocks Shale & sandstone Lacustrine sediments Andesite	Rhyolite Sandstone and shale Rhyolite	Rhyolite Sandstone? Rhyolite
Host Rock ^{*3}	Rhyolite (Dacite)	Dacite (Rhyolite)	Lacustrine sediments	Lacustrine sediments	Rhyolite	Rhyolite
K-Ar age of alteration ^{*4}	73–80 Ma	69–73 Ma	71–73 Ma	78–82 Ma	—	—
Minerals ^{*5}	Qz, Pyr, Ser, Ka, Da	Qz, Pyr, Ka, Ser, Da, Alu, Cor	Pyr, Qz, Ka, Da, Ser, Cor, Alu	Qz, Pyr, Ka, Di, Ser, Alu	Pyr, Qz, Ka, Ser, Da, Cor	Pyr, Qz, Ka, Ser, Da, Alu
Uses ^{*6}	Refractories, Insecticides, Cement, Tile	Glass fiber, Insecticides, White cement, Refractories, Tile	Glass fiber, White cement, Refractories, Tile	Refractories, Tile, Glass fiber	Refractories, Tile, Glass fiber	Glass fiber, Refractories, Craft products
References	*1: Matsumoto (1979) *2: Ishihara and Imaoka (1999) *3: Fujii et al. (1979) *4: Kitagawa et al. (1999)	*1: Matsumoto (1979) *2, 3, 5, 6: Hida (2000) *4: Kitagawa, Nishido, and Takeno (1988)	*1, 3: Koh (1996) *2: Kim and Nagao (1992) *4: Naito et al. (1999) *5, 6: Hida (2000)	*1, 2, 4: Kim and Nagao (1992) *3: Koh (1996) *5, 6: Hida (2000)	*1, 2, 3: Luo (1987) *5, 6: Sudo (1988)	*1, 2, 3: Luo (1987) *5, 6: Hida (2000)

*5: Pyr: Pyrophyllite, Qz: Quartz, Ka: Kaolinite, Di: Dickite, Ser: Sericite, Da: Diaspore, Cor: Corundum, Alu: Alunite.

Figure 7. Geological characteristics and occurrence of pyrophyllite deposits in East Asia

1971; Shibata and Kamitani 1974; Kitagawa et al. 1999); these range from 100 to 25 million years ago (Ma) (Cretaceous and Tertiary). Most of the pyrophyllite deposits in the Chugoku Province of southwest Japan range in age from 87 to 63 Ma (late Cretaceous and early Tertiary; Figure 5). In South Korea, pyrophyllite deposits are found in the southwest and southeast; the larger deposits are concentrated in the southwest, and their formation ages range from 92 to 51 Ma (Kitagawa, Nishido, and Takeno 1988). In China, the formation ages range from 100 to 91 Ma (Kitagawa et al. 1999). These data suggest that the formation ages decrease from China to South Korea to Japan.

In Russia, pyrophyllite is found in sulfide deposits scattered throughout a belt of approximately 2,000 km along the Ural Mountains (Figure 6). K-Ar radiometric dating of sericite in the deposits estimates the formation age at about 300 Ma near the end of the Carboniferous age (R. Kitagawa, personal communication).

Geologic Occurrence and Genesis

The shapes of pyrophyllite deposits can be roughly divided into massive, sheet, lenticular, and vein. The massive ore deposits tend to be the largest, as the name suggests, and also are the most common. Pyrophyllite is generally formed by hydrothermal alteration, and its primary origins are as follows: first, the hydrothermal alteration of volcanic rocks such as rhyolite, dacite, andesite, and tuffs, in which associated granites are assumed to be the heat source; second, the top or upper parts of an intrusive body, such as quartz por-

phyry, which acts as the heat source and is affected by hydrothermal alteration; and third, the alteration zone of metallic ore deposits.

In Japan, South Korea, and China, many deposits are distributed on the rim of circular structures with diameters of 10 to 35 km (Figure 7). These deposits are probably formed by hydrothermal activity at the marginal part of the caldera in a process closely related to caldron formation (Kim and Nagao 1992; Ishihara and Imaoka 1999).

Pyrophyllite from the alteration zone of metallic ore deposits, such as the Kuroko deposit in Japan, is not mined because of the small quantities present. By contrast, the body of pyrophyllite in the hydrothermal alteration zone of the Russian Ural sulfide deposits is large enough to be mined. Pyrophyllite has also been found in the quartz vein of a gold deposit in Russia, although too little is present for mining. In addition to the methods described above, pyrophyllite can be formed by alteration in a geothermal field; such deposits occur in Japan but are not mined (Kimbara 1991).

TECHNOLOGY

Exploration

Basic prospecting for pyrophyllite begins with selecting a suitable area for exploration using the available geological information. The geological features of the target area, such as lineaments, faults, and calderas, are then confirmed using satellite imagery and aerial photographs. The Advanced Spaceborne Thermal Emission and

Reflection Radiometer (ASTER) sensor onboard the Terra satellite measures light rays from visible to thermal infrared wavelengths, which allows the identification of rocks and minerals. This technique can be useful in exploration. In undeveloped areas, it is important to identify sites that might be dangerous or difficult to investigate. First, a broad geological survey is carried out in the target area with a topographic map, investigating the following parameters: the extent of the deposit and the host rock, the distribution of the surrounding rocks, and the geological structure of the area. Second, a more localized region is chosen for closer examination. A detailed geological survey, including drilling, is then used to determine the three-dimensional shape of the pyrophyllite deposit. Once drilling defines the deposit, underground development is performed. Third, a detailed map of the deposit is produced through analysis of the drill core and samples taken during the underground development. If the pyrophyllite deposit is near the surface, it is also useful to excavate trenches several meters wide. The most efficient methods for calculating the tonnage and grade are selected at this stage. The pyrophyllite deposits of East Asia are of relatively high quality and large scale and often show the characteristics listed below (Matsumoto and Yano 1995; Hida 2000):

- Found in rhyolitic or dacitic rock of Late Mesozoic age
- Marginal to, or overlapping part of, a volcanic basin or caldera
- Sited in the specific layer of overlaying shale or unaltered rhyolitic rocks
- Lenticular or stratified in structure concordant with the host rock
- Zonal distribution of the mineral assemblage
- Deposit controlled by faults and fissures

Evaluation

The results of the field survey, drilling, underground exploration, and trenching determine the geological structure, form, and zonal distribution of mineral assemblages. Mineral identification, chemical analysis, thermal analysis, and calcination testing then allow the grade distribution of the deposit to be determined in detail and the ore reserve to be calculated. The production grade can be predicted for the early, middle, and late stages of mining, and the mine plan can be made to fit user requirements for grade and quantity. It is important to evaluate the location of the mining area; in addition, the mine plan, investment requirements, and management strategy must all be accurately determined.

Mining

Pyrophyllite is mined using either open-pit or underground methods, both of which involve the use of large equipment. Bench-cut and inclined-slope techniques are used in open-pit mining. After blasting, the ore is classified on the basis of megascopic observations of the ore's size and quantities of alumina and iron present determined by chemical analysis. The blasted ore is loaded using hydraulic-power shovels, and dump trucks transport it to the processing plants. Some deposits must be mined using underground methods because of their shape and ore grade. The room-and-pillar method is generally used in relatively large mines. Underground mining is common in the Qingtian District of the Zhejiang Province of China and in part of the Nohwado island area of the Haenam District, Chollanam-Do Province, Republic of Korea. In East Asia, electric trolley trains, motorized bicycle-drawn carts, and dump trucks transport the extracted ore through transportation tunnels to processing plants outside the pits.

Ore Dressing and Processing

Both dry and wet processing methods are used in dressing pyrophyllite ores. The flow diagram in Figure 8 shows the dry and wet grinding processes used by the Shokozan Mining Co. Ltd., a major manufacturer of pyrophyllite powder products in Japan. This system is effective because the ores produced in the area are soft and contain relatively large amounts of clay-sized material. The ores are first crushed in a dry system to a particle size of less than 60 cm by a breaker at the working face or stockyard; they are then further reduced to 30 mm or less by a jaw-and-cone crusher. Particles of between 40 and 150 mm pass through the picking section, where corundum-bearing pyrophyllite and waste ore are sorted by hand; the former is valuable for use in specialized refractories and in some glass industries. Material less than 40 mm is screened to identify particles of the size required by manufacturers of tiles and refractories. Smaller clay particles (<1 mm) produced by drag classifiers and filter presses in the wet system are used in the manufacture of bricks, cement, and roof tiles. The water from the filter-press process is recycled to the screen process, and it is not discharged from the plant.

Pyrophyllite powder for use in agriculture and in the manufacture of glass fiber and plastics is produced by crushing ore to less than 30 mm and, for some customers, grinding it to -325 mesh in a roller mill. Accurate analysis of Al_2O_3 values and quality-control testing are essential when producing clay for glass-fiber applications; these processes account for a large proportion of the total cost of the products.

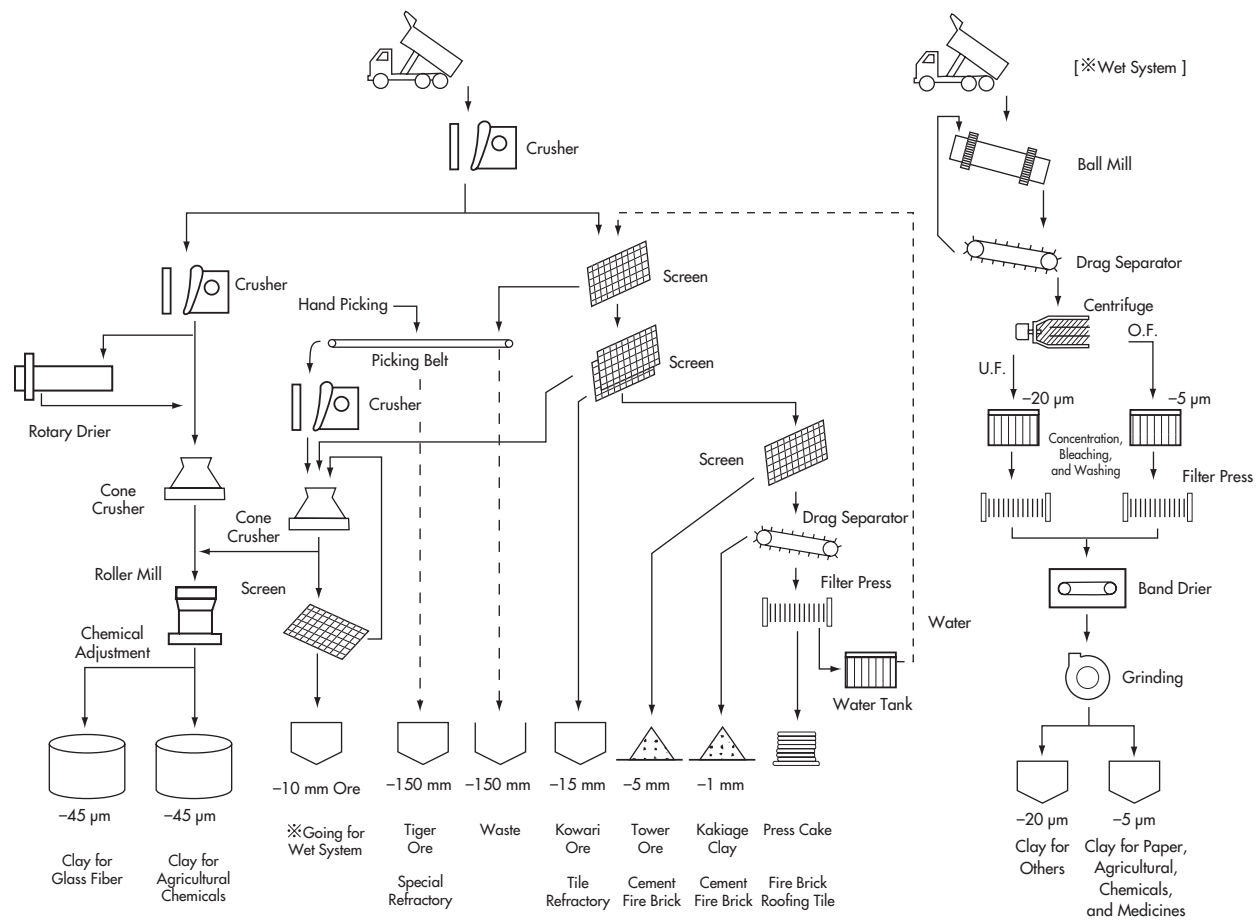
Pyrophyllite powder for use in medicines, paint, and construction materials is produced using wet processing. High-quality ore is crushed to a particle size of less than 10 mm and then ground in a tube mill. The fine pulverized powder, from which all quartz and heavy metals have been removed using a drag classifier, is then sent to a water tank, where aluminum sulfate is added to remove iron and bleach the powder. After being washed in clean water, passed through a filter press, dried to noodles, pulverized, and packed into bags, the powder is ready for shipment. The wet method is rarely used in East Asian countries, such as Japan, because of the costs of wastewater treatment; instead, dry grinding with a roller mill based on air elutriation is commonly used. By contrast, several of the beneficiation methods used to remove heavy metals and quartz in North Carolina (United States) and Newfoundland (Canada) are based on wet systems (Collings and Andrews 1990).

Packaging

Powder products are temporarily stored in product silos and packaged according to the exact specifications of the customer. Appropriate packaging materials for delivery to consumers include tank lorries, flexible container bags (500 to 1,000 kg), polypropylene (PP) bags (40 to 50 kg), and paper bags (20 to 25 kg). The automation of this process has improved rapidly in recent years with the development of automated equipment for both packing and loading. Automatic filling machines and flexible container bags have greatly reduced the labor and costs involved in the packaging process.

Transportation and Distribution

Using containers for the overseas transportation of pyrophyllite is beginning to expand. It is common to distribute material directly using tank trucks to larger customers in Japan; for smaller consumers, the networks of major trucking companies are often used, and some companies set up their own stock points in customer "hot spots" from which they distribute these products. Distribution costs are a significant issue for long-distance transportation, and one



Courtesy of Shokozan Mining Co., Ltd., Hiroshima, Japan.

Figure 8. Flowsheet for crushing, screening, and grinding of pyrophyllite ore

method of minimizing this expenditure is to take advantage of the backhaul to the area of the customers.

MARKETING

Uses

Pyrophyllite is used as a refractory raw material for various products, including pottery, porcelain, and tiles. It is also used as a clay material in cement, glass fiber, agricultural chemicals, building materials (mortar), paints, cleansers, rubber, medicinal clay (poultice), electrodes, resin fillers, and paper production as filler and coating. Strict quality control is necessary, both in the mine and during the crushing and grinding process, to ensure that the accessory mineral and trace element contents meet the specific requirements for different applications. Good care should also be taken to maintain product quality in transportation and other logistic operations. In the future, the range of uses of pyrophyllite is expected to expand with advances in the development of technologies in the chemical industry.

Specialized Uses

Pyrophyllite is occasionally associated with nacrite, barite, tourmaline, topaz, kyanite, zirconite, apatite, dumortierite, cookeite, vanbergite, or gold (Cornish 1983). Corundum-bearing pyrophyllite from the Shokozan Area of Japan is used for specialized refracto-

ries and in the glass industry. Diaspore-bearing pyrophyllite from the Mitsubishi Area of Japan, which is spherical or massive in shape, has applications in crucibles and specialized refractories. Dumortierite-bearing pyrophyllite from the Milyang deposit of South Korea is hand sorted for use in refractories. Kyanite-bearing pyrophyllite, which is chiefly mined in Brazil, is used in fillers and ceramics. Finally, relatively pure pyrophyllite from South Africa, or wonderstone, is used as a mold for artificial diamond production and in electric heaters and ceramics.

Product Grades and Specifications

To efficiently use pyrophyllite in industrial applications, it is necessary to identify and characterize all accompanying minerals and impurities. The different properties, grades, and specifications required for specific applications can be summarized as follows.

- **Refractory:** This requires an iron content of less than 1% and an absence of coarse quartz grains in the pyrophyllite ore. Fire resistance should exceed SK-30, and permanent expansion and good compaction on firing are necessary.
- **Pottery and tile:** For these applications, the siliceous pyrophyllite ore should have a high degree of whiteness and an iron content of less than 0.5%. In addition, high fire resistance, permanent expansion on firing, and low hydration expansion are required.

Table 7. Prices of pyrophyllite ores

Origin	Grade	Price Basis	Price, US\$/t	
			1996	October 2005
Australia	Filler grade, 300 mesh, milled	f.o.b. Sydney	230	342
South Korea	Ceramic grade, 15%–19% Al ₂ O ₃	f.o.b. Nohwado	27–44	27–44*
	Fiberglass grade, refractory grade, 18%–21% Al ₂ O ₃	f.o.b. Nohwado	59–65	59–65
	Clay filler grade, 21%–27% Al ₂ O ₃	f.o.b. Nohwado	110–150	110–150

Source: *Industrial Minerals* 1996, 2005.

* Minimal fluctuations in price over reporting period.

- **Cement:** This requires a pyrophyllite ore with low iron and alkaline contents and a high degree of whiteness after calcination.
- **Building materials:** A high degree of whiteness and a fine particle size are required for this application. Clays with high or low silica content are required for different products.
- **Glass fiber:** This requires clay with low iron, titanium, and alkaline contents, along with a fine particle size and high chemical stability and consistency.
- **Agricultural chemicals:** This grade of clay should contain stable particles and have high adherence and sticking tendencies. In general, it should have low specific gravity and moisture and be highly dispersible. A nearly neutral pH is required, as is stability over time when mixed with other chemicals.
- **Paper:** Pyrophyllite of this grade should have a high Al₂O₃ content, a low SiO₂ content, fine particles with no coarse elements, a stable particle distribution, and a high degree of whiteness.

In addition to the markets listed above, pyrophyllite ores and clay are also used in paint, plastics, colored aggregates, and medicines. The persistence of fine particles and chemical stability are valuable properties for most applications.

Prices

The price of pyrophyllite depends mainly on its Al₂O₃ content, although it is also affected by the presence of impurities such as iron and alkalis. Table 7 shows pyrophyllite prices in Australia and South Korea.

Competitive Substitutes

Chemical composition is of particular importance for ores used as raw materials in the manufacture of ceramics, cement, and long glass fibers. By contrast, physical properties—such as color, hardness, and particle size—are most significant for ores used in plastic fillers, paints, and construction materials. Stable pH value, particle size, and chemical composition are important for applications in pesticides and medicines. Although pyrophyllite was widely used as paper filler in the past, it has been largely replaced by soft kaolin, talc, and calcium carbonate in Japan.

INDUSTRY STRUCTURE AND ECONOMIC AND COMPETITIVE FACTORS

Infrastructure

In Japan, materials can be distributed by water, rail, and road. In recent years, motor vehicles have become the major form of trans-

portation because of advances in the maintenance of highways and the increasing demand for door-to-door services. Some observers, however, predict that rail transport in Japan, which was once considered a costly alternative, is becoming more competitive. Large port facilities allow a combination of sea and road transportation for the import and export of large consignments. South Korea has a complete network of water, rail, and road transport systems; however, because of the relatively small size, trucks are most commonly used. A main expressway system has been completed, and import and export ports are being constructed, although there are too few at present. In China, restricted water and road transport systems exist; however, international trade has rapidly expanded in recent years and a trade promotion policy has improved the transport infrastructure in urban areas and on the coast. In India, the railway and road haulage system—a result of the British heritage—is the major means of transport, and the infrastructure is continuing to improve, albeit slowly. The growth of coastal shipping systems and navigable waters in less developed countries invariably lags behind that of developed nations, and almost all ports and harbors in these countries fail to meet international standards.

Barriers to Entry

Strict rules and regulations concerning security, resources, and the environment, along with the enormous investment needed to develop a mine, make it difficult for newcomers to enter this industry. For example, in Japan, manufacturing commercial products for use in glass fibers requires highly specialized techniques for exploration, mining, grinding, and mixing; well-organized quality control; and accurate chemical analysis to produce good-quality pyrophyllite. In addition, customer requirements in the mining industry are often more demanding than those in other areas of commerce.

Economic Factors

The use of pyrophyllite in Japan has declined in recent years. At the same time, pyrophyllite production has become more difficult, manufacturing expenses have increased, and the price has decreased because of a lingering economic slump. Pyrophyllite bricks, once the mainstay of the refractory industry in Japan, have been almost entirely replaced by basic and high-alumina bricks. Low-grade bricks produced in China, where the manufacturing costs are lower, are being imported into Japan in increasing quantities. Similarly, in the tile industry, pyrophyllite consumption is decreasing and talc consumption is increasing, and the number of imported tiles is also growing. High-quality pyrophyllite powder for the manufacture of long glass fibers is increasingly being imported from South Korea and China; in addition, the costs of importing kaolin and silica clay into Japan have fallen recently, and these materials have begun to supplant pyrophyllite. In China, the production of refractories and glass fibers is rapidly expanding as a result of increased demand (Table 8).

Import Tariffs and Duties

The 2004 import tariffs on pyrophyllite ore in South Korea and Taiwan are 3.0% and 2.5%, respectively, and there are no import restrictions. Japan, Canada, and Australia do not impose import tariffs or restrictions on pyrophyllite, and the United States implements restrictions for only a few countries. In India, the breakdown of import duties is as follows: basic customs, 25%; special customs, 4%; and total customs, 30%. The import tariff in Brazil is about 5.5%, although the country has a complicated tax system and the tax ratios differ by state. China imposes an import tariff of 3.0% for selected countries such as South Korea, Japan, and the United

States, but the rate is 50% for all other nations; in addition, China emphasizes a protective trade policy.

By-Products

Most pyrophyllite containing high levels of iron and alkalis is discharged into waste piles or disposed of as unwanted stock. In Japan, some of this material is used in the production of eco-friendly goods and colored aggregates or in land reclamation. In other countries, including South Korea and China, the low-grade ores are partly used in eco-friendly goods, craft products, and road aggregates in the mining districts.

Depletion Allowance

Many countries, including the United States, Canada, Australia, and Europe, have a depletion allowance system to encourage mining, which recognizes that companies must continually acquire new mines and explore new prospects. Such allowances compensate companies for the loss of deposits or property, which gradually become depleted as the mines are operated. In Japan, there is no depletion-allowance system that resembles the ones in the United States and Europe, but the government allows mining companies either 12% of the sale proceeds from an ore or 50% of the income of a mining division to be reserved every year as a mine-prospecting reserve fund. This fund remains for 3 years and is then included in profits for taxation purposes. Pyrophyllite mining in Japan strictly follows this Japanese tax system.

Costs and Timing

Manufacturing expenses in the Japanese pyrophyllite industry have increased because of rising labor costs, investment in plants and equipment, resource conservation and environmental protection, and controls on dust produced during grinding. Regulations against overloading and exhaust control affect the costs of transportation. Despite increased manufacturing costs, the prices of most pyrophyllite products have declined in Japan. South Korea is also introducing stricter environmental regulations, although they are not as severe as those in Japan. In addition, the wages of workers in the mining industry are rising faster than wages in other sectors, leading to higher production costs. The prices of pyrophyllite products in South Korea are also increasing. Environmental regulations in China are less strict; however, it might be necessary to establish a reserve fund for the reclamation of mined land when mining rights are acquired. At present, China has comparatively little mechanization in rural areas, and most mining is performed by human power. China, however, is beginning to use modern equipment for crushing and grinding. Under the guidance of the government, improvements in the management of factors such as quality control, the maintenance of stable supplies, and safety issues in China are anticipated.

ENVIRONMENT

Safety, Health, and Environmental Sanitation

The stricter environmental regulations in Japan require greater efforts in the development of mines. In particular, safe working conditions during the mining, crushing, grinding, packing, and hauling processes are paramount. A company processing ore containing silica must use dust collectors, periodically measure the concentration of dust, and provide respirators for workers. In addition, periodic meetings about safety and health care are mandatory. Companies must recognize that managing the working environment is an important aspect of total quality control. Although these comments apply specifically to Japan, similar environmental requirements exist in several countries, albeit less stringent in some.

Table 8. Production of pyrophyllite ores for glass fiber in Fujian, China

Year	Output, t
1999	53,500
2000	73,500
2001	83,500
2002	143,500
2003*	170,000

Courtesy of Shokozan Mining Co., Ltd.

* Estimated.

Land Use and Restriction

In general, facilities must be designed to minimize pollution, and mining is restricted in some instances because of potential contamination problems. The Japanese Mining Act allows companies to acquire a maximum of 350 ha of land per mine, with few exceptions. To prevent pollution at landfill sites (waste rock reclamation), mining companies must perform routine maintenance and analysis of groundwater and must keep records of the results.

Mined Land Reclamation

When open-pit or underground mining ends, mining companies must take measures to prevent pollution and improve the appearance of the mined land. For underground mining, acid water flow from the mine must be neutralized before the water can be discharged into nearby watercourses. To avoid this problem, levels and shafts should be filled in completely, and pitheads should then be sealed. With bench cuts, which are popular in open-pit mining, revegetation is required on the filled site or the berm of the mine to prevent the bedrock from sloughing and to stop muddy water from flowing outside the mine during rainfall. Vegetation also improves the appearance of mined land, and trees and plants that can be acclimated to the natural features of the locality should be chosen for this purpose.

Pollution Control

All the processes involved in the manufacture of pyrophyllite products, including mining, dressing, grinding, packing, and hauling, can pollute; therefore, preventive or protective measures must be implemented at each stage. Blasting in open-pit mining can cause vibrations and noise, and fly rocks may be thrown outside the area of the mine; these factors can cause serious problems for nearby residences or roads. Frequent blasts of small charges are preferable to large-scale blasting. Watering haul roads in the mine controls dust, and workers must wear respirators when in a dusty environment. Side ditches or sand sedimentation tanks are used to settle suspended materials before the water is released into local channels.

Dust control is particularly important during dressing, grinding, and packing. Although adequate procedures and the routine maintenance of dust collectors can prevent mineral dust from dispersing to some degree, workers must wear respirators to ensure that they are protected from inhaling dust.

Finally, precise combustion- and emission-control systems to collect noxious gases are necessary to prevent air pollution during the drying of pyrophyllite. Anti-pollution procedures should also include taking routine measurements in the working environment, as specified by law.

OUTLOOK AND FUTURE TRENDS

Pyrophyllite deposits are concentrated in East Asia, with South Korea, China, and Japan predicted to remain major producers. In

China, in particular, the consumption and production of refractories, cement, glass fibers, and ceramics should increase significantly as industry and the economy develop further. The domestic demand for glass fibers in China has shown a strong increase over recent years, and this is likely to continue in the future. Kaolin and silica sand, which are also used in glass fiber applications, are abundant in United States and Europe; if these materials could be mined inexpensively in East Asia, they might be used along with pyrophyllite as a raw material for glass fibers. Chinese pyrophyllite remains highly competitive, however, because of its quality and low price. Pyrophyllite is also used in various agricultural applications, although its consumption is declining in Japan because of the acreage reduction policy in agriculture.

The pyrophyllite output of Brazil has remained relatively constant. Despite unstable economic conditions, production levels could increase if the prices fall below those of similar-grade materials produced in the United States. Significant reserves of pyrophyllite exist in the Indian states of Uttar Pradesh and Madhya Pradesh. The major domestic uses of Indian pyrophyllite are in tiles and ceramics. Despite low labor costs, India has yet to become competitive in the international pyrophyllite market, mainly because of high internal transportation costs. The production of wonderstone is increasing in the Republic of South Africa. Furthermore, a large deposit of pyrophyllite containing iron sulfide was recently identified in the Russian Ural province; this deposit was evaluated for use in refractories and ceramics, and further research and development is expected. Additional deposits exist in the Sikhote Alin Area of Russia, and near Fangchenggang in the Guangxi region of China. The future of the pyrophyllite industry worldwide depends on the continued exploration and development of new deposits and on the development of new markets.

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Rare Earth Elements

Stephen B. Castor and James B. Hedrick

INTRODUCTION

The rare earth elements (REEs), which include the 15 lanthanide elements ($Z = 57$ through 71) and yttrium ($Z = 39$), are so called because most of them were originally isolated in the 18th and 19th centuries as oxides from rare minerals. Because of their reactivity, the REEs were found to be difficult to refine to pure metal. Furthermore, efficient separation processes were not developed until the 20th century because of REEs' chemical similarity. A statement attributed to Sir William Crookes, a noted English scientist, betrays the frustrations of late 19th-century chemists with this group of elements (Emsley 2001):

The rare earth elements perplex us in our researches, baffle us in our speculations, and haunt us in our very dreams. They stretch like an unknown sea before us, mocking, mystifying and murmuring strange revelations and possibilities.

All of the REEs were finally identified in the 20th century. Promethium, the rarest, was not identified until 1945, and pure lutetium metal was not refined until 1953 (Emsley 2001). Commercial markets for most of the REEs have arisen in only the past 50 years.

Most REEs are not as uncommon in nature as the name implies. Cerium, the most abundant REE (Table 1), comprises more of the earth's crust than copper or lead. Many REEs are more common than tin and molybdenum, and all but promethium are more common than silver or mercury (Taylor and McLennan 1985).

Promethium, best known as an artificial element, occurs in very minute quantities in natural materials because it has no stable or long-lived isotopes. Lanthanide elements with low atomic numbers are generally more abundant in the earth's crust than those with high atomic numbers. Those with even atomic numbers are two to seven times more abundant than adjacent lanthanides with odd atomic numbers (Table 1).

The lanthanide elements traditionally have been divided into two groups: the light rare earth elements (LREEs)—lanthanum through europium ($Z = 57$ through 63); and the heavy rare earth elements (HREEs)—gadolinium through lutetium ($Z = 64$ through 71). Although yttrium is the lightest REE, it is usually grouped with the HREEs to which it is chemically and physically similar.

The REEs are lithophile elements (elements enriched in the earth's crust) that invariably occur together naturally because all are trivalent (except for Ce^{+4} and Eu^{+2} in some environments) and have

Table 1. REEs, atomic numbers, and abundances

Element	Symbol	Atomic Number	Upper Crust Abundance, ppm*	Chondrite Abundance, ppm†
Yttrium	Y	39	22	na‡
Lanthanum	La	57	30	0.34
Cerium	Ce	58	64	0.91
Praseodymium	Pr	59	7.1	0.121
Neodymium	Nd	60	26	0.64
Promethium	Pm	61	na	na
Samarium	Sm	62	4.5	0.195
Europium	Eu	63	0.88	0.073
Gadolinium	Gd	64	3.8	0.26
Terbium	Tb	65	0.64	0.047
Dysprosium	Dy	66	3.5	0.30
Holmium	Ho	67	0.80	0.078
Erbium	Er	68	2.3	0.20
Thulium	Tm	69	0.33	0.032
Ytterbium	Yb	70	2.2	0.22
Lutetium	Lu	71	0.32	0.034

* Source: Taylor and McLennan 1985

† Source: Wakita, Rey, and Schmitt 1971.

‡ na = not available.

similar ionic radii. An increase in atomic number in the lanthanide group is not accompanied by change in valence, and the lanthanide elements all inhabit the same cell in most versions of the periodic table. The similar radii and oxidation states of the REEs allow for liberal substitution of the REEs for each other into various crystal lattices. This substitution accounts for their wide dispersion in the earth's crust and the characteristic multiple occurrences of REEs within a single mineral. The chemical and physical differences that exist within the REEs group are caused by small differences in ionic radius and generally result in segregation of REEs into deposits enriched in either light lanthanides or heavy lanthanides plus yttrium.

The relative abundance of individual lanthanide elements has been found useful in the understanding of magmatic processes and natural aqueous systems. Comparisons are generally made using a

logarithmic plot of lanthanide abundances normalized to abundances in chondritic (ston y) mete orites. The use of this method eliminates the abundance variation between lanthanides of odd and even atomic number, and allows determination of the extent of fractionation between the lanthanides, because such fractionation is not considered to ha ve tak en place during chondrite formation. The method also is useful because chondrites are thought to be compositionally si milar to t he or iginal earth's mantle. Europium (Eu) anomalies (positive or negative departures of europium from chondrite-normalized plots) have been found to be particularly effective for petrogenetic modeling. In addition, REE isotopes, particularly of neodymium and samarium, have found use in petrogenetic modeling and geochronology.

HISTORY OF REE PRODUCTION

REEs wer e o riginally prod uced in min or amo unts from small deposits in gr anitic pegmatite, the geologic en vironment in which they were first discovered. During the second half of the 19th century and the first half of the 20th century, REEs came mainly from placer deposits, particularly t hose of the southeastern United States. With the exception of the most ab undant lanthanide elements (cerium, lanthanu m, and neodymium), in di vidual REEs were not commercia lly a vailable until the 1940s. Between 1965 and 1985, most of th e world's REEs came from Mountain Pass, California. Heavy mineral sands from placers in many parts of the world, however, were also sources o f b y-product REE minerals, and Australia was a major producer from such sources un til the early 1990s. Until recently, Russia also was an important REE producer from a hard rock source. During the 1980s, China emerged as a major producer of REE ra w materials, while the Austral ian and American market shares decreased dramatically (Figure 1). S ince 1998, more than 80% of the world's REE raw materials have come from China, and most of this production is from the Bayan Obo deposit in Inner Mongolia. Table 2 gives recent annual production figures by coun try, and Figure 2 sho ws locations of currently and recently productive REE mines.

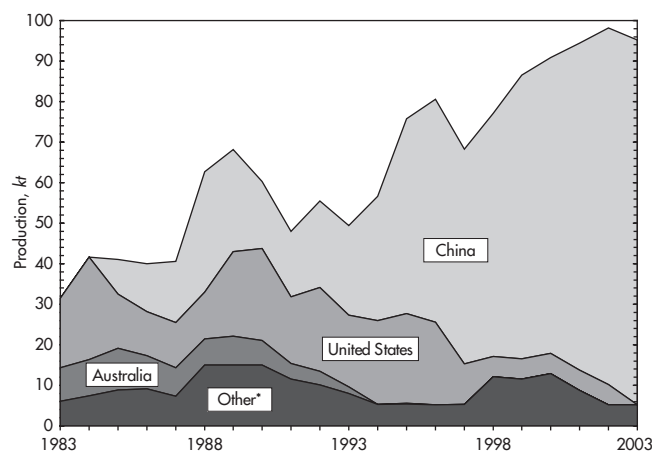
MINERALS THAT CONTAIN REES

Although REEs comprise significant amounts of man y minerals, almost all production has come from less than 10 minerals. Table 3 lists those that have yielded REEs commercially or have potential for production in the future. Extraction from a potentially economic REE resource is strongly dependant on its REE mineralogy. In the past, producing deposits were limited to those co ntaining REE-bearing minerals that are relatively easy to concentrate because of coarse grain size or other attributes. Minerals that are easily broken down, such as the car bonate bastnasite, are mo re desirable than those that are difficult to dissociate, such as the silicate allanite. Placer monazite, once an importa nt source of REEs, has been largely abandoned because of its high thorium co ntent. Recently, REEs absorbed on clay minerals in laterite have become important sources of REEs in Chin a. For more information on REE-bearing minerals, see works by Mariano (1989a); and Jones, Wall, and Williams (1996).

GEOLOGY OF REE DEPOSITS

Iron-REE Deposits

Some iron deposits contain REE resources, and such deposits have been exploited in only one area—Bayan Obo, China. These deposits constitute the largest known REE resource in the world (Table 4) and are no w the most important REE source in the world (Haxel, Hedrick, and Orris 2002).



*"Other" includes India, Brazil, Kyrgyzstan, Sri Lanka, Russia, Malaysia, and Thailand.

Figure 1. Production of REEs by China, the United States, Australia, and other countries, 1983–2003

Iron-LREE-niobium deposits at Bayan Obo in Inner Mongolia, China, were discovered by Russian geologists in 1927 (Argall 1980) when Inner Mongolia was under the control of the former U.S.S.R. REEs are recovered from iron-REE-niobium (Fe-REE-Nb) ore bodies that ha ve been m ined from more than 20 sites since mining started in 1957 (Drew, Meng, and Sun 1990). The two largest are the Main and East ore bodies (Figure 3), each of which incl ude iron-REE resources with more than 1,000 m of strike length and average 5.41% and 5.18% rare earth oxides (REOs), respectively (Yuan et al. 1992). Total reserves have been reported as at least 1.5 b illion t of iron (average grade 35%), at leas t 48 Mt of REOs (a verage grade 6%), and ab out 1 Mt of niobium (average grade 0.13%) (Drew, Meng, and Sun 1990). The REE ore consists of three major types: REE-iron ore, the most important type; REE ore in silicate rock; and REE ore in dolomite (Yuan et al. 1992). Massive REE-iron ore occurs in 100-m-thick lenses with local banded and breccia structures. Banded and streaky fluorite-rich REE-iron ore has the highest REE content, locally more than 10 % REOs. Major oxide chemistries of several Bayan Obo ore types are shown in Table 5. REEs are mainly in bastnasite and monazite, but at least 20 other REE-bearing minerals ha ve been identified (Yuan et al. 1992). Bayan Obo ore has e xtreme LREE enrichment with no europium anomalies (Figure 4) and lo w strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) (Nakai et al. 1989; Philpotts et al. 1989). Alkali-rich alteration (finitization), predominated by sodic amphibole and potash feldspar, is associated with the REE mineralization (Drew, Meng, and Sun 1990).

The Bayan Obo ore is hosted by dolomite of the Bayan Obo Group, a Middle Proterozoic clas tic and carbon ate sedimentary sequence (Qiu, Wang, and Zhao 1983; Chao et al. 1997) that occurs in an 18-km-long syncline (Drew, Meng, and Sun 1990). The Bayan Obo Group was deposited unconformably on 2.35-Ga migmatites, and, along with Carboniferous volcanics, was deformed during a Permian continent-to-continent collision event dominated by folding and thrusting (Drew, Meng, and Sun 1990). Intrusion of large amounts of Permian granitoid rocks also resulted from this collision.

The age of the REE mineralization is a matter of debate. It has been dated at 1600 Ma (Yuan et al. 1992) and 550 to 400 Ma (Chao et al. 1997). Most researchers agree that Fe-REE-Nb mineralization at Bay an Ob o took place over a long period of time.

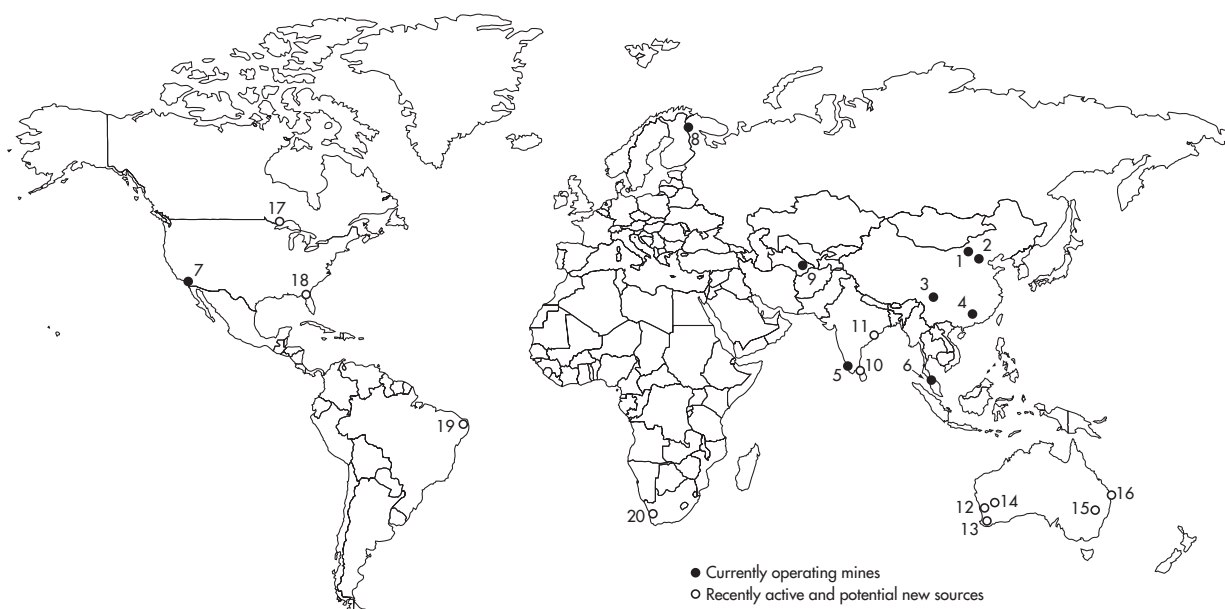
Table 2. Estimated annual world mine production of REEs, by country

Country	1983	1985	1987	1989	1991	1993	1995	1997	1999	2001	2003*
Metric Tons of REO Equivalent											
Australia	8,328	10,304	7,047	7,150	3,850	1,650	110	0	0	0	0
Brazil	2,891	2,174	2,383	1,377	719	270	103	0	0	0	0
China	na†	8,500	15,100	25,220	16,150	22,100	48,000	53,000	70,000	80,600	90,000
India	2,200	2,200	2,200	2,365	2,200	2,500	2,750	2,750	2,700	2,700	2,700
Kyrgyzstan	na	na	na	696	721	0	na	na	6,115	3,800	na
Malaysia	601	3,869	1,618	1,700	1,093	224	452	422	631	281	450
Mozambique	2	2	0	0	0	0	0	0	0	0	0
South Africa	0	0	660	660	237	237	0	0	0	0	0
Sri Lanka	165	110	110	110	110	110	110	110	120	0	0
Thailand	164	459	270	368	229	127	0	7	0	0	0
Russia	na	na	na	7,626	6,138	4,468	2,000	2,000	2,000	2,000	2,000
United States	17,083	13,428	11,100	20,787	16,465	17,754	22,200	10,000	5,000	5,000	0
Zaire	6	0	53	96	66	11	5	0	0	0	0
Total	31,439	41,047	40,541	68,155	47,978	49,449	75,730	68,288	86,566	94,381	95,150

Courtesy of USGS.

* Estimated. Some data have been added or modified using unpublished data from USGS files.

† na = not available.



Location No.	Location Name	Deposit Type	Location No.	Location Name	Deposit Type
1	Bayan Obo, China	Fe-REE-Nb deposit	11	Orissa, India	Monazite by-product, coastal placers
2	Weishan, China	Bastnasite-barite veins	12	Eneabba, Australia	Monazite by-product, coastal placers
3	Maoniuping, China	Bastnasite-barite veins	13	Capel and Yoganup, Australia	Monazite by-product, coastal placers
4	Xunwu and Longnan, China	Lateritic clay	14	Mount Weld, Australia	Lateritized carbonatite
5	Chavara, India	Monazite by-product, coastal placers	15	Dubbo, Australia	Altered alkaline complex
6	Perak, Malaysia	Xenotime by-product, tin placers	16	North Stradbroke Island, Australia	Monazite by-product, coastal placers
7	Mountain Pass, USA	Bastnasite-barite carbonatite	17	Elliot Lake, Canada	Uraniferous conglomerate
8	Lovozero, Russia	Loparite in peralkaline complex	18	Green Cove Springs, USA	Monazite by-product, placer
9	Aktus, Kyrgyzstan	Polymetallic deposit	19	Camaratuba, Brazil	Monazite by-product, coastal placers
10	Northern Sri Lanka	Monazite by-product, coastal placers	20	Steenkampsraal, South Africa	Monazite-apatite vein

Figure 2. Locations of the world's rare earth mines

Table 3. Minerals that contain REEs and occur in economic or potentially economic deposits

Mineral	Formula*	REO wt %†‡
Aeschynite	(Ln,Ca,Fe,Th)(Ti,Nb) ₂ (O,OH) ₆	36
Allanite (orthite)	(Ca,Ln) ₂ (Al,Fe) ₃ (SiO ₄) ₃ (OH)	30
Anatase	TiO ₂	3
Ancylite	SrLn(CO ₃) ₂ (OH)•H ₂ O	46
Apatite	Ca ₅ (PO ₄) ₃ (F,Cl,OH)	19
Bastnasite	LnCO ₃ F	76
Brannerite	(U,Ca,Ln)(Ti,Fe) ₂ O ₆	6
Britholite	(Ln,Ca) ₅ (SiO ₄ ,PO ₄) ₃ (OH,F)	62
Cerianite	(Ce,Th)O ₂	81§
Cheralite	(Ln,Ca,Th)(P,Si)O ₄	5
Churchite	YPO ₄ •2H ₂ O	44‡
Eudialyte	Na ₁₅ Ca ₆ (Fe,Mn) ₃ Zr ₃ (Si,Nb)Si ₂₅ O ₇₃ (OH,Cl,H ₂ O) ₅	10
Euxenite	(Ln,Ca,U,Th)(Nb,Ta,Ti) ₂ O ₆	<40§
Fergusonite	Ln(Nb,Ti)O ₄	47
Florencite	LnAl ₃ (PO ₄) ₂ (OH) ₆	32§
Gadolinite	LnFeBe ₂ Si ₂ O ₁₀	52
Huanghoite	BaLn(CO ₃) ₂ F	38
Hydroxylbastnasite	LnCO ₃ (OH,F)	75
Kainosite	Ca ₂ (Y,Ln) ₂ Si ₄ O ₁₂ CO ₃ •H ₂ O	38
Loparite	(Ln,Na,Ca)(Ti,Nb)O ₃	36
Monazite	(Ln,Th)PO ₄	71
Mosandrite	(Ca,Na,Ln) ₁₂ (Ti,Zr) ₂ Si ₇ O ₃₁ H ₆ F ₄	<65§
Parisite	CaLn ₂ (CO ₃) ₃ F ₂	64
Samarskite	(Ln,U,Fe) ₃ (Nb,Ta,Ti) ₅ O ₁₆	12
Synchisite	CaLn(CO ₃) ₂ F	51
Thalenite	Y ₃ Si ₃ O ₁₀ (OH)	63§
Xenotime	YPO ₄	61§
Ytrotantalite	(Y,U,Fe)(Ta,Nb)O ₄	<24§

* Source for mineral formulas: Mandarino 1999, with Ln = lanthanide elements.

† Sources for REO content: Frondel 1958; Overstreet 1967; Anon. 1980; Kapustin 1980; Mazzi and Munno 1983; Mariano 1989a.

‡ Where more than one analysis is available, the analysis with the highest REO content is reported (e.g., REO for monazite from the Mountain Pass carbonatite is reported; monazite from pegmatites and metamorphic rocks generally has lower REO).

§ Stoichiometric calculation of REO content.

Recent research points to ore formation during hydrothermal replacement of sedimentary dolomite, possibly related to one of the following:

- Alkaline or carbonatite magmatism (Drew, Meng, and Sun 1990; Campbell and Henderson 1997; Smith and Henderson 2000; Smith, Henderson, and Campbell 2000)
- Original emplacement of both the host dolomite and ore as igneous carbonatite with subsequent tectonic deformation (Le Bas, Spiro, and Yang 1997)
- Formation of host and ore by marine exhalation of alkalic or carbonatite-related fluids

Whatever its origin, the Bayan Obo deposits now dominate worldwide REE production and probably will do so for many years to come.

The Pea Ridge iron deposit in Missouri contains an undeveloped high-grade REE resource of unknown but probably small size in breccia pipes associated with 1.48-Ga granite and syenite (Kisvarsanyi, Sims, and Kisvarsanyi 1989). Bulk samples of REE-rich breccia, which contain monazite and xenotime, average about 12% REEs (Nuelle et al. 1992). Although the Pea Ridge resource is LREE-dominated, it also contains significant HREEs.

Mill tailings from processing magnetite deposits in Precambrian gabbro and syenite at Mineville, New York, are an REE resource of unknown size. They contain apatite that averages more than 11% REOs, including about 2% Y₂O₃ (McKeown and Klemic 1956).

The important magnetite and hematite deposits at Kiruna, Sweden, average 0.7% and 0.5% REOs, respectively, and other Swedish iron deposits contain similar amounts of REOs (Parak 1973). The REEs in these deposits are reportedly in apatite and monazite.

The huge Middle Proterozoic Olympic Dam copper-uranium-silver-gold deposit, South Australia, may also be included in this deposit type because most of the ore is breccia that contains 40% to 90% hematite along with quartz, sericite, fluorite, barite, sulfides, and REE minerals (Oreskes and Einaudi 1990). Olympic Dam is a potential source of by-product REEs, but typical content is about 0.5% total REEs, and there are no plans for REE production from the deposit. Extremely fine-grained monazite and bastnasite are the most abundant REE minerals, and the LREE/HREE ratio is high in Olympic Dam ore.

Carbonatite Deposits

Many carbonatite intrusions are enriched in REEs; Orris and Grauch (2002) list more than 100 carbonatite occurrences that contain REE minerals. Brief descriptions of REE mineral occurrences in carbonatites worldwide may be found in works by Mariano (1989a), Woolley (1987), and Wall and Mariano (1996).

Despite the abundance of REE-bearing carbonatites, REEs have been produced from only one, the Mountain Pass deposit in California. Although the Mountain Pass mine and plant did not operate in 2003, REE products were shipped from stockpile (Hedrick 2004a). Beginning in 1954, the Mountain Pass deposit was mined exclusively for REEs by Molycorp, Inc. (originally Molybdenum Corp. of America and now a subsidiary of Unocal). In 1987, proven and probable reserves totaled 29 Mt with an average grade of 8.9% REOs based on a 5% cutoff grade (Castor 1991). Current reserves are in excess of 20 Mt of ore at similar grade (Castor and Nason 2004). The ore typically contains 10% to 15% bastnasite, 65% calcite or dolomite, and 20% to 25% barite. Other gangue minerals, such as strontianite and talc, are present in significant amounts locally. Galena is locally abundant, but other sulfide minerals are rare. Bastnasite is the only mineral processed, although nine other REE minerals occur at Mountain Pass (Castor and Nason 2004). Mountain Pass ore has high LREEs and HREEs (Figure 4). The major oxide chemistry of Mountain Pass REE ore types is shown in Table 5.

The Mountain Pass carbonatite, which has been dated at about 1.4 Ga (DeWitt, Kwak, and Zartman 1987), is a moderately dipping, tabular intrusion (Figure 5) into granulite-grade gneiss. It is associated with ultrapotassic alkaline plutons of similar age, size, and orientation, as well as with abundant carbonatite and alkaline dikes, and is in a narrow north-trending zone of ultrapotassic alkaline igneous rocks at least 130 km long (Castor 1991; Castor and Nason 2004).

Elsewhere in the western United States, carbonatites have been investigated as possible sources of REEs, but none rival the Mountain Pass deposit as a REE resource. Similar to the Mountain

Table 4. Size and grade of some productive and potentially productive REE deposits

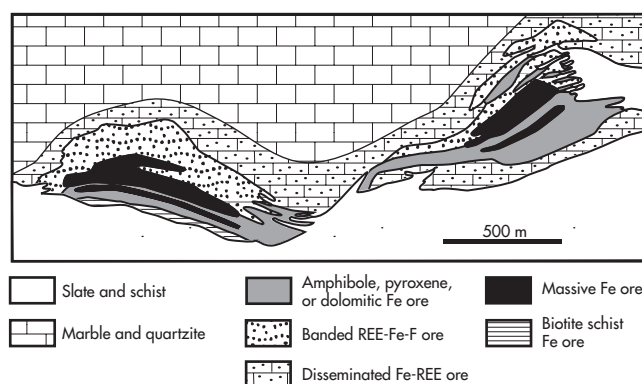
Deposit or District	Country	Size, t REO	Grade, % REO	Deposit Type	Recent Production	Reference
Bayan Obo	China	48,000,000	6	Iron-rich	Yes	Drew, Meng, and Sun 1990
Araxá	Brazil	8,100,000	1.8	Carbonatite laterite	No	Morteani and Preinfalk 1996
Mountain Pass	United States	1,800,000	8.9	Carbonatite	Yes	Castor and Nason 2004
Mount Weld	Australia	1,700,000	11.2	Carbonatite laterite	No	Mariano 1989b
Dubbo	Australia	700,000	0.86	Trachyte	No	Australian Zirconia Ltd. 2000
Mrima Hill	Kenya	300,000	5	Carbonatite laterite	No	Orris and Grauch 2002
Nolan's Bore	Australia	150,000	4	Vein	No	Anon. 2003
Xunwu and Longnan	China	Unknown	0.05–0.2	Laterite	Yes	Wu, Yuan, and Bai 1996
Lovozero	Russia	Unknown	0.01	Peralkaline syenite	Yes	Hedrick, Sinha, and Kosynkin 1997
Maoniuping	China	Unknown	2	Vein	Yes	Wu, Yuan, and Bai 1996
Weishan	China	Unknown	1.6	Vein	Yes	Wu, Yuan, and Bai 1996
Aktyus	Kyrgyzstan	Unknown	0.25	Unknown	Yes	Geological Survey of Kyrgyzstan 2004
Eneabba	Australia	Unknown	0.001	Placer	Yes	Griffiths 1984

Pass carbonatite, most have high LREE/HREE ratios. The large Cambrian Iron Hill carbonatite in the Powderhorn District of Colorado has been considered a possible source of REEs, but Armbrustmacher (1980) reported a grade of about 0.5% REEs. Carbonatite dikes in the Powderhorn District that contain up to 3% REOs constitute a resource of unknown size (Olson and Hedlund 1981), and dikes in the nearby Wet Mountains constitute a small resource with a grade of about 2.5% REOs (Armbrustmacher 1988). Phanerozoic carbonatite dikes that contain as much as 21% REOs (Crowley 1960), mainly in monazite, allanite, and ancylite (Heinrich and Levinson 1961), are present in the North Fork Area on the Idaho–Montana border, but the size of this resource is probably small because dikes with high REO contents are generally less than 1 m thick.

Carbonatite complexes in eastern Canada also contain REE mineralization. A biotite-bearing carbonatite dike in Mesozoic carbonatite at Oka, Quebec, is an REE resource of unknown size and grade (Mariano 1989a). Bastnasite and monazite zones containing up to 4.5% LREEs have been identified in the Late Proterozoic St-Honore Complex in Quebec, with one 80-m drill intercept averaging more than 3% REOs (Vallee and Dubuc 1970).

Brazilian carbonatites contain significant REE resources but have yielded only minor production to date. Niobium ore in the Barreiro Complex at Araxá, Minas Gerais, which comprises 5450+ Mt averaging 2.5% Nb₂O₅, contains about 4.4% REOs (Issa Filho, Lima, and Souza 1984).

African carbonatites also contain LREE-dominated deposits that are largely unexploited. Kangankunde Hill, Malawi, is underlain by carbonatite dikes in which the main REE phase is monazite that is almost thorium-free (Garson 1966). The dikes are thought to contain a resource of several hundred thousand tons of monazite at an average grade of more than 5% (Deans 1966). Mariano (1989a) suggested that monazite in Kangankunde Hill carbonatite is of primary igneous origin like the bastnasite at Mountain Pass, but subsequent work indicated that the monazite, as well as associated bastnasite and florencite–goyazite, was formed from an original REE phase during hydrothermal activity (Wall and Mariano 1996). Carbonatite dikes at Wigu Hill, Tanzania, contain up to 20% REOs as monazite and REE fluorocarbonate minerals of possible hydrothermal origin (Deans 1966). The Palabora carbonatite in South Africa, which occurs in a large Early Proterozoic potassic alkaline complex, has significant copper and apatite production and has been evaluated as a source of REEs. Potential by-product from apatite



Adapted from Chao et al. 1997.

Figure 3. Geologic map of the Main and East iron-REE-niobium ore bodies at Bayan Obo, China

concentrates that contain 0.4% to 0.9% REOs has been estimated at 4,250 tpy (Notholt, Highley, and Deans 1990).

Sill-like lenses of bastnasite-fluorite-barite rock as much as 30 m thick with about 5% REEs are associated with carbonatite at Kizilçören, Turkey (Hatzl et al. 1990). The carbonatite occurs in dikes associated with intrusive Tertiary phonolites and trachytes along with alkaline pyroclastic rocks. The unexploited Kizilçören resource is dominantly LREEs (G. Morteani, personal communication).

Lateritic Deposits

Lateritic deposits that occur over low-grade primary sources, such as carbonatites and syenites, have been studied as potential REE sources since the 1980s. Such deposits may constitute large resources and some have high REE contents; however, only two deposits in China have been exploited to date.

REEs have been produced in increasing quantities in recent years from surficial clay deposits in southern China, and Orris and Grauch (2002) list 18 Chinese occurrences of such material. In 1992, REEs from these deposits comprised 14% of Chinese production (Wu, Yuan, and Bai 1996), and this source has had a strong impact on yttrium supplies since 1988. The deposits reportedly form weathering crusts over granite (Ren 1985; Wu,

Table 5. Major oxide chemistry of ore samples from Bayan Obo and Mountain Pass

Samples	Bayan Obo [*]					Mountain Pass [†]					
	Mfe	Ffe	AeFe	RiFe	MDT	7B30-20	7B30-45A	7B30-28B	7B31-10	85-4	R-724
SiO ₂	4.81	2.18	23.86	10.79	8.74	na [‡]	na	na	na	0.40	1.63
TiO ₂	0.27	0.62	0.56	0.55	0.28	1.00	0.15	0.23	0.08	0.01	0.01
Al ₂ O ₃	0.22	0.66	1.55	0.83	0.74	0.06	0.25	0.17	0.26	0.01	0.01
Fe ₂ O ₃ [§]	74.73	39.29	31.61	44.59	11.69	7.72	13.87	37.17	5.00	0.24	1.77
MnO	0.79	0.12	0.07	5.95	1.18	0.01	0.03	0.02	0.01	0.24	0.45
MgO	0.99	0.31	0.30	3.52	13.23	<0.03	0.07	0.25	0.12	0.04	6.41
CaO	8.78	26.26	11.59	16.15	27.09	27.98	27.98	3.92	8.67	21.30	11.73
SrO	0.36	3.90	5.67	1.15	0.25	0.05	0.10	0.07	0.09	14.15	2.49
BaO	na	na	na	na	na	0.04	3.80	2.79	2.46	14.63	25.12
Na ₂ O	0.25	0.25	4.06	0.62	0.12	na	na	na	na	0.05	0.07
K ₂ O	0.09	0.08	0.57	0.92	0.58	<0.24	<0.24	<0.24	<0.24	0.05	0.09
P ₂ O ₅	0.94	2.71	2.85	1.16	1.47	na	na	na	na	0.04	0.29
F	5.89	16.83	7.25	8.31	1.83	17.00	14.4	1.68	4.49	0.70	1.40
CO ₂	na	na	na	na	na	na	na	na	na	19.84	18.26
SO ₃	na	na	na	na	na	na	na	na	na	18.26	15.43
LOI	2.89	5.15	5.62	5.60	25.23	na	na	na	na	na	na
RE ₂ O ₃	2.73	9.49	7.72	3.24	3.98	19.32	8.67	10.89	42.75	9.89	13.18
Nb ₂ O ₅	na	na	na	na	na	0.36	0.02	0.05	0.53	0.001	0.004
Total	103.74	107.85	103.28	103.38	96.41	73.54	69.34	57.24	64.46	99.85	98.34

Source: Yuan et al 1992; Chao et al. 1997; Castor and Nason 2004.

^{*} Bayan Obo:

Mfe = massive REE-Fe ore

Ffe = fluorite REE-Fe ore

AeFe = aegerine REE-Fe ore

RiFe = riebeckite REE-Fe ore

MDT = magnetite-dolomite ore

7B30-20 = high-REE, low-Fe banded ore

7B30-45A = bastnasite-apatite-pyroxene-fluorite ore

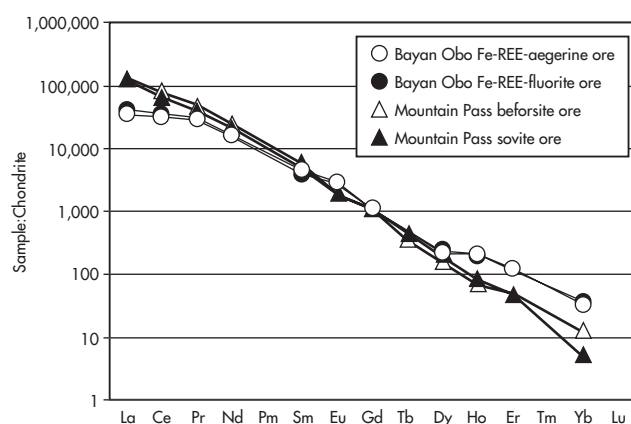
7B30-28B = high-Fe, REEs, and fluorite ore

7B31-10 = high-REE, low-Fe, and low-F ore

[†] Mountain Pass:

85-4 = bastnasite-barite sovite, Sulphide Queen ore body

R-724 = bastnasite-barite beforite, Sulphide Queen ore body.

[‡] na = not available.[§] All Fe as Fe₂O₃.

NOTE: REE data not normalized to 100% prior to chondrite normalization.

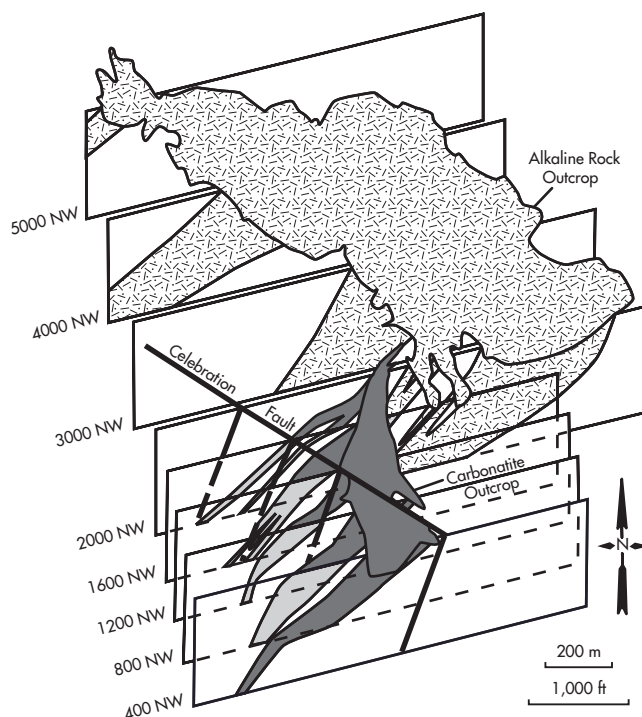
Figure 4. Chondrite-normalized plot of REEs in ores from Bayan Obo, China, and Mountain Pass, United States (data sources: Castor 1986; Yuan et al. 1992)

Yuan, and Bai 1996). The ore, referred to as REE-bearing ionic absorption clay, mostly comes from two sites in Jiangxi Province—Longnan and Xunwu, the former yielding HREE- and yttrium-rich material and the other, LREE-rich material (O'Driscoll 2003). Ore from Longnan has an HREE-dominated

distribution pattern very similar to that of xenotime, whereas ore from Xunwu is relatively enriched in lanthanum (Hedrick 1992; Figure 6). Both ores have relatively low cerium content, suggesting deposition from REE-bearing groundwater with depleted cerium that results from the element's insolubility in the oxidized (Ce⁴⁺) state. The ore bodies are 3 to 10 m thick and occur mainly in a wholly weathered zone composed of halloysite and kaolinite with residual quartz and feldspar; grades are reported at 0.05% to 0.2% REOs (Wu, Yuan, and Bai 1996). The deposits are considered to be laterites and show similarities to a number of other lateritic deposits formed over alkaline igneous rocks and carbonatite (Morteani and Preinfalk 1996).

REE-enriched lateritic material overlying carbonatite is present in many sites worldwide, mostly in the tropics. Orris and Grauch (2002) list more than 50 such occurrences, but, other than the Chinese deposits, none have produced significant amounts of REEs.

The Mount Weld REE deposit in southern Western Australia is in the lateritized cap over a large carbonatite (Figure 7) dated at 2.0 Ga (Duncan and Willett 1990). Although LREE/HREE ratios are generally high, the laterite is locally enriched in HREEs and yttrium. Published reserve figures are 15.4 Mt with 11.2% REOs + Y₂O₃ (Mariano 1989a), and 2.3 Mt with 18.0% REOs (Willis 2002). Large volumes of ore contain an average of 0.33% Y₂O₃, and niobium and tantalum enrichment has also been reported (O'Driscoll 1988). Data from Lottnermoser (1990) indicate that unweathered carbonatite at depth contains 0.1% to 0.2% REOs. REE enrichment at Mount Weld is thought to have been caused by



Adapted from W. Buckovic, personal communication.

Figure 5. Stacked cross sections through the Mountain Pass REE carbonatite ore body (gray) and a major associated alkaline rock mass (patterned)

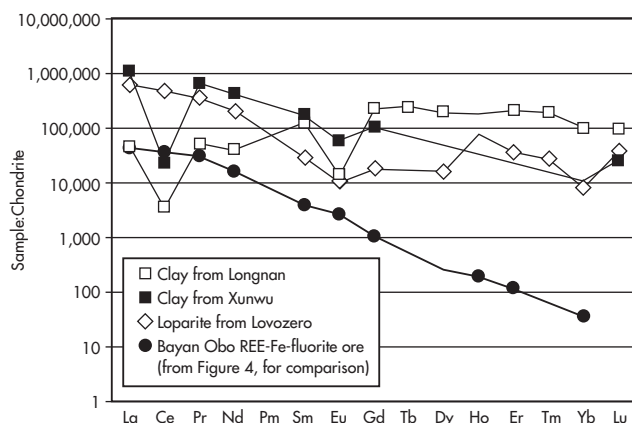
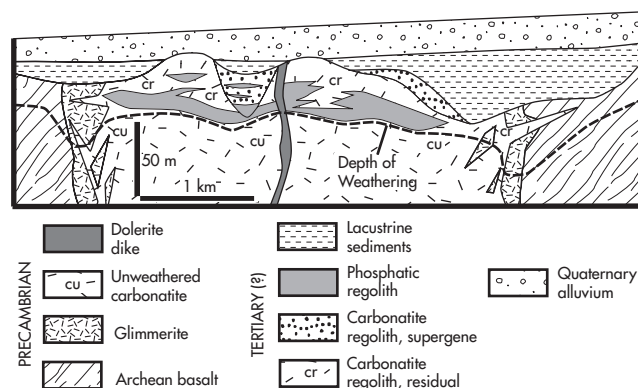


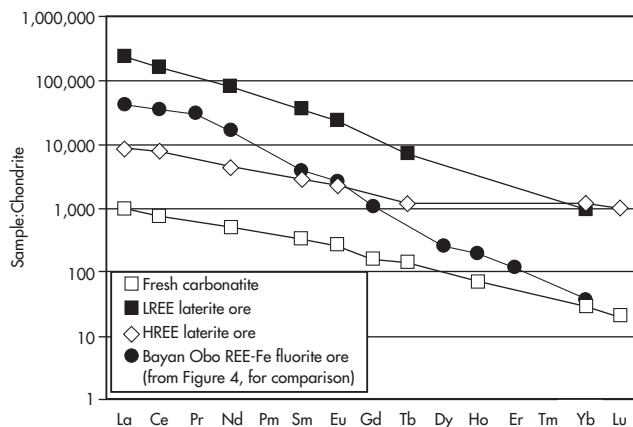
Figure 6. Chondrite-normalized plot of REE distribution (normalized to 100%) in ion absorption clay ores from China and loparite from Russia (data source: Hedrick 1992)

long-term leaching and redeposition by groundwater; it mainly consists of REE phosphates (Mariano 1989a), including the yttrium-rich mineral churchite (Lottermoser 1988). During the formation of the weathered profile since Permian glaciation, LREEs were incorporated in phosphate and alumino-phosphate minerals in the upper part of the profile, and HREEs and Y were deposited as churchite at lower levels (Lottermoser 1990), leading to the formation of both LREE- and HREE-enriched ore (Figure 8). The Yangibana REE



Adapted from Duncan and Willett 1990.

Figure 7. East-west geological cross section through the Mount Weld carbonatite and its weathered cap



NOTE: REE data not normalized to 100% prior to chondrite normalization.

Figure 8. Chondrite-normalized plot of REEs in laterite and carbonatite from Mount Weld, Australia (data source: Lottermoser 1990)

prospect in northern Western Australia, a gossan containing as much as 11% REOs (O'Driscoll 1988), is thought to have been formed by weathering from a carbonatite associated with Early Proterozoic alkaline rocks.

The Araxá carbonatite complex in Brazil contains 800,000 t of supergene-enriched laterite that averages 13.5% REOs, mainly in the phosphate minerals gorceixite and goyazite (Mariano 1989a). In the Catalão I Complex about 300 km southeast of Araxá, phosphatic laterite comprises a resource of about 2 Mt averaging 12% REOs. The REEs are mainly in secondary phosphate minerals, such as gorceixite (Mariano 1989a; Morteau and Preinfalk 1996). Laterized carbonatite in the Maicuru Complex, Pará, northern Brazil, contains phosphatic material with as much as 17% REEs (Costa et al. 1991). Cerro Impacto, a large circular structure thought to be a deeply weathered carbonatite that is located in the Amazon region of Venezuela, contains as much as 11% REEs in thick laterite (O'Driscoll 1988).

Deeply weathered Brazilian carbonatites that contain large titanium resources in the form of a natase with associated REE phosphate minerals are also a potential source of by-product REEs

with high LREE/HREE ratios (Mariano 1989a). Titanium concentrates from a pilot plant contain more than 3% REEs that must be removed to produce commercial titania. Reserves are known to be substantial; the largest deposit, at Serra Negra, Minas Gerais, contains 200 Mt averaging 27.7% TiO_2 (Anon. 1984). Other poorly explored carbonatites in the Amazon region of South America are known to host supergene REE mineralization (Mariano 1989b).

REE-enriched laterites occur at 17 sites in Africa (Orris and Grauch 2002). The most thoroughly investigated deposit is probably monazite-rich laterite that includes 6 Mt of material with about 5% REOs that overlies carbonatite at Mrima Hill, Kenya. REE enrichment in the form of secondary hydroxylbastnasite and other minerals has been reported in karst-related lateritic deposits in Europe, such as upper Jurassic bauxite deposits in Montenegro (Maksimović and Pantó 1996).

Placer Deposits

Most placer accumulations with significant amounts of REE minerals are Tertiary or Quaternary deposits derived from source areas that include granitic rocks or high-grade metamorphic rocks; however, paleoplacer deposits that are as old as Precambrian contain REE resources. Orris and Grauch (2002) list more than 360 REE-bearing placers. Most commercial deposits are in sands of marine origin along or near present coastlines and consist of titanium mineral placers with by-product zircon and monazite; some contain xenotime. In the 1980s, monazite and xenotime from titania-zircon paleobeach placers in Australia were the third most important source of REEs in the world, but Australia currently exports little or no REE minerals from such sources, owing to their high thorium content.

Placer rutile-zircon-ilmenite deposits at Eneabba on Australia's west coast north of Perth, which produced about 2,500 t of monazite annually, were brought into production in the late 1970s. These deposits are still productive, but little or no monazite is currently marketed from them. Heavy minerals comprise about 6% of the sand mined at Eneabba, and monazite makes up 0.5% to 7.0% of the heavy minerals (Shepherd 1990). The heavy mineral sands lie 30 m or more above present sea level and were deposited in late Tertiary or early Pleistocene time (Lissiman and Oxenford 1975). Archean metamorphic rocks in the interior provided heavy minerals to Mesozoic sedimentary rocks that were reworked to form these deposits. In the Geographe Bay area near Capel, ilmenite-zircon paleobeach deposits that have been mined since the mid-1950s occur along a strike length of about 50 km in Pleistocene to Recent sands (Welch, Sofoulis, and Fitzgerald 1975). The setting and source are similar to those described for Eneabba. Although the average heavy mineral grade of Geographe Bay deposits is somewhat higher than at Eneabba, the monazite content of heavy mineral concentrates is lower, at 0.04% to 1.1% (Welch, Sofoulis, and Fitzgerald 1975).

Minor amounts of monazite were once produced from placers along Australia's east coast. Rutile and zircon are the main mineral products from these operations, which exploit Quaternary beach placers and sand dunes. Heavy mineral content in some of these deposits is less than 0.5% (Griffiths 1984), and monazite comprises less than 1% of the heavy mineral concentrate (McKellar 1975). The WIM 150 deposit, a placer in an interior basin in Victoria, contains large REE mineral resources. A 14-m-thick titanium and zirconium mineral sand deposit, underlies an extensive area amenable to dredging. Estimated REE mineral reserves exceed 580,000 t monazite and 170,000 t xenotime (O'Driscoll 1988).

In addition to Australia, by-product monazite has been extracted from beach deposits in Brazil, India, Malaysia, Thailand,

China, Taiwan, New Zealand, Sri Lanka, Indonesia, Zaire, Korea, and the United States. Present-day production is from India, Malaysia, Sri Lanka, Thailand, and Brazil. In India, monazite production from titania-zircon placers is government controlled, and a domestic plant processes monazite concentrate into REE products. In southeast Asia, monazite and xenotime are won from concentrates produced during placer tin, zircon, and titania mining. Prior to 1988, when China began to dominate yttrium production, xenotime from Malaysia was the largest source of yttrium in the world. Approximately 500 t of monazite per year were produced from 1952 to 1994 as a by-product of titania-zircon production from Pleistocene sands near Green Cove Springs in Florida.

Prior to large-scale exploitation of the Mountain Pass deposit, REE production in the United States came almost exclusively from nonmarine placers, although none comes from such sources now. The Carolina monazite belt, from which a total of about 5,000 t of monazite was produced between 1885 and 1917, has considerable placer reserves that average 0.25 kg/m³ of monazite (Overstreet 1967). In Idaho, REE minerals were produced in the 1950s from placers. Dredging operations near Cascade produced about 7,000 t of monazite from gravels containing about 1 kg/m³, and monazite reserves are estimated at 38,000 t (Overstreet 1967). Bear Valley, Idaho, where monazite and yttrium-bearing euxenite were mined by dredging, contains an estimated 10,000 t of REOs along with significant niobium and tantalum, on the basis of data from Kline et al. (1953). Some Idaho placers contain xenotime, particularly those in northern Idaho, and REEs are a possible by-product of placer gold mining in that area.

Metamorphosed Early Proterozoic conglomerate mined for uranium at Blind River, Ontario, Canada, contains REEs in monazite, uraninite, and brannerite (Roscoe 1969), and was the source of minor REE production from the 1950s to 1970s and again from 1986 to 1990. The heavy minerals in this ore are believed to be primarily of placer origin with possible enrichment during metamorphism or hydrothermal activity. Of the approximately 230 Mt of ore averaging 0.1% U_3O_8 estimated to be present in the district in 1973 (Robertson 1981), perhaps half remained unmined in the early 1990s, even though uranium mining didn't end until 1996.

At Music Valley in Southern California, xenotime- and monazite-rich zones with as much as 16% REOs (including 6% Y_2O_3) in Precambrian gneiss are thought to have originated as placer accumulations (Evans 1964). At Bald Mountain, Wyoming, a paleoplacer monazite resource was identified in Cambrian conglomerate (Borrowman and Rosenbaum 1962).

REE distribution plots of monazite and xenotime from most placer deposits have pronounced negative europium anomalies (Figure 9), indicating derivation from sources containing plagioclase. In addition, placer monazite has relatively high HREE contents compared with the strongly LREE-dominated hard-rock deposits at Bayan Obo and Mountain Pass.

HREE Deposits in Peralkaline Igneous Rocks

Although many REE deposits occur in peralkaline igneous rocks and resources can be large, most such deposits are relatively low grade, and only a single deposit in Russia has been mined. Peralkaline REE deposits are typically enriched in yttrium, HREEs, and zirconium. Future development of such deposits is dependent on the markets for these elements.

REE-bearing loparite has been produced for about 50 years from nepheline syenites in the peralkaline Paleozoic Lovozero massif on the Kola Peninsula in Russia. The massif is layered and is composed of four rock suites (Vlasov, Kuz'menko, and Yes'kova 1966). The upper 30% of the massif is eudialytic syenite.

The bottom, loparite-bearing section of the massif, over 1,000 m thick, comprises 65% of its volume and consists of alternating layers of nephelinites, nepheline syenites, and associated rocks. Late syenites occur as relatively small intrusions, and late mafic dikes are rare. The main rock-forming minerals are nepheline, microcline, and aegirine with accessory arfvedsonite, hydrosodalite, natrolite, and sodalite.

The loparite mostly occurs as 0.2- to 0.6-mm grains and rarely as larger crystals (Smirnov 1977; Vlasov, Kuz'menko, and Yes'kova 1966). Loparite contents are highest in areas of greatest differentiation and in rocks enriched in nepheline. It is found primarily in porphyritic rocks with concentrations in the urtites and their feldspar-aegirine equivalents, juvite, and malignite. The ore, in banded horizons from several centimeters to several meters thick, grades 2% to 3% loparite (Hedrick, Sinha, and Kosynkin 1997). The loparite contains 38.5% titanium oxide, 30% to 36% REOs, and 10% to 12% niobium and tantalum oxides. In the 1990s, 30,000 tpy of loparite were concentrated locally from ore from two mines and shipped to Estonia and Kazakhstan for processing (Kogarko et al. 1995). Loparite mining has ceased in recent years, but renewed production is being considered. The loparite REE distribution is weakly enriched in LREEs relative to HREEs (Figure 6).

During the 1980s when yttrium demand exceeded supply, exploration for yttrium-rich REE deposits led to the discovery of zirconium and HREE-dominated resources that are associated with peralkaline syenitic and granitic rocks. Some have associated beryllium, niobium, and tantalum. These resources are large but have low REE contents compared with commercial LREE-dominated deposits. Richardson and Birkett (1996) give an overview of Canadian peralkaline rock-associated deposits and compare them with similar deposits worldwide.

An HREE-zirconium deposit at Pajarito Mountain in New Mexico containing 2.4 Mt of rock with 0.18% Y_2O_3 and 1.2% ZrO_2 (Scherer 1990) consists of a 10-km² dome-shaped syenite intrusion (Kelley 1968). The main zirconium-REE phase was found to be eudialyte (Mariano 1989a).

Foliated syenite at Kipawa Lake, Ontario, includes a 1,300-by-100-m zone of yttrium- and zirconium-rich rock that contains eudialyte, mosandrite, and britholite (J. Allan, personal communication). The Y_2O_3 content of this deposit is comparable to that at Pajarito Mountain, but grade varies widely within the deposit, which was intensely deformed during the Grenville orogeny.

The Strange Lake zirconium-HREE-niobium-beryllium deposit in Quebec-Labrador is in a circular peralkaline granite complex about 6 km in diameter (Currie 1985). Reserves are reported at 5 Mt containing 0.5% yttrium and 3% zirconium along with beryllium, niobium, and tantalum credits (Miller 1988), and total reserves in the complex could be much larger. Most of the REEs are in gadolinite, bastnasite, and kinosite (A.N. Mariano, personal communication). Alkaline complexes in the Shallow Lake and Letitia Lake areas in Labrador, about 250 km southeast of Strange Lake, also include rocks with high yttrium content (Currie 1976; Miller 1988). Granite- and syenite-associated HREE resources with Y_2O_3 contents of about 0.2% have also been identified at Bokan Mountain in southeastern Alaska (Barker and Mardock 1988) and at Thor Lake in the Northwest Territories, Canada (Trueman et al. 1988; Taylor and Pollard 1996).

A Late Proterozoic peralkaline syenite complex at Ilmaussaq in southern Greenland contains layers with as much as 27% eudialyte (Ferguson 1970); the discovery of ore bodies containing 0.12% Y_2O_3 and 1.2% ZrO_2 has been reported (O'Driscoll 1988). The richest layer is 3.5 m thick and contains about 1 Mt of rock that

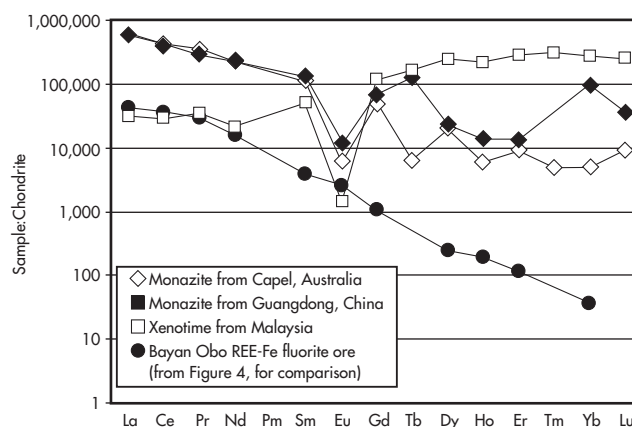


Figure 9. Chondrite-normalized plot of REE distribution (normalized to 100%) in placer monazite and xenotime (data source: Hedrick 1992)

averages 4% ZrO_2 (Steenfelt 1991). At Norra Kärr, Sweden, Middle Proterozoic eudialyte-bearing peralkaline syenite has been evaluated as a source of zirconium (Lundqvist 1980). Eudialyte from Norra Kärr contains 1.3% yttrium (Fryer and Edgar 1977).

Four Saudi Arabian deposits carrying REEs and zirconium occur in alkaline granites. The deposits include both LREE- and HREE-rich types, and estimated sizes range from 6 to 440 Mt with yttrium contents from 0.13% to 0.52% (Drysdaal et al. 1984). The Brockman deposit in northern Australia has been evaluated for zirconium, yttrium, HREEs, niobium, and tantalum. The deposit, in metamorphosed lower Proterozoic rhyolite tuff, consists of 9 Mt containing 1.3% zirconium, 0.15% Y_2O_3 , and 0.12% HREEs (O'Driscoll 1988). A deposit of altered Jurassic intrusive trachyte at Dubbo, New South Wales, Australia, is probably in this class. It contains 83 Mt with 1.9% zirconia, 0.14% Y_2O_3 , 0.12% REOs, and tantalum credits (Australian Zirconia Ltd. 2000). At Pocos de Caldas, Brazil, a Mesozoic or Early Tertiary peralkaline syenite complex 30 km in diameter (Woolley 1987) contains local concentrations of eudialyte. On the Kola Peninsula, Russia, Paleozoic peralkaline syenite complexes at Khibina and Lovozero contain large amounts of eudialyte-bearing rock (Gerasimovsky et al. 1974; Kogarko et al. 1995).

Vein Deposits

REE deposits in veins are typically small in comparison to the commercial hard-rock deposits at Bayan Obo and Mountain Pass. Nevertheless, REEs were produced from two vein deposits in Africa in the past, and more recently from two such deposits in China.

In recent years, Chinese vein deposits have become important REE sources. In 1992, production from the Maoniuping mine, Sichuan Province, and the Weishan mine, Shangdong Province, together accounted for 24% of Chinese REE production (Wu, Yuan, and Bai 1996). Both are described as bastnasite-barite-carbonate veins associated with quartz syenite. The y may be carbonatite dikes; published descriptions are not conclusive. The Maoniuping deposit, which is reportedly the second largest REE deposit in China (Pu, Chen, and Yang 2001), consists of swarms of veins and adjacent veinlets as much as 1,000 m long and 20 m wide that average about 2% REOs (Wu, Yuan, and Bai 1996). The ore mineral is coarse-grained bastnasite. Other REE minerals include chevkinite, xenotime, britholite, allanite, and monazite. Gangue minerals are barite, calcite, quartz, fluorite, feldspars, aegirine-augite,

and sulfide minerals. Ore at the Weishan mine occurs in veins as much as several hundred meters long and 1 m wide, with an average grade of 1.6% REOs. The mineral assemblage is similar to that at Maoniuping but also includes dolomite, amphiboles, thorite, titanium minerals, and niobium minerals (Wu, Yuan, and Bai 1996).

In South Africa, more than 50,000 t of monazite were produced in the 1950s and 1960s at Steenkampskraal (Neary and Highley 1984) from a monazite-apatite-quartz vein in Proterozoic granite. The vein, which occupies a shear zone, is about 300 m long and 1 m thick (Andreoli et al. 1994). Monazite comprises as much as 75% of the vein material (Overstreet 1967), accompanied by apatite, magnetite, and sulfide. The ore contains as much as 39% REOs with LREEs dominating HREEs and a pronounced negative europium anomaly (Andreoli et al. 1994). A similar monazite-apatite vein cuts Precambrian granite near Crescent Peak in Nevada about 30 km east of the Mountain Pass REE deposit (Castor 1991).

At Karonge, Burundi, in east Africa, quartz-barite-bastnasite-monazite stockwork veins that cut Precambrian quartzite and schist have produced small amounts of REEs (Notholt, Highley, and Deans 1990). The bastnasite and monazite have high LREEs typical of carbonates, but secondary cerianite and rhabdophane have abnormally high or low cerium contents because of oxidation (Van Wambeke 1977). In South Africa, small REE reserves have been estimated for britholite-bearing veins in the Pilanesberg peralkaline complex (Lurie 1986).

REE- and thorium-bearing quartz veins scattered over an area of about 250 km² at Lemhi Pass on the Idaho-Montana border in the United States comprise a REE resource of 370,000 t (Staatz, Sharp, and Hetland 1979). The mineralization is mostly LREE-dominated and averages less than 1% REOs, but some veins contain as much as 0.3% Y₂O₃ and 2.0% total REOs. A small area at Diamond Creek about 50 km northwest of Lemhi Pass contains veins with similar mineralogy but with low LREE/HREE ratios. The Snowbird occurrence in northwestern Montana is an REE resource of unknown size with 0.1% to 0.2% Y₂O₃. The REE minerals are in a Cretaceous quartz-carbonate-fluorite-parisite vein considered to be of hydrothermal origin (Metz et al. 1985). Thorite-bearing quartz-carbonate-fluorite veins at Hall Mountain near Port Hill in northernmost Idaho contain as much as 0.2% Y₂O₃. The Tertiary Bear Lodge trachyte-phonolite complex in Wyoming contains a minor REE resource in veins that average about 3% REOs (Staatz 1983), but the veins are narrow and commercial development is unlikely.

Veinlike deposits of apatite at Nolan's Bore, near Alice Springs in Australia, contain a significant amount of REEs. An inferred resource of 3.8 Mt of ore contains 4.0% REOs and 17% P₂O₅ (Anon. 2003). The REEs reportedly occur in the apatite and in REE minerals, with the latter possibly occurring as cross-cutting zones of cheralite.

Other Deposits

Some REE accumulations that do not fit into the deposit types previously discussed have had REE production or have been evaluated as possible sources. In recent years, a deposit near Aktyus in the Tien Shan Range of Kyrgyzstan has seen significant REE production. Although little information on this deposit exists in the literature, the deposit is said to contain complex ore from which lead, molybdenum, silver, and bismuth are also produced (Geological Survey of Kyrgyzstan 2004). The average REE content of the ore is reported to be 0.25%, with yttrium and HREEs making up 43.7% of the total REEs. The deposit consists of two stock-shaped bodies that contain synchisite-(Y), bastnasite, monazite, xenotime, and zircon (Roskill Information Services Ltd. 1996).

Some fluor spar deposits offer potential for REE production from associated REE minerals or from REEs that substitute for calcium in fluorite. Fluor spar mining at Naboomspruit in South Africa produced a small amount of monazite in the 1980s (Hedrick and Templeton 1991). About 65 t of bastnasite concentrate were produced from a fluor spar deposit in the Gallinas Mountains, New Mexico, in the 1950s (Adams 1965).

Near-economic HREE-uranium mineralization occurs as xenotime accumulations in sandstone of the Late Proterozoic Athabasca Group near Wheeler River in Alberta, Canada. Similar accumulations of HREEs and uranium are in quartzite in Western Australia (Mariano 1989a).

REE deposits in Vietnam are reported to contain several million tons with grades that range from 1.4% to 5% REOs with LREE- to moderate HREE-enriched distributions. The deposits have been described as crushed zones in Proterozoic limestone affected by metasomatic processes (Premoli 1989).

Marine phosphorites have been proposed as a potential source of REEs (Altschuler, Berman, and Cuttitta 1967). Certain members of the Permian Phosphoria Formation, which are mined for phosphate in large quantities in Montana and Idaho, contain significant amounts of REEs, including as much as 0.1% yttrium (Gulbrandsen 1966).

Pegmatite REE deposits are common but generally too small or too low in grade to be commercially exploited. Production of REEs from pegmatite mined for other minerals, such as feldspar or mica, however, is possible. Allanite-bearing pegmatites are relatively common, generally with high LREE/HREE ratios. In Australia's Northern Territory, a pegmatite deposit containing 1 Mt with 4% allanite was investigated as a source of REEs (O'Driscoll 1988).

ORIGIN OF DEPOSITS

The concentration and distribution of REEs in natural deposits are dependent on several petrogenetic processes, including enrichment and complexing in late-stage magmatic or hydrothermal fluids, fractionation into mineral phases, oxidation or reduction, and redistribution during weathering. LREE enrichment in igneous rocks generally is ascribed to fractionation of HREE into minerals such as garnet and pyroxene during partial melting of source materials or during fractional crystallization. In addition, an anomalously low europium/chondrite contents, a common feature in highly evolved igneous rocks of crustal derivation, are considered to be the result of Eu fractionation into plagioclase. Eu/Eu* (measured europium divided by europium calculated from interpolation between samarium and gadolinium; Henderson 1984) generally is near unity in mantle-derived rocks such as carbonatites but low in granitic rocks thought to have been derived by partial melting of crustal materials.

Lanthanum/gadolinium (La/Gd), as a measure of LREEs/HREEs, plotted against Eu/Eu* (Figure 10) is helpful in the classification of REE deposits and the interpretation of their origin. Whole rock and mineral plots for carbonatite REE deposits and laterite derived from carbonatite fall in a field of high La/Gd and Eu/Eu*. Carbonatites are considered to be mantle-derived rocks with little or no contribution from the crust. By comparison, monazite concentrates from Australian, Chinese, and Florida placer deposits plot in a tight cluster with high La/Gd and low Eu/Eu*, probably reflecting derivation from rocks that contained plagioclase or were produced by partial melting of plagioclase-bearing crustal rocks. HREE deposits in peralkaline rocks plot in a diffuse field with relatively low La/Gd and Eu/Eu*, probably because of derivation of the host peralkaline rocks from plagioclase-bearing crustal sources, and placer xenotime from Malaysia plots near the peralkaline field.

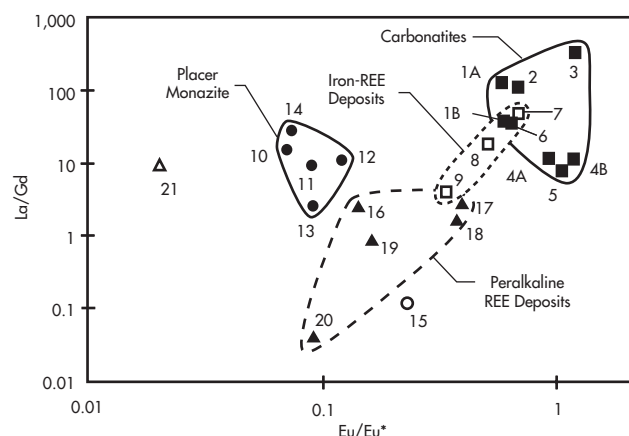
Some iron-REE deposits occupy a linear field that appears to connect the carbonatite and peralkaline HREE deposit fields, suggesting mixed crustal and mantle sources for the REEs, whereas ore from the Bayan Obo deposit plots within the carbonatite field, suggesting mantle derivation.

Most significant natural concentrations of REEs in nature are in, or associated with, alkaline igneous rocks and carbonatites. For deposits such as those at Mountain Pass, Mount Weld, Araxá, Pea Ridge, and Lovozero, this association is clear. At Bayan Obo, which emerged as the world's most important source of REEs in the 1990s, the association is less clear. Some researchers believe that the Bayan Obo deposits originated as carbonatite (Bai and Yuan 1985; Le Bas, Späth, and Yang 1997). Others believe that the deposit is hydrothermal, but call on an alkaline igneous or carbonatite source for the fluids (e.g., Drew, Meng, and Sun 1990; Yuan et al. 1992; Campbell and Henderson 1997). Still others call on mobilization of lower crustal REEs and deposition by hydrothermal activity during a protracted period of subduction (Chao et al. 1997). In addition, the Bayan Obo iron deposits have been compared to banded-iron formation deposits (Qiu, Wang, and Zhao 1983).

Hitzman, Oreskes, and Einaudi (1992) proposed a class of dominantly Proterozoic iron oxide (copper-uranium-gold-REE [Cu-U-Au-REE]) deposits that includes the Bayan Obo, Olympic Dam, Kiruna, and Pea Ridge deposits. They suggested that these deposits formed at relatively shallow crustal levels (< 4 to 6 km) from igneous-hydrothermal systems tapped by deep crustal structures associated with global rifting, possibly during break-up of a Proterozoic supercontinent. Hitzman, Oreskes, and Einaudi (1992) did not call for mantle or carbonatite-related fluids for this class of deposits, instead proposing release of large volumes of magmatic-hydrothermal fluid during magmatic underplating of the crust. By contrast, Chao et al. (1997) proposed a protracted Paleozoic lower crustal origin for REE-rich fluids at Bayan Obo on the basis of ages of amphiboles related to REE deposition. Smith (2001) noted evidence that the Olympic Dam deposit was formed from hypersaline brines and proposed that it should be placed in a separate category from Bayan Obo, which shows no evidence of such fluids.

The Mountain Pass deposit shares features with other carbonatites in the world: (1) textural and structural features that support igneous intrusive origin (Olson et al. 1954); (2) associated alkali-rich fenitic alteration; and (3) low $^{87}\text{Sr}/^{86}\text{Sr}$ (Powell, Hurley, and Fairbairn 1966; E. DeWitt, personal communication). But the shape of the carbonatite ore body, its ultrapotassic alkaline association (most carbonatites are associated with alkaline rocks that are dominantly sodic), and chemistry (it is unusually low in iron, phosphorus, and niobium for REE-rich carbonatite) suggest that its source was different than that of most other carbonatites (Castor and Nason 2004). The chemistry of the ultrapotassic alkaline rocks at Mountain Pass suggests that they were derived from primitive or depleted mantle mixed with an enriched mantle or crustal component, and the carbonatite likely came from a similar source. The Mountain Pass LREE deposit occurs in a northeasterly-trending belt of anorogenic Middle Proterozoic plutonism that crosses the North American continent (Anderson 1983) and contains eight Middle to Late Proterozoic REE deposits (Castor 1993, 1994).

Although there are mineral and chemical similarities between the Mountain Pass and Bayan Obo deposits, there are also major differences. Like the Bayan Obo ore, the Mountain Pass carbonatite ore has extreme LREE enrichment with no europium anomalies (Figure 4) and low $^{87}\text{Sr}/^{86}\text{Sr}$. As at Bayan Obo, alkali-rich alteration is associated with the Mountain Pass carbonatite; in both areas, alteration assemblages include sodic amphibole and potash feldspar



Location No.	Deposit Name and Type	Location No.	Deposit Name and Type
1A	Mountain Pass bastnasite	12	South China placer monazite
1B	Mountain Pass monazite	13	Florida placer monazite
2	Kangankunde REE-rich carbonatite	14	Brazil placer monazite
3	Kizilçören REE-rich carbonatite	15	Malaysia placer xenotime
4A, 4B	Salitre II perovskite and anatase	16	Strange Lake peralkaline igneous HREE deposits
5	Mount Weld carbonatite	17	Kipawa Lake eudialyte
6	Maicuru REE-rich carbonatite	18	Bokan Mountain peralkaline igneous HREE deposits
7	Bayan Obo ore	19, 20	Jabal Sa'id and Jabal Tawlah peralkaline igneous HREE deposits
8	Pea Ridge breccia	21	Crescent Peak vein deposit
9	Mineville apatite		
10, 11	Western and Eastern Australia placer monazite		

Figure 10. Plot of La/Gd against Eu/Eu* for some REE-rich mineral concentrate and rock samples (data sources: Deans 1966; Fryer and Edgar 1977; Qiu, Wang, and Zhao 1983; Drysdall et al. 1984; Hedrick 1985; Roeder et al. 1987; Barker and Mardock 1988; Nelson et al. 1988; Mariano 1989a; Costa et al. 1991; G. Morteani, personal communication; L. Tucker, personal communication)

(Olson et al. 1954; Drew, Meng, and Sun 1990). The Bayan Obo and Mountain Pass deposits are both enriched in barium and fluorine (Wu, Yuan, and Bai 1996; Castor and Nason 2004). Samples of Bayan Obo ore, however, have an average BaO content of about 2.4%, and a maximum barium content of 7.7% (based on data from Chao et al. 1997), much lower than Mountain Pass ore (Table 5). The fluorine content of Bayan Obo ore, which averages more than 9%, is much higher than that of Mountain Pass ore, and Bayan Obo ore also has higher phosphorus and niobium contents (Table 5). Deposits such as those at Bayan Obo, Pea Ridge, and Mineville are clearly different from Mountain Pass in their association with large amounts of iron. Whereas Mountain Pass ore contains about 10 times as much bastnasite as monazite, Bayan Obo deposits contain approximately equal amounts of bastnasite and monazite (Y. Qiu, personal communication), although bastnasite-rich ore is selectively mined. REE-chondrite patterns for Bayan Obo show enrichment in HREEs relative to Mountain Pass (Figure 4). Finally, the ultrapotassic alkaline intrusions that are associated with the Mountain Pass carbonatite are not found at Bayan Obo. On the basis of its relatively high P, Fe, and Nb contents, if the Bayan Obo deposit has a carbonatite-related origin, it is probably to a nepheline-carbonatite system rather than to an ultrapotassic-carbonatite system as at Mountain Pass.

The chemical compositions and mineral assemblages of most vein-type REE deposits suggest a genetic relationship with carbonatite-alkaline complexes. Such a relationship has been proposed for

the Karonge, Burundi, veins (Van Wambeke 1977). The monazite-apatite vein at Crescent Peak, Nevada, though, has REE distribution that includes a prominent negative europium anomaly that suggests a different origin than the Mountain Pass deposit 30 km away.

Although REE minerals are considered to be relatively unaffected by weathering, some lateritic REE deposits show signs of mobilization and redeposition of REEs. Residual concentration of REE minerals such as monazite is possible in laterite, and Morteani and Preinfalk (1996) reported that the REEs behaved as rather immobile elements in laterites at Araxá and Catalão in Brazil. Differences in REE distributions in different lateritic deposits may result from differences in parent rocks. For instance, Morteani and Preinfalk (1996) noted that REE distributions in the Araxá and Catalão laterites mirrored those in underlying alkaline rocks, and the very different REE distributions in the Xunwu and Longnan deposits in southern China (Figure 6) may be caused by different REE distributions in the parent rocks. As noted by Mariano (1989a), however, development of REE mineralization in laterites does not require derivation from independent REE minerals in the parent rock but may come from REEs in minerals that are less resistant to breaking down during weathering. Fractionation of the REE elements clearly takes place during weathering, as indicated by differences in REE distributions at different levels in the weathering cap above the Mount Weld carbonatite (Lottermoser 1990; Figure 8). The production of cerium anomalies (either positive or negative) during the breakdown of REE-bearing minerals in an oxygen-rich environment is to be expected; however, laterite deposits may or may not show such fractionation (compare Figure 8 with Figure 6). Mariano (1989b) proposed that differences in the mineral assemblages in carbonatite-derived laterites may result from factors other than parent rock composition, such as age, depth of weathering, and geomorphology.

TECHNOLOGY

Exploration Techniques

Geologic conditions favorable for REE deposits are widespread, but most of the world's hard-rock deposits are restricted to areas underlain by Precambrian rock. The Bayan Obo deposits, which are in Proterozoic rock, were originally discovered as ridge-forming surficial deposits of dark brown and black iron oxide (Argall 1980). Carbonatite REE deposits and many HREE deposits occur in or are associated with alkaline rocks in circular complexes, generally in Precambrian host rocks. Such complexes may be identified using aerial photography, even in deeply weathered and highly vegetated areas. Although isolated alkaline-carbonatite complexes such as Mount Weld in Australia do occur, most are in clusters or linear belts like those associated with rift zones in eastern Africa and the Araxá-Catalão belt in Brazil.

Sources for placer REE deposits include granitic rocks or high-grade metamorphic rocks, or both. Coastal monazite-bearing placers in Western Australia, Brazil, India, Sri Lanka, and the southeastern United States were derived from highly metamorphosed Precambrian shield rocks; whereas monazite and xenotime-producing placers in Eastern Australia, Malaysia, Indonesia, China, and Korea were eroded from Phanerozoic granites, including tin-rich granites. Sources of monazite, euxenite, and xenotime in Idaho placers include both highly metamorphosed Precambrian rocks and Mesozoic granitic rocks.

Because REEs are associated with thorium and uranium, radiometric exploration techniques are extremely useful in REE exploration. REE-rich carbonatite at Mountain Pass was discovered during surface prospecting for uranium using a geiger counter (Olson et al. 1954). Many other REE deposits were found by surface or airborne radiometric surveying. Although most placer REE

deposits yield only subtle radiometric signatures, careful data collection and analysis can be used to locate favorable intrabasin areas or horizons.

Geochemical prospecting using heavy-mineral concentration of active stream sediments can be very effective because most REE minerals are relatively heavy and resistant. Concentrates made by hand panning, mechanized gravity concentration, or heavy media separation can be analyzed for REEs using inexpensive multielement analytical techniques. Because many REE minerals are resistant to chemical breakdown, use of analytical methods that do not require dissolution, such as x-ray fluorescence or neutron activation analysis, is desirable, or care must be taken to use methods that assure total dissolution when using a technique such as inductively coupled plasma (ICP) spectroscopy. During prospecting for REE placer deposits in Idaho, the senior author found that favorable basins yield heavy-mineral concentrates with 1% or more cerium and 0.1% or more yttrium. Splittings of heavy-mineral concentrates taken during exploration should be saved so mineral determinations can be performed using microscopic or other techniques.

Regional geochemical surveys can be used to find igneous rocks that are likely to host or be associated with REE deposits. Carbonatite deposits were delineated in Greenland using multielement analysis of fine stream sediment samples collected at a density of 1 sample/30 km² (Steenfelt 1991). The Magnet Cove alkaline-carbonatite complex in Arkansas was delineated using REEs, titanium, and fluorine contents of stream silt samples collected at a density of 1 sample/10 km² (Sadeghi and Steele 1989). Peralkaline rocks that host HREE deposits in Greenland were delineated using niobium content in fine stream sediments collected at 1 sample/6.25 km² (Steenfelt 1991). The Strange Lake deposit in Canada was discovered using regional lake water and sediment surveys, with subsequent tracing of glacially transported boulders that were initially recognized 20 km from their source (Richardson and Birkett 1996).

Biogeochemical prospecting may be useful in defining buried REE targets. REE contents of plant ash have been analyzed in areas that contain pegmatitic and vein occurrences in Finland and Canada, and extreme LREE enrichment has been noted in plant ash from the Bayan Obo area (Dunn 1995).

Normal surface exploration techniques, such as trenching and pitting by heavy equipment, are used to evaluate poorly exposed REE deposits. Exploratory dredging is used to locate beach placer deposits. In countries with low labor costs, hand pitting may be used to evaluate placer deposits or unconsolidated deposits such as those in laterite.

Drilling techniques utilized for hard-rock REE exploration and prospect evaluation are mainly core drilling and dual-tube rotary or hammer drilling. The method of choice for most heavy-mineral placer evaluations is dual-tube rotary drilling. The collection of large samples, such as are necessary to evaluate gold placers, generally is not needed because the nugget effect is not a factor in most heavy-mineral sands that contain REEs.

Because of the economic importance of differences in processing REE-bearing minerals, identification of the REE-bearing phases in prospective deposits is important. Light-colored REE minerals, such as bastnaesite and monazite, may generally be distinguished by a green luminescence when illuminated by a mercury vapor light (Murata and Bastron 1956). A conventional black light with the purple filter removed may be used for this test. This luminescence, which is caused by absorption and indicates the presence of significant amounts of neodymium, has been used successfully for preliminary REE-grade determination during core logging at Mountain Pass. Because the test is based on neodymium content,

HREE minerals may not respond. Absorption bands in the visible spectrum may also be used to distinguish REE minerals with the aid of a hand spectroscope (Mertie 1960).

Geophysical methods that can be used to search for buried iron-REE deposits and some REE carbonatite deposits include gravity surveys and airborne or surface magnetic surveys. The effectiveness of such methods is based on anomalous density and magnetic susceptibility of a deposit and the associated rocks. Because many carbonate complexes have a central carbonatite mass surrounded by mafic alkaline rocks, a common signature is a magnetic bull's-eye with high central values combined with a centrally located gravity low and a concentric gravity high. The Mountain Pass carbonatite, however, does not follow this pattern because of its high density (caused by abundant barite and bastnaesite) and lack of magnetite. The Mount Weld carbonatite was discovered during interpretation of a regional aeromagnetic survey, and its detailed magnetic expression exhibits concentric zoning (Gunn and Dentith 1997). Other geophysical techniques include seismic surveys, which may be used in conjunction with drilling to determine the depth to bedrock of placer deposits.

Mining

At Mountain Pass, REE ore was mined until October 2001 in an open pit approximately 150 m deep using 80-t haul trucks and a 10-m³ shovel. Blast holes drilled at 3 to 4 m spacing were assayed for total REOs and other elements by x-ray fluorescence methods. Approximately 300,000 tpy were mined with a stripping ratio of 5:1 or higher. The ore was crushed using jaw and impact crushers at the upper lip of the pit and fed to an adjacent mill. Mining operations may be restarted in 2006 following governmental approval for pit expansion and a new tailings disposal site; however, newly enacted California mining regulations could block the resumption of mining.

At Bayan Obo, iron and REE ore is mined from two large open pits at a rate of at least 15,000 tpd using electric shovels and rail haulage (Argall 1980). Because water is lacking near the mine, crushed ore is hauled about 150 km by railroad to milling facilities at Baotou. According to Argall (1980), there was no selective mining at Bayan Obo to maximize production of any group of minerals. Originally, REO minerals may have been recovered from iron ore waste. According to Jackson and Christiansen (1993), however, REO in the iron ore is locked in slag during refining and is not recovered, and REO is produced strictly from bastnaesite ore that occurs in certain zones. According to L. Drew (personal communication), during the late 1980s, REE ore came from areas mined specifically for REE production, although iron ore and REE ore were hauled on the same trains to Baotou, where most cars were routed to steel mills and some to nearby REE processing facilities. During the 1990s, REE ore enrichment by hand cobbing was witnessed at the mining operation.

Russia's loparite was mined as a primary product by underground and open-pit methods from ore bodies in the Lovozero alkali massif near the city of Revda. The mining company, Lovozersky GOK, has plans to reopen and expand its mining capacity to 2.6 Mtpy of ore; however, problems with downstream processing of loparite concentrate in Estonia probably precludes expansion in the near future.

REE placer mining is done by either dry land mining or by dredging techniques. Although Australia does not currently export monazite from titanite and zircon placer operations, descriptions of the placer mining operations in that country are probably representative of placer mining that yields monazite and xenotime elsewhere. Dredges with capacities of as much as 2,800 tpy (Anon.

1987) were used in the 1980s to mine beach and dune sand deposits, particularly along the east coast. Dry land techniques, including loader and truck, scraper, drag line, or bucket wheel mining, are used for most of the heavy mineral sand mining in Western Australia (Griffiths 1984).

Processing

Flotation was used at Mountain Pass to make a bastnaesite concentrate containing about 60% REOs until late in 2001. Figure 11 is a simplified flow chart for concentrate production at Mountain Pass. This concentrate was used either (1) on site as feed for chemical separation of REEs; (2) leached with dilute HCl to produce a 70% REO concentrate; or (3) shipped as is. Current sales are from stockpile. Flotation that produces concentrate containing about 60% REOs is used at Baotou to process REE ore from the Bayan Obo deposit. In Russia, loparite ore was processed using gravity and electromagnetic separation methods to produce a 95% loparite concentrate. The mill has the capacity to produce about 6,500 t of contained REOs in loparite concentrate annually, and an expansion to 12,500 t of capacity is planned.

REE minerals are separated commercially from associated minerals in placer deposits using a combination of gravity, magnetic, and electrostatic techniques (Griffiths 1984). Figure 12 is a typical beneficiation flow diagram for monazite and xenotime. Gravity methods include the use of jigs, spiral and cone concentrators, and shaking tables. Sizing and preconcentration commonly is performed at the mine site by trommels, shaking screens, and gravity separation. Many dredges have such facilities on board or utilize floating preconcentration plants.

REE extraction from monazite and xenotime is accomplished by dissolution in hot concentrated base or acid solutions. During past processing of monazite ore, REEs were extracted using a concentrated solution of sodium hydroxide at 140 ° to 150 °C (Kaczmarek 1980). After cooling, hydroxides of REEs and thorium were recovered by filtration, and thorium was separated by dissolution and selective precipitation. Monazite and xenotime also have been processed using hot sulfuric acid digestion and water leaching to remove phosphate. This is followed by selective precipitation of thorium during dilution and precipitation of REEs as double sulfates.

At Mountain Pass, bastnaesite was calcined to drive off CO₂ and fluorine and leached with HCl to dissolve most of the trivalent REEs (Figure 11). The residue, which consists mostly of CeO₂, was sold as a polishing abrasive. At Baotou, Bayan Obo REE mineral concentrate is baked with sulfuric acid at 300 °C to 600 °C and leached with water, taking REEs into solution and precipitating other elements as waste (Chegwidden and Kingsnorth 2002). REEs are then precipitated as double sulfates and converted to hydroxides, which are leached with HCl for purification using solvent extraction (SX) and other methods. Because this method is very similar to placer monazite processing, the Bayan Obo concentrate is assumed to contain significant amounts of monazite.

Russian loparite concentrate is produced by a mill with the capacity to generate about 6,500 tpy. The concentration process uses gravity and electromagnetic separation methods, and yields a concentrate containing 95% loparite. The mill also produces aegirine and nepheline-feldspar concentrates. If mining expansion plans move forward, expansion of the mill will produce 3,000 t of loparite concentrate in a pilot phase followed by 12,500 t in the commercial phase. Additional expansion, if warranted, would increase loparite concentrate capacity to 25,000 tpy.

Russian loparite concentrate is processed using gaseous chlorination at high temperature in the presence of reducing agents

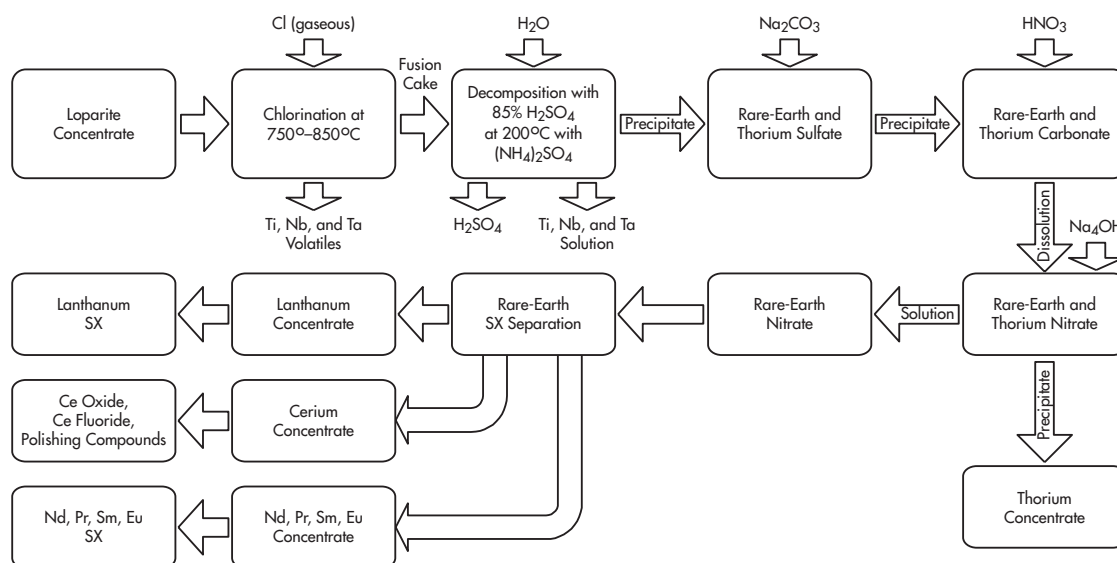


Figure 13. Loparite refinery flow diagram (Irtys, East Kazakhstan Oblast, Kazakhstan, and Sillamjõe, Estonia)

(Mikhailichenko, Mikhlin, and Pattrikeev 1987). The more volatile chlorides of titanium, niobium, and tantalum are separated from the less volatile chlorides of REEs and other elements, which remain as a fusion cake (Figure 13). The fusion cake is dissolved in hot sulfuric acid in the presence of ammonium sulfate (Kosynkin et al. 1993). The solution is diluted with water, dropping out double sulfates of rare earths and thorium that are converted to carbonates by the addition of sodium carbonate. The carbonate is dissolved in nitric acid, and thorium is precipitated by raising solution alkalinity (Hedrick and Sinha 1994) or by solvent extraction. The remaining rare earth nitrate solution is separated and purified by selective precipitation and solvent extraction.

Because of their chemical similarity, the trivalent REEs are difficult to separate. Although fractional crystallization and ion-exchange techniques are used to separate them in small amounts, commercial separation generally is done using liquid-liquid solvent extraction (Kaczmarek 1980). This process consists of addition of a solvent composed of a mixture of organic compounds to the pregnant aqueous solution in a series of mixing/settling cells that allow repetitive fractionation during a more-or-less continuously flowing process. Figure 14 is a simplified diagram of the SX process used at Mountain Pass. Following precipitation and drying, specific REE compounds with purities in excess of 99.99% can be produced by this process. At Mountain Pass, a REE fraction produced during SX was treated to separate europium by reduction to the divalent state, with ultimate purification as europium oxalate (D. Witham, personal communication). Other individual REE compounds were precipitated as hydroxides, carbonates, and oxalates following complex iterative SX processes.

Specifications and Testing

Specifications for REE mineral concentrates, compounds, and metals vary depending on use. Purity specifications for some compounds may be determined by reference to Table 6. Testing of REE products mainly consists of purity determinations. In addition to specific wet chemical analytical procedures, the most effective techniques used to test products for individual REE content are x-ray fluorescence, ICP emission spectroscopy, and instrumental

neutron activation analyses. Impurities, such as phosphate, silica, lead, and thorium, may be deleterious to product utilization or the environment. The need to limit such impurities depends on use. Physical specifications, such as particle-size distribution, color, and moisture content, also are important for some products.

Advances in processing in recent years have removed markets for some relatively low-spec REE products. For instance, a 90% cerium oxide product used mainly by the glass industry and manufactured cheaply for years at Mountain Pass has been supplanted by higher-grade cerium products with little or no price increase.

ECONOMIC FACTORS

Prices

REE mineral concentrates and intermediate compounds had relatively steady price and production increases from the 1960s through the 1980s, when markets were created in response to new technologies (Castor 1994), while REE sources remained relatively steady. In recent years, prices for REE concentrates and intermediate compounds can be considered expensive when compared with many other mineral products (Table 6) and have lagged behind inflation. REE production increases accelerated following significant Chinese impact on the market in the 1990s (Figure 1), while prices for all REE commodities have decreased (Table 7). Therefore, despite a total annual production increase on the order of 300% since the early 1980s, the overall dollar value of the REE market has probably remained static or even decreased.

Prices for individual REOs and metals were generally lower in the late 1990s and early 2000s than in the 1960s, 1970s, and 1980s. Individual REE compounds vary widely in value (Table 7), mostly because of relative abundance and production costs. The most expensive REE is the heaviest—lutetium, which sold as the high-purity oxide for as much as \$9,000/kg in 1989 (Hedrick 1991a) and declined to a low of \$2,400/kg in 2003. Metallic REEs typically have higher prices than their equivalent oxides or other compounds. Mischmetal, a mixture of metallic REEs, was quoted at \$12.35/kg at the end of 1989 (Hedrick 1991a). During the 1980s, individual REE prices generally were static or increased slightly, but, since then, market changes have caused price decreases for individual

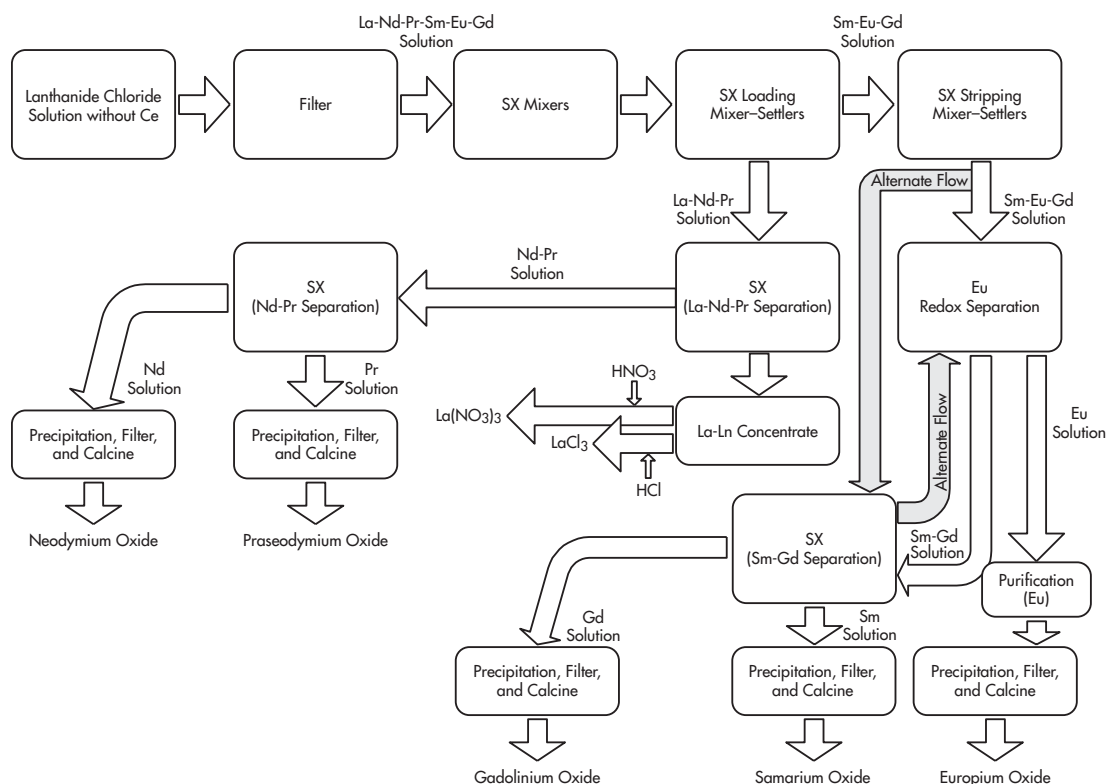


Figure 14. Rare earth SX flow diagram (Mountain Pass, California)

Table 6. U.S. prices for rare earth concentrates and compounds in 2003

Product	Purity,* %	Quantity, kg	Price,† \$/kg‡
Concentrates§			
Bastnasite concentrate, unleached	58–63	500	3.64 (contained LnO basis)
Bastnasite concentrate, leached	68–73	500	4.08 (contained LnO basis)
Bastnasite concentrate, leached and calcined	85–90	500	5.51 (contained LnO basis)
Lanthanum hydrate	75 minimum	907	5.51 (contained LnO basis)
Lanthanum-lanthanide chloride	46	159	3.20 (contained LnCl basis)
Oxides**			
Lanthanum	99.5	1	12.00
Cerium	99.5	1	18.00
Praseodymium	99.5	1	30.00
Neodymium	99.5	1	18.00
Samarium	99.9	1	58.00
Europium	99.99	1	1,120.00
Gadolinium	99.9	1	55.00
Terbium	99.9	1	440.00
Dysprosium	99.5	1	90.00
Holmium	99.9	1	245.00
Erbium	99.9	1	135.00
Thulium	99.9	1	1,950.00
Ytterbium	99.9	1	360.00
Lutetium	99.9	1	2,400.00

* Purity as total lanthanide (Ln) oxides equivalent.

† Prices are nominal and subject to change on a daily basis, priced on a contained Ln oxide or Ln chloride basis.

‡ Prices for metric-ton quantities or long-term contracts are typically lower.

§ Rare earth concentrate prices from Molycorp, Inc., free on board (f.o.b.) Mountain Pass, California.

** REO prices from Hefa Rare Earth Canada Co. Ltd., 1 kg quantity, f.o.b. Vancouver, Canada.

Table 7. Comparative U.S. prices for rare earth metals and oxides, US\$/kg

Oxides*	Year				
	1963†	1973‡	1983§	1993**	2003††
Lanthanum	12	10	19	19	12
Cerium	17	11	20	23	18
Praseodymium	88	71	130	37	30
Neodymium	66	26	80	88	18
Samarium	99	66	130	66	58
Europium	1,411	992	1,900	992	1,120
Gadolinium	176	99	140	121	55
Terbium	860	606	1,200	827	440
Dysprosium	187	88	110	132	90
Holmium	254	265	650	485	245
Erbium	187	99	200	143	135
Thulium	2,756	2,205	3,400	2,750	1,950
Ytterbium	331	187	225	220	360
Lutetium	7,661	4,409	5,200	5,500	2,400
Yttrium	119	66	94	80	52

Metals‡‡	Year				
	1963§§	1973***	1983†††	1993†††	2003§§§
Lanthanum	309	88	125	150	25
Cerium	304	88	125	350	30
Praseodymium	386	353	310	540	70
Neodymium	386	220	260	340	30
Samarium	397	298	330	300	80
Europium	3,307	5,952	7,500	7,600	1,600
Gadolinium	463	463	485	500	78
Terbium	2,315	1,543	2,800	2,800	630
Dysprosium	661	265	300	500	120
Holmium	661	606	1,600	1,400	350
Erbium	664	309	650	725	180
Thulium	8,378	5,291	8,000	6,500	3,000
Ytterbium	1,047	507	875	1,200	484
Lutetium	9,370	12,125	14,200	13,000	4,000
Yttrium	717	309	430	340	96

* REO prices from U.S., French, and Chinese producers.

† Cerium and lutetium prices from American Potash & Chemical Corp., 2–99-lb quantity, f.o.b. Chicago, Illinois; all other REO prices from Michigan Chemical Corp., 2–99-lb quantity, 99.9% purity, f.o.b., St. Louis, Missouri.

‡ REO prices from Research Chemicals, Inc., 2–49-lb quantity, 99.9% purity, f.o.b., Phoenix, Arizona.

§ REO prices from Research Chemicals, Inc., 1–5-kg quantity, 99.9% purity, f.o.b., Phoenix, Arizona.

** Holmium, thulium, ytterbium, lutetium, and yttrium oxide prices from Rhône-Poulenc Basic Chemicals Co., 1-kg quantity, f.o.b. Phoenix, Arizona; all other oxide prices from Molycorp, Inc., 25–300-lb quantity, f.o.b. Mountain Pass, California.

†† REO prices from Hefa Rare Earth Canada Co. Ltd., 1-kg quantity, 99.5%–99.99% purity, f.o.b. Vancouver, Canada.

‡‡ Rare earth metal prices from U.S., French, and Chinese producers.

§§ Rare earth metal prices from American Potash & Chemical Corp., 1–4-lb quantity, f.o.b., Chicago, Illinois.

*** Rare earth metal prices from Research Chemicals, Inc., converted from 2–10-lb ingot price, f.o.b., Phoenix, Arizona.

††† Rare earth metal prices from Research Chemicals, Inc., 1–5-kg quantity, ingot price, f.o.b., Phoenix, Arizona.

‡‡‡ Rare earth metal prices from Rhône-Poulenc Basic Chemicals Co., 1–5-kg quantity, ingot price, f.o.b., Phoenix, Arizona.

§§§ Rare earth metal prices from Hefa Rare Earth Canada Co. Ltd., 1-kg quantity, 99.5%–99.99% purity, f.o.b. Vancouver, Canada.

Table 8. REE uses and applications by industry

Automotive	Catalysts for pollution control; catalytic converter catalyst substrate; rechargeable batteries; fuel cells; colored plastics
Ceramics	Oxygen sensors; structural ceramics for bearings; jet engine coatings; investment molds; refractories; pigments
Chemicals	Oil refinery fluid cracking catalysts; pharmaceuticals; water treatment; catalysts; moisture control, dryers, and detection
Defense	Lasers; missile guidance and control; visual displays; radar; electronic countermeasures; communication; shielding
Electronics	Capacitors; cathodes; electrodes; semiconductors; thermistors; traveling wave tubes (TWTs); radio frequency circulators and toroids; yttrium iron garnet (YIG) ferrites
Glass	Polishing compounds; decolorizing; coloring; increase refraction; decrease dispersion; radiation stabilization; absorber
Illumination	Trichromatic fluorescent lamps; mercury lamps; carbon arc lamps; gas mantles; auto headlamps; long-glow phosphors
Magnets	Speakers and headphones; linear motors; antilock braking systems; tape and disk drives; gauges; electric motors; pumps; ignition
Magnetostrictive	Sonar systems; precise actuators; precision positioning; vibratory screens; speakers; ultrasonics to kill bacteria
Medical	Contrast agents; magnetic resonance imaging (MRI); positron emission tomography (PET); radioisotope tracers and emitters
Metallurgy	Alloying agents in aluminum, magnesium, iron, nickel, and steel alloys; superalloys; pyrophoric alloys; lighter flints; armaments
Phosphors	Cathode-ray tubes (CRTs); fluorescent lighting; radar and cockpit displays; x-ray intensifying screens; temperature sensors
Other	Simulated gemstones; textiles; magnetic refrigeration; hydrogen fuel storage; lubrication; photography; nuclear uses

REE commodities. Samarium oxide, for which demand often exceeded supply during the late 1980s, sold for \$187/kg in 1988 but currently is available at \$58/kg because neodymium-iron-boron magnets have supplanted much of its market share. Europium oxide also has decreased in price from about \$2,000/kg in 1980 to \$1,120/kg in 2003. REE prices are generally lower for metric-ton quantities or long-term contracts.

Yttrium raw materials varied greatly in price during the 1980s, selling for as much as \$50/kg for contained Y₂O₃ in a 60% concentrate in the mid-1980s, retreating to \$32/kg by 1989. In the 1990s, yttrium-enriched ion-adsorption lateritic clays from southern China began supplying increasing amounts of low-cost yttrium oxide, significantly reducing demand for other yttrium concentrates derived from monazite and xenotime. The availability of low-cost yttrium oxide (\$7 to \$10/kg in metric-ton quantities in 2003) has essentially eliminated the competition in yttrium concentrate.

Rare Earth Uses and Markets

REEs are used in a wide variety of applications (Table 8). Comprising one of the widest ranges of consumer products of any element group, their usage is believed to be a significant economic indicator. Traditional REE applications in lighter flints, carbon arc lighting, and iron and steel additives have declined from 75% of the overall international REE market in the 1950s to about 20% in the 2000s.

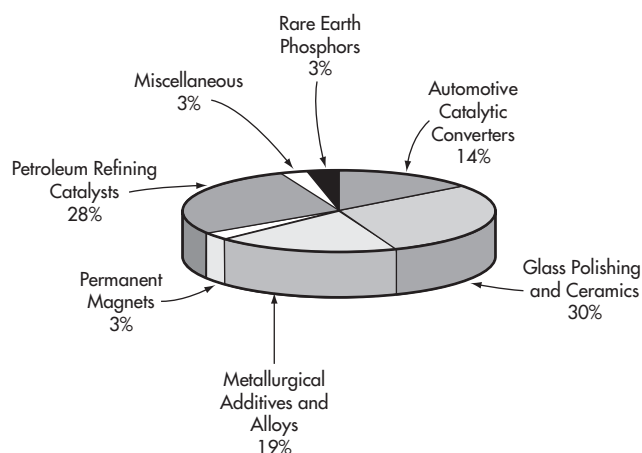


Figure 15. Rare earth markets by weight

Uses in glass polishing and ceramics are the largest market for REE commodities by weight (Figure 15). Substantial amounts of cerium concentrates and cerium oxide are used in glass-polishing applications. The automotive catalyst industry also consumes significant REEs by weight, using cerium carbonate and cerium oxide in the catalyst substrate and as a component of the converter's oxidizing catalyst system. During the 1980s, REE production increases resulted from the rising use of cerium in automotive catalytic converters (O'Driscoll 1988). The use of lanthanum-rich mixed REE compounds in fluid cracking catalysts (FCCs) in petroleum refining also has been a major market (Figure 15). Although this application initially declined substantially in the mid-1980s when legislation mandated the use of unleaded fuels, the yield of gasoline and other light-fraction products was so reduced that consumption of REE-containing FCCs were restored. Phosphors, electronics, and laser crystals provide relatively minor markets by weight, although most are high value.

Although it only comprises 3% of REE production by weight, the phosphor market is probably the most important in terms of dollar value. Beginning in the 1960s, color television manufacturers spurred demand for high-value REE phosphors based on yttrium and europium; later, gadolinium and terbium compounds were added as phosphors. More recently, their use in trichromatic phosphors in fluorescent lighting resulted in increased production.

The introduction of high-strength samarium-cobalt permanent magnets developed by Karl Strnat in the 1970s, particularly for use in small electric motors and headphones, created a dynamic new REE market. Although higher-strength, lower-cost neodymium-iron-boron permanent magnets are now substituted for the more expensive samarium-cobalt magnets in most applications, samarium-cobalt magnets are still used in applications requiring higher temperatures.

Proposed new uses have increased a awareness of potential profits in REE raw materials. Superconducting substances containing lanthanum or yttrium have been in the spotlight since 1986. Volume markets for these substances, however, await further technological breakthroughs. New methods have been devised for REEs used in hydrogen-based refrigeration and energy storage. Market expansion for yttrium has provided an incentive for increased production from HREE deposits. In addition to its use in television, computer, and lighting phosphors, yttrium has found increased use in stabilized-zirconia ceramics applied in structural parts, bearings,

oxygen sensors, simulated gemstones, golf clubs and shoe cleats, shirt buttons, and coatings in the exhaust section of jet engines.

Although worldwide demand for REEs has had a general upward trend for many decades, REEs' economics are as complex as their chemistry. Because individual REEs occur together in most deposits in fixed ratios, the economic riddle is how to balance production against market demand. To accomplish this, each REE must be assigned a factor based on its natural abundance in the ore mineral in order to develop marketing equations, such as determination of price. Complexity of these equations are enhanced by variations in separation and purification costs between the REEs. In addition, markets for individual REEs may change rapidly because of technological changes and other factors. Marketing variability may also lead to stockpiling of unmarketable REE fractions and products by producers.

The principal source of REE ores is China, with smaller amounts available from India, Kazakhstan, Kyrgyzstan, Malaysia, Russia, Thailand, and the United States. Refined rare earth products, including compounds, metals, and alloys, are primarily produced in China and France.

U.S. imports were dominated by Chinese material in 2003, with 75% of domestic imports, by weight. France, with 10%, was the next largest source of U.S. imports (down from 30% in 2000), and Japan was third, with 4%. France and Japan, however, do not mine REEs and source the majority of their supplies from China. Therefore, the amount of Chinese REEs that the United States actually imported in 2003 was probably 89%. For the rare earth trade categories of domestic imports, the percentage of shipments supplied by China, by weight, were as follows:

- Cerium compounds: 84%
- Yttrium compounds: 63%
- Individual REE compounds (except cerium): 64%
- Mixtures of REOs (except cerium): 97%
- REE metals (intermixed or interalloyed): 73%
- Mixtures of REE chlorides: 94%

China was the leading source of materials for all rare earth import categories except ferrocerium and other pyrophoric alloys, a small volume trade category supplied mainly from France, at 82% of the import market.

In the mid-1980s, U.S. imports exhibited a very different distribution, at lower quantities because of high REE production from Mountain Pass. The leading supplier of domestic imports in 1985 in each category by percentage of shipments by weight, were as follows:

- Cerium compounds (except oxide): France, 89%
- Cerium oxide: France, 98%
- Individual REOs (excluding cerium): France, 84%
- REE alloys (including mischmetal): Brazil, 87%
- REE metals: former U.S.S.R., 65%
- Other REE metals: Federal Republic of Germany, 21%
- Ferrocerium and other pyrophoric alloys: France, 59%

In 1985, the majority of rare earth imports came from France, at 48%, with China supplying only about 1%.

Domestic production trended upward from the 1960s, when bastnasite production from Mountain Pass became commercially available, to the 1990s. Concentrate production at Mountain Pass ceased during 2001, when the mine and mill were put on standby status. Stocks of bastnasite concentrates and some REE intermediate and purified compounds are available from stockpiles, however.

Table 9. Harmonized Tariff Schedule for rare earth commodities imported into the United States in 2004

Heading/ Subheading Codes	Article Description	Normal Trade Relations	Non-normal Trade Relations	Special Program Codes*
2530.90.8050	Mineral substances not elsewhere specified or included; rare earth metal ores, e.g., xenotime (complex phosphate) and gadolinite, ytterbite, and cerite (complex silicates)	Free	0.3¢/kg	
2612.20.0000	Thorium ores and concentrates; rare earth metal ores, e.g., monazite (thorium and rare earth phosphate)	Free	Free	
2805.30.0000	Rare earth metals, including scandium and yttrium, whether intermixed or interalloyed, ad valorem	5.0% ad valorem	31.3% ad valorem	Free A+, CA, CL, D, E, IL J, JO, MX, 3.7% (SG)
2846.10.0000	Cerium compounds, including oxides, carbonates, hydroxides, nitrates, sulfates, chlorides, oxalates, and so forth	5.5% ad valorem	35% ad valorem	Free A, CA, CL, E, IL, J, JO, MX, 4.1% (SG)
2846.90.2010	Mixtures of rare earth oxides, including yttrium and scandium, other than cerium oxides	Free	25% ad valorem	
2846.90.2050	Mixtures of rare earth chlorides, except cerium chloride	Free	25% ad valorem	
2846.90.4000	Yttrium-bearing materials and compounds containing by weight >19% but <85% yttrium oxide equivalent	Free	25% ad valorem	
2846.90.8000	Rare earth compounds, including individual REOs, rare earth hydroxide, rare earth nitrate, and other compounds (excludes cerium compounds, mixtures of REOs, and mixtures of rare earth chlorides)	3.7% ad valorem	25% ad valorem	Free A, CA, CL, E, IL, J, JO, K, MX, SG
2844.40.0020	Other radioactive elements, isotopes, and compounds (includes promethium, gadolinium 157, and so forth)	Free	Free	
3606.90.3000	Ferrocium and other pyrophoric alloys	5.9% ad valorem	56.7% ad valorem	Free A+, CA, CL, D, E, IL, J, JO, MX, 4.4% (SG)
7202.99.5040	Other ferrosilicon alloys, containing by weight not more than 55% silicon, other (e.g., rare earth silicide)	Free	4.4¢/kg on silicon content	

* Products eligible for special tariff treatment:

A = Generalized System of Preferences (GSP) (duty-free treatment).

A+ = Only imports from least-developed beneficiary developing countries eligible for GSP under that subheading (duty-free treatment).

CA = North American Free Trade Agreement (NAFTA) for Canada (duty-free treatment).

CL = Chile Special Rate.

D = Africa Growth and Opportunity Act (duty-free treatment).

E = Caribbean Basin Initiative (CBI).

IL = Israel Special Rate (duty-free treatment).

J = Andean Trade Preference Act (ATPA).

JO = Jordan Special Rate.

K = Agreement on Trade in Pharmaceutical Products (duty-free treatment).

MX = NAFTA for Mexico (duty-free treatment).

SG = Singapore Special Rate.

Although REE raw material production is dominated by one country, worldwide REE commodity markets are complex because of the variety of ores and commodities. Also, REE separation facilities are located in various countries that import all of their plant feed material, which means that high-purity REE products may be shipped back to the countries that originally produced the REE raw material. France and Japan, which have no internal REE raw material sources, are major producers of processed REE commodities, exporting approximately \$20 million and \$15 million worth, respectively, of REE compounds and metals to the United States in 2003. Separated REE production in France is by a single company, Rhodia Electronics & Catalysis. Originally, it utilized monazite and xenotime from Australia and the United States; however, restrictions on the disposal of thorium waste forced Rhodia to shift to intermediate REE thorium-free compounds, including rare earth chlorides and nitrates. Sixteen European countries exported REE commodities to the United States in 2003: Austria, Belgium, Estonia, France, Germany, Hungary, Ireland, Italy, Liechtenstein, the Netherlands, Norway, Russia, Spain, Sweden, Switzerland, and the United Kingdom. At least 20 companies in Japan produce REE commodities that are used by that country's steel, auto, and electronics industries. Japanese REE producers have used increasing amounts of Chinese raw and purified REE materials for their industry.

GOVERNMENTAL CONSIDERATIONS

Tariff Rates, Depletion Provisions, and Government Policies

The classification of China as a most favored nation in 1978 by the United States had a strong impact on REE markets, and the U.S.

government has shown little interest in protecting domestic producers. U.S. tariff rates are shown in Table 9.

While keeping the value of its currency low, the Chinese government has aggressively promoted its REE industry. Peking University is reported to have a research staff of 1,400 scientists working on all facets of REE production and marketing (D. Witham, personal communication). Development of Chinese REE deposits does not seem to have been impeded by normal market considerations, leading to significant overproduction of REEs in recent years. Many of China's REE mines, processing facilities, and manufacturing plants are said to be underfunded (O'Driscoll 2003). In 2003, the Chinese government announced that it would assert control over its REE industry, setting up two oversight groups: one centered on the Bayan Obo-Baotou operations in the north and one that will be developed mainly around the lateritic (ionic clay) REE deposits in southern China.

Environmental Concerns

In the United States, REE mines and processing plants are required to meet the same environmental quality guidelines as other mining and chemical facilities. The U.S. Environmental Protection Agency (EPA) is responsible for setting air-, water-, and soil-quality standards for such operations nationwide, but standards for some individual states are more stringent. Reclamation requirements for mining are under state authority and differ from state to state; however, reclamation on federally owned land is overseen by agencies such as the U.S. Forest Service and U.S. Bureau of Land Management.

REE ores and commodities, as well as by-products and waste materials from REE processing, are naturally radioactive, mostly because of contained thorium. The thorium content of monazite typically ranges from 4% to 10% ThO_2 , where as thorium comprises less than 1,000 ppm in bastnasite from Mountain Pass (Mariano 1989a) and may be even lower in Chinese REE concentrate. Handling, shipping, storage, and disposal of such materials are controlled by federal and state agencies. Less than 10 t of thorium commodities, all from imported or stockpiled material, are consumed in the United States annually (Hedrick 2004b). Therefore, thorium produced during REE processing presents an expensive disposal problem for the industry.

The Rhodia plant in Freeport, Texas, extracted REEs from largely imported monazite until 1992, when the feedstock was switched to Chinese REE concentrates. Production from this operation has declined substantially in recent years. The company's La Rochelle, France, plant is now the world's only significant REE separation plant outside of China, and it imports most of its REEs as carbonates, chlorides, and nitrates from China (Chegwidden and Kingsnorth 2002).

Although the bastnasite produced by Molycorp, Inc., at Mountain Pass has relatively low thorium, chemical processing was suspended by the California EPA in 1998, mainly because of the radioactive element content of waste involved in a spill incident. Between 1998 and the present, Molycorp has sold REE commodities from stockpile and has purchased, tested, and resold imported REE commodities. The company plans to resume production at Mountain Pass and its environmental impact statement is currently under review.

Environmental concerns centered on the disposal of radioactive waste have precluded the development of REE extraction plants in Australia, where environmental policies are mainly under state control. A processing facility in Western Australia designed to produce REEs from 15,000 t of monazite annually, originally slated to begin production in 1989, was not constructed because of lack of approval from the Environmental Protection Authority of Western Australia. Groups concerned about radioactive contamination of the environment have become active worldwide, as shown by protests of plans to begin processing REEs in Malaysia in the late 1980s. Malaysian production of xenotime ore ceased in 1994 because of environmental regulatory compliance problems, along with the collapse of market prices for xenotime.

On the other hand, consumption of REEs in automotive and industrial emission catalysts is directly dependent on environmental regulations for air pollution control. Use and composition of REE-containing refinery FCCs are functions of both the feedstock and the fuel quality required, both of which also relate back to air pollution regulations.

FUTURE TRENDS

The future use of REEs is expected to increase, especially in automotive pollution catalysts, FCCs, and permanent magnets. Rare earth applications are expected to need greater amounts of higher-purity mixed and separated products, requiring specificity in their unique properties. Strong demand for cerium, lanthanum, and neodymium is expected to continue throughout the decade as automotive and electronic usage expands with population growth. Future growth also is forecast for REEs used in lasers, fiber optics, and medical applications that include MRI contrast agents, PET scintillation detectors, medical isotopes, and dental and surgical lasers. On the other hand, demand is expected to decline over the next decade for REE phosphors used in CRTs, as flat-panel display use increases. A slight decline also is forecast for rechargeable

nickel-hydride batteries, as lithium ion batteries gain wider use in portable electronics. Long-term growth is forecast for REEs utilized in magnetic refrigeration alloys and other technologies that exhibit energy efficiency and cost benefits.

World reserves are sufficient to meet forecast world demand well into the 21st century. Several world-class REE deposits in Australia and China (Mount Weld and Maoniuping, respectively) have yet to be fully developed and contain substantial reserves. Production may resume at idle deposits that produced in the past, such as Mountain Pass, United States, and Steenkampskraal, South Africa. Other substantial reserves are contained in heavy-mineral sands deposits worldwide. As demand continues to increase, future development of new REE deposits is likely.

U.S. companies have shifted away from using radioactive REE ores, which has negatively affected monazite-containing mineral-sands operations worldwide. The cost to dispose of radioactive waste products in the United States is expected to continue to increase, severely limiting domestic use of low-cost monazite and other thorium-bearing REE ores. Worldwide demand for monazite is expected to increase in the long term, however, because of its abundant supply and its recovery as a low-cost by-product.

World REE markets are expected to continue to be very competitive in response to China's large resources, competitive prices, low-cost wages, inexpensive utilities, and minimal environmental and permitting requirements. China is expected to remain the world's principal rare earth supplier. In addition, economic growth in several developing countries will provide new and potentially large markets in Southeast Asia and Eastern Europe.

The long-term outlook is for an increasingly competitive and diverse group of REE suppliers. As research and technology continue to advance the knowledge of REEs and their interactions with other elements, the economic base of the REE industry is expected to continue to grow. New REE applications are expected to continue to be discovered and developed.

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Salt

Susan R. Feldman

Sodium is an unstable, silver-colored, metallic element that reacts violently in the presence of water, and chlorine is a dangerous and potentially lethal, greenish-colored gaseous element. Yet combined, these two elements form sodium chloride, commonly known as salt, which is a white-colored compound essential to life itself. Salt is perhaps the only mineral in the world that is used by virtually every human being. World history is peppered with examples of salt's profound influence. Sources of salt have even determined the location of cities, such as Salzburg, Austria; Salzgitter, Germany; and Saltville, Virginia. Populations have migrated in search of salt, and wars have been fought to obtain or to protect it.

Although there is no record of when prehistoric civilization first discovered salt, cultures appreciated its unique and distinctive taste. They also noticed animals attracted to salt springs and salt licks, satisfying their innate cravings. Hunters and gatherers knew that where there was salt, they would find animals. Because prehistoric people were not aware of their physiological need for salt, they automatically received their salt requirements from eating the meat of animals. A Mesopotamian tale tells of a wounded pig that ran into the ocean and drowned. After being recovered from the ocean, where it was saturated in the salt brine, the pork was found to taste better than unsalted meat. It was not until civilization graduated from a nomadic to an agricultural society and vegetables and cereals were introduced into the diet, that the need for additional supplements of salt was realized. The Sumerians ate salted meat and used salt to preserve food about 3500 BC. In approximately 1000 BC, the Trojans learned to use salt for preserving fish. The maritime civilizations, such as the Phoenicians, engaged in an extensive salt trade throughout the Mediterranean.

Many superstitions, customs, and traditions surround the religious, social, economic, and political aspects of civilization. Although some commodities have provided the basis of some ageless metaphors and clichés (i.e., heart of gold, strong as steel, eyes of coal), none are more commonly used as those pertaining to salt. Being “the salt of the earth” referred to a person's worthiness, as referenced in Matthew 5:13 of the Bible. Someone “not worth his salt” reportedly was used in ancient Greece in bartering salt for slaves. When laborers were worth their salt, they were paid a “salary” (*sal* is Latin for salt), a term still in use today that dates back to Roman times when part of a soldier's pay was paid in salt rations. Fearing those around him, the Roman leader Pompey was known to add a grain of salt to his drinks as a supposed antidote to poison.

Hence, “taking it with a grain of salt” is to regard something with suspicion. Kurlansky (2002) mentions that Haitians broke spells and brought zombies back to life with salt.

The earliest known record of salt production was in China about 2000 BC when Emperor Yu decreed that salt had to be supplied to the court as a tribute. Because salt was a commodity that had universal demand, governments often intervened to control salt production and distribution to generate revenue for major national projects. State-run salt monopolies were common in history—for example, in Rome about 506 BC. Revenue was also derived from taxes levied on salt sales. The word *gabelle* refers to the direct salt tax used in France. This tax was so despised that it was a major cause of the French Revolution. Although the tax was repealed in 1790, it was reinstated in 1805 to raise revenue for Napoleon's wars. France continued to use the *gabelle* until 1945. Because of the unique properties of preservation for food stores, salt became one of the first international trade commodities.

Salt making was an important economic activity in many areas of the world. Archaeological evidence indicates that salt was quarried from hills near the Dead Sea before the Bronze Age. At Hallstatt in the eastern Alps of Austria, rock salt was mined as early as 1400 BC. Solar salt was being produced in the northern Yucatan peninsula by the Mayan civilization about 1000 BC to AD 300; however, even earlier Mexican saltworks were found in Oaxaca. By the 1500s, salt was in such demand by civilizations that during the war beginning in 1568 between Spain and the Dutch, the Dutch were cut off from their supply of Spanish salt. They were able to confiscate Spanish salt from the beach at Araya in Venezuela and from sea salt ponds in Bonaire in the Dutch Antilles. The Spanish also lost salt to the British on Tortuga, another Caribbean island close to Venezuela. In 1541, when Hernando DeSoto, the explorer, was traveling up the Mississippi River, he remarked in his log that salt was collected along the river, marking the rudimentary solar salt gathering works by the native Indians of that region.

Other than the prehistoric use of salt in the southwestern part of the United States by Native Americans, the first production of salt by the American colonists began in June 1614 on Smith's Island, Virginia, 7 years after the founding of the Jamestown colony. The short-lived activity was in response to the high price of salt being charged by ships' captains who brought salt over as ballast from England.

History in the Americas is filled with salt wars. This trend continued until after the Civil War. The early Aztecs held power

over their enemies by denying them access to salt. Although Nathaniel Loomis, in 1790, is credited with starting the first commercial inland salt production in the United States at New York's Onondaga Lake, salt had been made by individuals for private use many years earlier. Indians had long known of the salt springs in the Kanawha Valley of Virginia (now West Virginia). In 1755, Mary Ingles, a white settler, was kidnapped by Indians and was forced to make salt from the saline springs. After her escape, she told other settlers how to make salt. At Saltville, Virginia, Arthur Campbell began making salt in 1782 by boiling brine obtained from salt springs. In 1799, William King sank a shaft about 3.0 m (9.8 ft) in diameter down about 61.0 m (200.1 ft) to the underlying Saltville salt deposits. The shaft flooded before he could extract any rock salt; however, King has the distinction of digging the shaft of the first salt mine in the United States. Figures 1 and 2 show the King site as it appears today in Saltville, Virginia. Production of brine from the shaft continued until 1892. Settlers moved into the Kanawha Valley in 1785, but it wasn't until 1806 that Elisha Brooks established the first commercial salt works in Kanawha.

GEOLOGY

In 1849, J. Usiglio, an Italian scientist, illustrated the sequence for precipitation of chemical compounds from sea water using water collected from the Mediterranean Sea. His order of precipitation was iron hydroxide, calcium carbonate, calcium sulfate, sodium chloride, and the soluble salts of potassium and magnesium in the mother liquors. Although the deposit at Strassfurt, Germany, is a classic example of this sequence, this sequence was not correct.

Mineralogy

Pure sodium chloride contains by weight 39.34% sodium and 60.66% chlorine. The mineralogical name for salt is halite, from the Greek word *hals*, meaning salt. Because of its simple crystal structure, it was the first structure to be analyzed by x-rays. Salt has the following properties:

Formula: NaCl

Crystallography: isometric, hexoctahedral, 4/m 32/m

Cell contents: Na₄Cl₄

Habit: usually cubic, rarely octahedral; massive, granular to compact

Physical properties:

Refractive index: 1.554

Twinning: observed on {111}

Cleavage: {001} perfect

Fracture: conchoidal, brittle

Hardness: Mohs hardness of 2

Specific gravity: 2.168

Melting point: 804°C (1,479°F)

Boiling point: 1,413°C (2,575°F)

Luster: vitreous, normally colorless to white, but occasionally red, yellow, blue, and purple

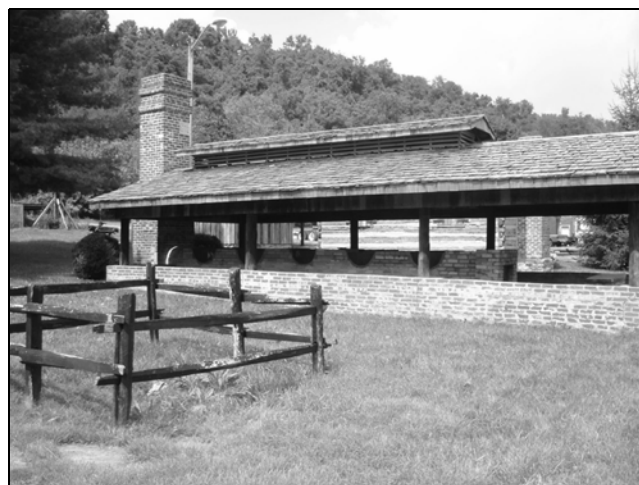
Solubility: 0°C: 35.7 parts per 100 parts of water
100°C: 39.8 parts per 100 parts of water

Classification of Deposits

Salt deposits are found in solution or in a solid state. It is the method of recovery from these two forms that categorizes salt as rock salt, solar salt, salt brine, or vacuum pan salt.

Solution

Solutions of salt are found in the oceans, lakes, natural brines, and groundwater.



Courtesy of Dave Hubbard.

Figure 1. Location of the first salt mine in the United States, Saltville, Virginia (within fenced area). The shaft was filled in many years ago for safety reasons. Note the rebuilt salt-boiling block, patterned after one used during the Civil War to produce salt for the Confederacy.



Courtesy of the Museum of the Middle Appalachians, Saltville, Virginia.

Figure 2. View of Saltville, Virginia, circa 1900, showing the fenced area of the King salt mine (arrow)

Oceans. The oceans provide us with the largest resource of salt in the world. The world's oceans contain about 530 million km³ of water. About 42% of salt is dissolved in the oceans. One cubic kilometer of seawater contains 93 Mt of dissolved matter, of which 78 Mt is salt. To visualize what this quantity of salt looks like, it would take about 18 Vertical Assembly Buildings (the world's largest building in terms of volume) like the one at the Kennedy Space Center at Cape Canaveral, Florida, to hold all the salt contained in a single cubic kilometer of seawater.

The salt content of the oceans varies from 1% to 5%, depending on the location, depth, and external influences, but it averages about 3.5%. In coastal areas, where evaporation rates exceed precipitation rates, solar evaporation of sea water may be the more advantageous method to produce salt. In certain countries that have limited technology and markets, the operations may be crude and

relatively unchanged from methods their ancestors used. Some facilities in arid regions take advantage of natural, shallow depressions along the coastlines. The seawater is introduced during high tides or storms and evaporated during dry periods, leaving a dry crust of salt on the surface. Most of these operations are small and the salt is marketed for local consumption. In other nations, modern operations that use more advanced scientific techniques to improve product quality and quantity while maintaining low production costs have become major competitors in world markets.

Lakes. Lakes are the result of natural accumulations of water in topographical depressions, or behind natural obstructions. Usually water carries dissolved material whose composition depends on the type and solubility of the rocks and material exposed to dissolution by the ground and surface waters. Clarke (1924) classified mineralized lakes as follows

- Sodium chloride lakes
- Natural bittern lakes—magnesium salts dominate
- Sulfate water lakes
- Sulfate-chloride lakes
- Alkaline lakes; carbonate lakes, carbonate-chloride lakes, chloride-sulfate-carbonate lakes

Sodium and calcium cations that dominate most mineralized lake deposits give rise to deposits rich in sodium sulfate (both mirabilite and thenardite), burkeite, gaylussite, trona, and halite. Landes (1960) reported that the sodium chloride lakes are “either separated bodies of ocean water or they owe their composition to the presence of salt within the rocks that floor the watershed.” Land-locked bodies of saline water provide a natural source of salt to develop, such as the Great Salt Lake in Utah, where several solar salt evaporation facilities have been constructed. Alkaline lakes, such as Searles Lake and Owens Lake, both in California, are more noted for their sodium carbonate content than their sodium chloride potential.

Groundwater. Groundwaters are classified as either connate or meteoric water. Connate waters are those that are trapped in the country rock at the time of formation and reflect the composition of the water at the time. Most sedimentary rocks were deposited at the bottom of the sea, so a substantial quantity of connate water could have been entrapped during the process. However, sedimentary rocks are also formed in freshwater lakes and interior salt lakes.

Meteoric, or rainwater, is fresh as it is precipitated; however, it absorbs soluble material as it descends through the air, and into the soil, rocks, and so forth. Depending on the environment, the composition and the salinity of groundwater vary. The salinity of the groundwater can increase on contact with sodium chloride-rich strata. Clarke (1924) classified groundwaters into the following groups: chloride, sulfate, carbonate, mixed (chloride-sulfate, chloride-carbonate, sulfate-carbonate, chloride-sulfate-carbonate), siliceous, borate, nitrate, phosphate, and acid.

Groundwaters range in chemical content from practically nil to as much as 254,000 ppm. Many groundwaters that were saturated with salt provided the source of surface salt springs that were used by animals and prehistoric man. The salt-bearing groundwaters in New York, Virginia, and West Virginia were commercialized to take advantage of this resource. Some brines are not processed for the salt but for their bromine or magnesium contents.

Solid Salt

Crystalline salt is found in playa lake deposits, bedded salt deposits, and salt domes. Halite may be the dominant mineral; however, it also may be commingled with other sedimentary minerals.

Playa Salts. A playa is a naturally occurring sandy, salty, mud-covered floor of a desert basin, according to Grabau (1913). During

an influx of rain, the playa may be covered with rainwater, which dissolves part of the soluble playa surface. After the water evaporates, a soluble evaporite remains that may be concentrated in one part of the playa. With subsequent periods of additional precipitation and evaporation, salts dissolved from the playa surface will deposit out as crystals of various substances, the majority of which is sodium chloride. The crystal's surface promotes the continued growth of the size of the crystalline deposit. Searles Lake in California is considered one example of a crystal body in a playa lake.

Playa lake deposits generally are common in arid regions. Saline playas are formed from the evaporation of a mineralized lake that was created by the leaching of the rocks in the area surrounding the enclosed basin. Sodium chloride-bearing solutions contribute to the salt content of the playa. The presence of certain other minerals may indicate that other geologic processes occurred in the area. For example, the presence of borates would indicate recent volcanism in the area.

Salt is not the only mineral found in playa deposits. The mineralogical composition of a playa may vary considerably. Several playa lakes in California illustrate this clearly. Cadiz Lake is predominantly composed of calcium chloride, while Bristol Lake is predominantly salt and Owens Lake is chiefly sodium carbonate. Searles Lake contains a mixture of many compounds, primarily salt, sodium carbonate, sodium sulfate, potash, and borates.

Bedded Salt Deposits. Salt is also found as sedimentary, bedded deposits of varying thicknesses. It is usually associated with other sedimentary rocks, such as shales, limestone, dolomites, gypsum, anhydrite, and so forth. Salt deposits are found in every geologic period from the Cambrian to the Tertiary, and evidence indicates that some deposits are Precambrian. Table 1 lists examples of salt deposits in the different geologic periods.

Although bedded salt deposits are found in many countries throughout the world, geologists have been intrigued with the origin of the very thick deposits, such as Paradox Basin, some of which exceed several hundred meters in thickness and cover many hundreds of square kilometers. The concept of the time span and the amount of evaporation required to produce that magnitude of salt overpowers the imagination.

Various theories have been developed to explain the formation of bedded salt deposits. None of the ideas adequately account for the extremely thick beds, or for the concept of how salt may be the dominant mineral in one basin with gypsum-anhydrite in another. The generally accepted theory of formation involves the precipitation of salt from an evaporating body of salt water. Landes (1960) outlined the classification of the various theories as follows

- I. Terrestrial type: Evaporating interior sea becomes saline as a result of
 - A. Primary sodium chloride produced as a weathering product.
 - B. Flushing of connate water from sedimentary rocks cropping out above water level in drainage basin.
 - C. Leaching of salt from sedimentary rocks cropping out in the drainage basin.
- II. Marine type: Concentration of ocean water in cutoff sea:
 - A. Without further enrichment
 - B. With enrichment by
 1. Wind-blown salt
 2. Ocean water
 - a. Marginal salt pans
 - b. Marine salinas
 - c. Barred lagoons
 - d. Silled downwarping basins

Table 1. Ages of salt deposits

		Location
Cenozoic Era		
Recent		Mexico, United States* (solar salt operations and playa lakes)
Pleistocene		Israel, Mexico, United States (CA, NV), Russia
Pliocene		Italy, Jordan, United States (NV, UT)
Miocene		Algeria, Cyprus, Czech Republic, Dominican Republic, Egypt, Iran, Iraq, Morocco, Poland, Spain, Sudan, Syria, Trucial States, Turkey, Russia
Oligocene		France, Germany, Iran, Iraq, Spain, Turkey
Eocene		Belize, Iran, Morocco, Pakistan,† United States (Green River Basin, WY)
Mesozoic Era		
Cretaceous		Angola, Bolivia, Brazil, Colombia, Congo, Gabon, Libya, Mexico, Morocco, Nigeria, Peru, Senegal, United States (FL), Russia, Democratic Republic of Congo
Jurassic		Aden, Chile, Cuba, Germany, Kuwait, Tanzania, United States (ID, Gulf Coast area)
Triassic		Algeria, Bolivia, Bulgaria,† Ethiopia, France, Germany, Greece,† Libya, Mexico (Isthmus of Tehuantepec), Morocco, the Netherlands, Peru, Portugal, Spain, Switzerland, Tunisia, United Kingdom
Paleozoic Era		
Permian		Australia,† Brazil, Denmark, Germany, Greece,† the Netherlands, Mexico, Peru, Poland, United Kingdom, United States (Permian Basin, Supai Basin, Williston Basin), Russia
Pennsylvanian		Brazil, United States (CO, UT, Paradox Basin)
Mississippian		Canada (New Brunswick, Nova Scotia), United States (VA, Williston Basin)
Devonian		Australia, Canada, United States (Williston Basin, WY), Russia
Silurian		Canada, United States (Salina Basin)
Ordovician		Bolivia,† United States (Williston Basin, WY)
Cambrian		Australia, Canada (Northwest Territories), Iran, Pakistan,† Russia
Precambrian Era		
		Australia, Iran, Pakistan†

Adapted from Lefond 1969.

* See Figure 3 for more information on U.S. deposits.

† Unconfirmed.

Landes (1960) also suggests the following stages for the formation of a major bedded salt deposit:

1. Peneplanation of the continental platform so that it is a nearly flat land of very little elevation above the sea.
2. Submergence of wide areas beneath the sea. Shallow ocean waters spread over a considerable part of the continent.
3. Beginning or renewed downwarping of a basin marginal to this epicontinental sea.
4. Sedimentation of both basin and epicontinental sea. Mainly clastic and organic (reef) deposits.
5. Lowering of sea to approximately sill level. Period of evaporite deposition. Enrichment by seawater flowing across sill. Because of the shallowness of the water, and the distance from the open ocean in such areas as the Michigan Basin, the brine crossing the sill may have been abnormally strong. Some enrichment could also take place by wind-blown salt, for the flat topography and scantiness of land vegetation no doubt resulted in incessant winds of considerable magnitude.

As more salt and/or sediments are deposited onto the layer of salt crystals on the sea floor, the water is squeezed out and the salt crystals become compacted or recrystallized into massive salt beds. Other theories of salt formation suggest that salt may have been deposited from deep density-layered brine contained in basins that did not dry up. This theory raises more questions than it resolves.

Salt Domes. One of salt's properties is that it will flow plastically when compressional forces are exerted on competent strata that contain salt beds. The forces may be due to the static weight of

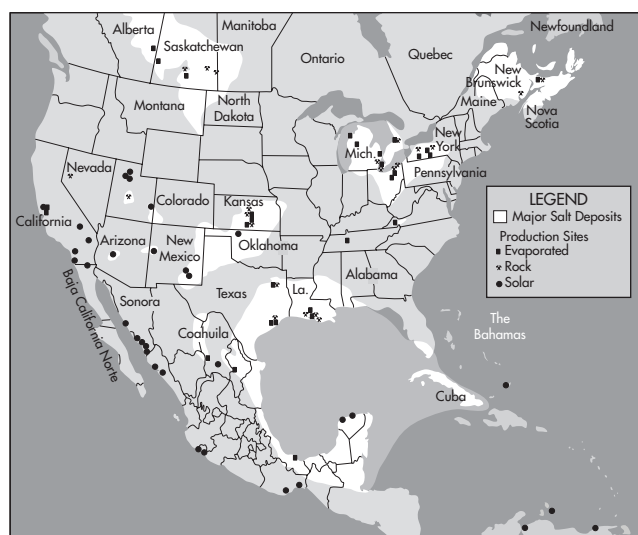
the overlying sediments, or other tectonic factors. If the pressure increases, the salt will flow into zones of decreased pressure, usually vertically upward through the overlying sediments. The salt will resemble "domes" or "diapiric folds." Salt domes are found in the Gulf Coast of the United States and in the Paradox Basin of Colorado-Utah. They are also found in Algeria, Germany, Iran, Mexico, Romania, Tunisia, and elsewhere. Some times the salt dome reaches the surface and appears as a circular expression, such as the Avery Island, Louisiana, salt dome. A salt dome can also flow like a glacier onto the surface, such as the Kuh-i Namak salt plug in the Persian Gulf area.

Distribution of Major Deposits

Solid deposits of salt or salt-bearing solutions are found in virtually every country in the world. Although the world contains abundant reserves of salt, the location and size of the deposits in relation to the location and size of the salt markets are important factors to consider when developing a commercial salt operation. For example, transportation is a variable in the total cost to the purchaser. To remain competitive, these types of added expenses must be evaluated to determine whether a business in a particular location makes sense economically.

The United States

The United States is the world's largest salt producer. Its domestic salt resources are located primarily in four depositional basins covering an area totaling about 1.3 million km² (0.5 million mi²) in 18 states. Figure 3 shows the distribution of domestic (North



Adapted from Salt Institute 2004.

Figure 3. Major salt deposits and dry salt production sites in North America

American) salt resources. Although large regions of the country are underlain with bedded, dome, or brine salt deposits, the northwest and most of the eastern States are devoid of salt. For consumers located in these regions, salt must be imported. The total identified resource of salt in the United States is estimated at 49.8 trillion t. At the present rate of mining, only 45 Mt are being depleted annually from this resource.

The four depositional basins are (1) the Gulf Coast of Permian-Jurassic age, which covers part of Alabama, Arkansas, Florida, Mississippi, eastern Texas, and all of Louisiana; (2) the Permian of Permian age, which includes part of Colorado, Kansas, New Mexico, Oklahoma, and western Texas; (3) the Salina of Silurian age, which covers part of Michigan, New York, Ohio, Pennsylvania, and West Virginia; and (4) the Williston of Ordovician-Permian age, which includes portions of North and South Dakota, Montana, and Wyoming. The Salina and Williston basins extend into Canada while the Gulf Coast and Permian basins reach into Mexico.

There are also a few other minor basins that contain salt. They are (1) the Supai of Permian age, in part of eastern Arizona and western New Mexico; (2) the Paradox of Pennsylvanian age, in southeast Utah and southwest Colorado; (3) the Sevier, in central Utah; and (4) the Green River of Eocene age, in southwest Wyoming. There is also some bedded salt in the overthrust area of Utah/Wyoming.

World

Salt is produced in Canada in the provinces of Alberta, New Brunswick, Nova Scotia, Ontario, Quebec, and Saskatchewan. Although Canada has large reserves of salt, about 62% of Canadian salt production is in Ontario, where transport economics are the dominant market force.

Rock salt deposits in Mexico occur near Monterrey, Coatzacoalcos, and Punta Gorda. Salt domes and salt anticlines are associated with the deposit at Coatzacoalcos. At Monterrey, the salt is solution mined and used as feedstock for the one local synthetic soda-ash plant. Although there were extensive solar works in the northern Yucatan peninsula that had been used by the early Mayan

civilization, the major solar salt production in Mexico today is at Guerrero Negro along the Pacific coast of Baja California.

Brazil has large salt reserves in the Amazon basin, Sergipe, and in offshore salt domes. Salt is also found in Argentina, Chile, and Colombia. Except for the underground salt mine at Zipaquirá, Colombia, the majority of salt produced in South America is from playa lake deposits or solar salt pans.

The salt industry of Europe can be traced back to early Roman times. The Romans introduced open-pan evaporation of seawater to England. Salt has been produced in Austria since the eighth century, and the rock salt mine at Wieliczka, Poland, has been in continuous operation since the thirteenth century. England, France, Germany, Italy, the Netherlands, Poland, and Romania, and Russia are the major salt-producing countries of Europe. Approximately one-fourth of the salt produced is rock salt, and most of the remainder is salt brine for use by the European chemical industry.

One of the major salt deposits in Europe is the Zechstein (Permian) salt formation that extends from eastern England to western Poland. In Germany, the Keuper (Triassic) salt beds are well developed. Salt beds of the Miocene, Oligocene, and Jurassic periods are found in several European countries. Solar salt is produced along the coasts of France, Greece, Italy, Portugal, and Spain.

Although rock salt deposits are found in Africa, most salt is produced by solar evaporation from seawater and saline lakes. The countries that are known to produce salt include Algeria, Benin, Burkina Faso, Djibouti, Egypt, Ghana, Kenya, Libya, Madagascar, Mali, Mauritania, Mauritius, Morocco, Mozambique, Namibia, Niger, Senegal, Sierra Leone, Somalia, the Republic of South Africa, Sudan, Tanzania, Tunisia, and Uganda.

China is the largest salt-producing nation in Asia and the second largest in the world. Coastal solar salt works and inland drilling for salt brines have been conducted since about 2000 BC. Though a major salt user, Japan has no indigenous rock salt or salt spring deposits; therefore, it must depend on imports to satisfy most of its salt requirements. Japan does, however, produce food-grade salt by processing seawater using ion-exchange electrodialysis technology, which is very energy intensive. The improper climate and lack of available coastal land make solar salt production impractical. Rock salt deposits in Asia are found in China, India, Pakistan, and Thailand. Within the last decade, countries such as India, Pakistan, Thailand, Vietnam, and many African coastal nations have begun to explore the commercial aspects of solar salt production, and many have developed production sites.

TECHNOLOGY

Exploration and Development

Many salt deposits were discovered while exploring for oil, gas, and potash. For example, salt was found in Morocco's Mohammédia region by a United Nations exploration team searching for commercial-grade potash in the Khemisset-Berrechid basins. Accidental discoveries of salt occurred in Brazil, France, Morocco, Portugal, and Thailand.

Although many reconnaissance projects have located salt resources, it is the task of the exploration geologist to delineate the ore zone and attempt to quantify the salt reserves. The exploration method is governed to a large extent by the proposed method for recovering the salt—that is, by either conventional underground room-and-pillar mining or by solution mining, including the projected use of the resultant cavity.

If the salt body is to be dry mined, the exploration project must be more extensive and greater care taken in delineating the

results than if the deposit were to be mined using solution-mining techniques. The extra care is necessary because of the greater capital investment incurred with underground dry mining than is incurred in developing a brine field.

Evaluation of Geologic Factors

When evaluating a salt deposit for dry mining, the geologic conditions surrounding the deposit are almost as important as the deposit itself. These conditions include

1. *Groundwater.* The quantity of groundwater and its hydrostatic head will have a direct influence on the method and cost of shaft sinking. If the groundwater is a potable water supply for a community, the protection of the aquifer requires careful hydrological investigation. Shaft sinking difficulties will increase if an aquifer contains brine or significant amounts of hydrogen sulfide, ammonia, or hydrocarbon gases, or if the hydrostatic pressure is very high.
2. *Overburden characteristics.* Considering the overburden as the alluvium plus the rock sequences above the salt deposit, it is essential that the physical characteristics of these horizons be known as fully as possible. It is particularly important that this information is gathered from the area in which the shaft or shafts are to be sunk. The data should include the thickness and hardness of the beds, drillability, fracture pattern, friability, and tendency to oxidize. Contractors that sink the shafts frequently make physical examinations of the drill cores themselves.
3. *Physical characteristics of rocks associated with the salt.* The structural integrity of the sedimentary rocks underlying and overlying the salt bed is particularly important. The roof spans, pillar size, percentage of extraction, mine layout, and the roof-bolting program are some of the mine features that will be dictated by the character of the rocks surrounding the deposit.
4. *Faults.* Fault systems, common to many salt formations, can create numerous serious problems and should be defined as carefully as possible during the exploration project (Jacoby 1969). Salt domes in the United States gulf coastal area have many faults associated with the spines that characterize their upper limits. These vertical or near-vertical fractures often contain brine, oil, and/or gases. Failure to develop mining patterns to a void creating differential stresses across these features to seal off the liquid intrusions often results in great expenditures of time, energy, and money.
5. *Facies changes.* Major and minor facies changes may occur in salt beds over relatively short distances. This has been documented in the Michigan Salina salts; the Realmonte, Sicily salts; and the potash salts of the Khemmiset Basin of Morocco. In Michigan, the A-1 salt changes from a pure anhydrite on the basin's edge near Detroit to an almost pure salt in East China Township, Michigan, and finally to a heavily contaminated potash salt at Midland. In the Khemmiset Basin, salts grade from a lean potash ore at Berrechid to a 98.3% sodium chloride in Mohammadia. Although the salt at Realmonte, Sicily, is metamorphosed, it shows a similar gradational change from lean potash mineralization to a pure halite. Most salt consumers prefer a product of uniform chemical composition; therefore, the exploration program must define the limits of the various salt grades laterally and vertically within the bed and the reserves of a uniform or standard product.
6. *Attitudes and position.* The attitude and position of bedded salt and the flowage lines in salt domes influence the mining

system, the percentage of extraction, the depth of the mining level, the selection of a shaft versus an inclined entry, and the rock mechanics of superimposing pillars where multiple level systems are contemplated. Whenever the internal features of the deposit or the continuity of the salt quality is questionable, a mill sample should be obtained by a bored shaft or inclined entry. Structures within a salt bed, such as folding (e.g., Cane Creek potash mine in southern Utah), can also add problems to underground mining. In the case of Cane Creek, this structural change caused the owners to switch to solution mining from underground mining. When solution mining is considered, exploration is conducted concurrently with the expansion or replacement of the current brining facilities. Evaluating the regional geology leads to the selection of the brine field site. Based on previously published information, a decision may be made on whether or not geophysical information would be beneficial in guiding subsequent drilling. Where domes are involved, or where the beds are known to have been altered by diapirism or faulting, geophysical studies may have distinct value (Mattox 1968).

7. *Chemical composition.* The deposit generally should have a minimum sodium chloride content of 95% to be commercially acceptable. The northeastern section of the United States has an average sodium chloride content of 97%. Salt obtained from southern salt domes or from solar evaporation has a higher sodium chloride content of about 99%. Depending on the salt end use, various trace elements such as boron, chromium, copper, iron, and vanadium, as well as ammonia, and water insolubles, such as gypsum, must be considered.

Drilling and Coring

If seismic or other geophysical data show a uniform top elevation of the salt, the drilling fluid can be changed from water to saturated brine just above the top of the salt formation. Where zones of lost circulation have been encountered "up the hole," a casing point is usually selected above the top of the salt and a string of protective casing installed. Depending on the well design and the economics, the casing is either set temporarily on a packer or permanently cemented in the hole. When drill holes expose shales that swell, spall, or slough in the presence of freshwater, early conversion to a saturated salt-brine drilling fluid often is justified.

A clean and fully saturated or supersaturated brine drilling fluid is very important so that the salt is not etched or leached. The solubility of salt at different temperatures is also very important.

Once the drill rig cuts and recovers the cores, the cores are cut into 0.33 m (1 ft) lengths and halved. One section is halved again to form a quarter, which is crushed and ground for chemical tests. Physical testing is usually done on a second quarter of the core.

Once the core hole is completed, it should be logged with gamma-neutron, sonic, or 3-dimensional equipment. The logs are then correlated with the physical core sections and the geograph that records the rate of drill penetration. Because faults, especially low-angle thrust faults, are difficult to recognize in cores of salt beds, the correlation with logs will often show repeat sequences of rock strata. Subsequently, a core reexamination may indicate a fine-grained granular halite section of core that was previously unrecorded. Sonic logging differentiates anhydritic dolomite from dolomitic anhydrite, while gamma-neutron will clearly depict salt from anhydrite (Leroy 1951).

Evaluation of Deposits and Plant Siting

Jacoby (1972) outlined a good procedure for evaluating a salt deposit with respect to its development using solution mining:

- I. Preliminary considerations
 - A. Plant requirements
 1. Quantity of brine
 2. Quality of brine
 3. Degree of saturation required
 - B. Subsurface factors
 1. Geology
 2. Rock mechanics
 3. Hydrology
 4. Previous extractive operations and environment
 - C. Surface factors
 1. Environment
 2. Topography
 3. Property boundaries
 4. Plant-brine field relationships
 - D. Feasibility study
 1. Preliminary brine-field layout
 2. Capital investment
 3. Cost of capital
 4. Operating cost
 5. Brine treatment cost
 6. Taxes and tax incentives
 7. Return on investment
- II. Preliminary engineering
 - A. Property
 1. Acquisition
 - a. Option of surface and mineral rights
 - b. Rights of well sites
 - c. Ingress and egress rights
 - d. Right-of-way for roads, pipelines, and power lines
 - e. Storage rights
 - f. Conditions of abandonment
 - B. Water supply
 1. Environmental considerations
 - a. Groundwater table
 - b. Salt water encroachment
 - c. Effect on local agriculture, industry, and domestic use
 2. Supply characteristics
 - a. Volume (continuity and cyclic variations)
 - b. Quality
 - C. Salt supply
 1. Exploration
 - a. Geophysical surveys
 - (1) Seismic
 - (2) Gravity
 - b. Drill holes
 - (1) Cores
 - (2) Geophysical logs
 - (3) Hydrological tests
 2. Design data development
 - a. Analyses of well logs and cores
 - b. Physical testing of cores
 - c. Water supply evaluation
 - d. Equilibrium studies
- III. Design and cost analysis
 - A. Brine-field layout and cost
 1. Salt wells design and cost
 2. Subsidence grid system design
 3. Roadways and well sites
 4. Pipelines and power lines
 5. Cathodic protection

6. Pump and pump facilities
7. Feedwater treatment facilities
8. Reservoirs and aeration
9. Security
- B. Supervision costs
- C. Operating costs
- D. Maintenance costs
- E. Taxes and insurance
- F. Depletion and depreciation
- G. Cost of capital
- H. Return on investment

Methods of Recovery

Data pertaining to commercially produced salt in the United States have been reported since 1797. A good reference for this is Kaufmann (1960). Table 2 lists domestic salt production, by type, from 1990 through 2002.

Underground Mining

Mining underground bedded salt or salt dome deposits includes constructing and developing underground rock salt mines, solution mining of the subsurface solid salt, or producing and developing natural saline brines.

Rock Salt Mining. All U.S. and Canadian rock salt mines use the room-and-pillar method of underground mining. The height of the pillars is limited to the thickness of the salt bed and the vertical section of salt that can be economically and safely extracted. Usually a certain amount of salt is left behind in the floor and the roof to avoid mining into the underlying and overlying non-salt beds that would contaminate the quality of the salt being mined. Bedded salt deposits generally are vertically restrictive but laterally unrestricted, while salt dome deposits are laterally restricted but vertically unrestricted. Room heights can range from about 3.0 m (9.8 ft) in a bed to more than 30.0 m (98.4 ft) in a dome. The height of pillars in salt domes, therefore, can be substantially higher than those in bedded

Table 2. Salt production in the United States, kt*

Year	Vacuum Pans and Open Pans	Solar†	Rock‡	Brine§	Total**
1990	3,660	2,990	12,800	17,400	36,800
1991	3,650	2,810	11,200	18,700	36,300
1992	3,810	3,220	11,400	17,600	36,000
1993	3,860	2,960	14,300	18,100	39,200
1994	3,960	3,020	15,100	18,000	40,100
1995	3,950	3,540	14,000	20,600	42,100
1996	3,920	3,270	13,500	21,500	42,200
1997	3,980	3,170	12,900	21,400	41,400
1998	4,040	3,190	12,900	21,100	41,200
1999	4,190	3,580	14,400	22,700	44,900
2000	4,200	3,801	15,000	22,500	45,600
2001	4,120	3,310	17,000	20,400	44,800
2002	4,100	3,390	13,500	19,300	40,300

Source: U.S. Geological Survey 2004.

* Production data are actual production data.

† Includes bulk, packaged, compressed pellets, and pressed blocks.

‡ Includes bulk, packaged, and pressed blocks.

§ Tons of anhydrous salt contained on a bulk basis.

** Data may not add to totals shown because of independent rounding.



Courtesy of Fonville Winans.

Figure 4. A 1939 view of Cargill Salt's Avery Island rock salt mine

salt operations. The room widths are basically a function of the thickness of the overlying incompetent rocks and the physical characteristics and thickness of the salt that forms the roof. Figure 4 shows a view of Cargill Salt's Avery Island rock salt mine with its rooms that are 30.0 m (98.4 ft) high.

The pillar widths are controlled by the percentage of extraction permissible at the various depths and room widths. Most room-and-pillar operations recover about 45% to 65% of the resource, with the remainder left behind as pillar supports. Most mines in bedded deposits use roof bolts to support their haulage ways, shaft entries, and permanent work areas. Roof bolts are used in bedded salt mines to prevent roof collapses. They are effective safety devices when properly applied. The length, diameter, and spacing of the bolts vary with the circumstances. Most mines use bolts 1.1 m (3.6 ft) to 3.0 m (9.8 ft) long on 1.1 m (3.6 ft) spacing centers. Very little roof bolting is done in salt dome mines because of the problems encountered in bolting in salt. Bolt holes in salt have a smooth, slick surface that form poor seats for bolt anchors, and that deforms plastically over time because of the pressures.

The majority of domestic rock salt mining uses conventional mining equipment because of the physical properties of salt. Continuous mining equipment, which uses rotating drum heads fitted with tungsten-carbide cutting tips, has been tested in some mining operations, but it tended to pulverize a lot more of the salt into useless fine particles. Newer types of continuous mining equipment have improved to such a degree that they are finding wider acceptance in salt mining. In conventional mining, the working face is first horizontally undercut about 3.0 m (9.8 ft) into the face to produce a keel. This allows a smoother floor to work from later on. Next, a drill rig is used to drill a series of horizontal (or slightly angled) holes about 3.0 m (9.8 ft) deep into the salt. Explosives, usually ammonium nitrate and fuel oil (ANFO), are pneumatically blown into the drill holes and set off electrically later after the working shift is over. One Kansas mine has experimented successfully with making the first horizontal cut at the ceiling level, rather than along the floor. The result is a smooth ceiling.

After the salt is blasted free, front-end loaders pick up the loose rock salt and transport it to a breaker-feeder unit that crushes and conveys the salt on belt conveyors to other underground crushing and screening stations. The salt can be stockpiled underground or hoisted to the surface and stored in silos or bins for processing at

a later time. Some operations prefer to crush and screen the salt to different sizes at the surface.

In 2004, eight companies operated 14 rock salt mines in the United States. The plant locations span Kansas, Louisiana, Michigan, Nevada, New York, Ohio, and Texas. Rock salt mining accounted for 400 Mt, or 66% of total U.S. salt production in 2002.

Solution Mining. The practice of solution mining is more than 2,200 years old; however, the concept remains the same today although there have been a few improvements made since 1965. Solution mining involves injecting a solvent to dissolve and recover underground soluble minerals. Before 1955, all solution mining used either "annulus injection" that employed a pair of concentric pipes (one carried the solvent downward and the other contained the brine upward) or "tubing injection" that introduced the solvent at the bottom of the tube. Several holes are usually drilled and the solvent (usually water) is pumped into the holes under pressure, dissolving the salt and leaving the insolubles in the bottom of the resulting cavity. The saturated brine can be pumped to the surface for recovery and further processing. One advantage of this technique is that specific beds can be mined, thereby reducing any subsidence.

Hydraulic fracturing has been used in the oil and gas industry for many years and was adopted by the salt industry. This technology was preferred for the following reasons:

1. It altered the cavity configuration from the "morning glory" shape to hemispheres and ellipsoids, thus increasing the stability of openings and reducing the likelihood of subsidence.
2. It increased the percentage of extraction from less than 5% to something in excess of 40%.
3. It reduced brining costs in most operations by 50%.
4. It increased the productive capacity of wells from approximately 3 L/s (50 gpm) to about 31 L/s (500 gpm) or more.
5. It reduced well maintenance costs to less than 5% of their former amount.

Solution mining is used to obtain a sodium chloride feedstock for vacuum-pan salt production and for synthetic soda ash, chlorine, and caustic soda manufacture. Only the quantity of manufactured vacuum-pan salt is reported. The amount of underground salt that is dissolved and recovered is not reported. The quantity of brine used to make chloralkali chemicals is reported as either the amount of captive brine used or brine sold. The chemical industry is the largest consumer of salt brine in the world, using about 45% of total salt sales. Brine represented about 89% of the salt feedstock for the chemical industry. Although the same companies that use it produce most salt brine, many chloralkali manufacturers now purchase brine from independent brine supply competitors.

Most salt and chemical companies use contract drillers to drill brine wells. Almost all new wells are constructed with rotary drilling equipment. Steel-cased pipes are inserted in the drill holes and cemented on the outside back to the surface. Most companies use a series of well pairs to establish a brine field. One well pair consists of (1) an injection well, in which the water solvent is introduced, and (2) a production well, in which the salt-bearing solution is pumped to the surface for processing. Some chemical companies have turned over the routine responsibility of operating and maintaining the brine field and pipelines to brine supply companies. The chemical producers are charged by the meter for how much brine they receive.

The cavities created during solution mining are often used for underground storage of a variety of products. The empty caverns

provide an inert and sealed environment to store hydrocarbons, ethylene dichloride, and compressed air.

Solar and Mechanical Evaporation

Other than recovering salt from underground deposits, salt can be obtained from seawater along coastal margins, and from landlocked bodies of natural saline water and artificial brines. Salt production uses the wind and sun to evaporate water, leaving behind relatively pure crystals of salt. Solar salt production is restricted to regions of the world that have high evaporation rates and low precipitation. The practice of solar salt production from sea water can be traced back many hundreds of years and has not changed much throughout history. Laborers in some countries today, such as Colombia, India, Jordan, and Thailand, continue to produce solar salt in the same manner as their ancestors.

Seawater Evaporation. Seawater contains various dissolved salts that will separate depending on their relative solubilities. Calcium carbonate, which is the least soluble, will separate out first. Highly soluble magnesium salts tend to separate last. The mineral salt separation order from seawater, from first to last, is calcite, gypsum, halite, astrakanite, epsomite, kainite, hexahydrate, kieserite, carnallite, and bischofite.

In the United States, solar salt production from sea water is restricted to the San Francisco Bay area and southern California. Seawater from the Pacific Ocean is collected and allowed to evaporate in specially constructed concentration and evaporation ponds. The initial step concentrates the brine to raise the salinity and to allow various calcium, magnesium, and iron compounds to precipitate from solution. The brine circulates among a network of interconnecting gravity-fed ponds, with salinity increasing with each transfer. It takes approximately 2 to 5 years from the time seawater is initially introduced before the first salt is ready for harvest.

The brine is treated with lime to remove excess sulfate as calcium sulfate and then pumped to evaporation ponds and harvesting ponds to permit the salt to crystallize. After about 85% of the salt has crystallized, the remaining supernatant liquid, called "bittern," is drained. Some companies pump the bittern to adjacent ponds for subsequent extraction of magnesium, potassium, bromine, and sodium compounds. Depending on the location of the plant, frequency of harvest can vary. In most industrialized countries, solar salt is harvested by mechanical harvesting equipment. Less industrialized countries still use manual labor to obtain the salt.

Inland Solar Evaporation. Solar salt is produced from the Great Salt Lake in Utah, which is an example of a landlocked body of salt water. The principles of solar salt concentration and production are similar to those along coastal margins except that salinity of inland lakes usually is greater than that of seawater and a yearly crop of salt can be harvested. As water flows over or beneath the surface, it dissolves minerals from underlying soils and rocks. The salt lakes are topographically lower than most of the surrounding areas and, therefore, become excellent sumps for mineral accumulation. For example, the Great Salt Lake receives about 2 Mt of new minerals annually by this process. The salt percentage in the lake varies, depending on the influx of freshwater.

A second form of inland solar evaporation includes evaporating artificial brines that were discharged as waste products into containment ponds. One example is the solar salt operations in New Mexico that are associated with potash mining. Underground-commingled deposits of halite and sylvite are mined for the potash, and the salt is discharged during potash processing as a brine to tailing ponds and left to evaporate. Over the years, many feet of salt have accumulated and various companies have been attracted to recover and sell the salt. Although a network of concentration and evaporation ponds is

not required in this case, the harvesting equipment is similar. The arid location permits virtually year-round harvesting.

The total quantity of solar salt produced in 2002 in the United States was 3.4 Mt, or 8.4% of U.S. salt production. Nine salt companies operated 14 solar evaporation facilities in the United States. Solar salt from seawater was harvested in California. Solar salt from inland solar evaporation was produced in Arizona, California, New Mexico, Oklahoma, and Utah.

Vacuum Pan Salt

Vacuum pan salt is solution- or dry-mined and is produced using mechanical evaporation technology. Although any of the other three types of salt may be dissolved to make vacuum pan salt (i.e., rock salt, solar salt, and salt brine), virtually all domestic vacuum pan salt is obtained by solution mining underground salt formations.

Salt is obtained by dehydrating the incoming brine using heat alone or in combination with a vacuum. The vacuum pan process conserves energy by using multiple-effect evaporators connected to vacuum pumps. A saturated salt solution will boil at a higher temperature than freshwater; however, when a vacuum is applied, the brine boils at a lower temperature, enabling the generated superheated vapor to act as the heating medium for the next evaporator.

Another mechanical evaporation process used in the United States on a small scale is the open-pan process. Round and rectangular pans with steam-heated immersion coils are used to evaporate the water from the brine. Rotating rakes scrape the salt that has accumulated on the pan bottom into a sump, or up a ramp depending on the method, and onto conveyors for dewatering and drying. The open-pan process produces a flake-shaped crystal rather than the typical cubic form. Flake salt is preferred to produce cheese, butter, and baked goods. The Alberger process is a modified open-pan technique that produces flake salt that possesses a hopper shape in complete crystals.

Five companies operated 19 vacuum-pan salt plants, accounting for 10% of total U.S. salt production in 2002. Vacuum pan salt is produced in California, Kansas, Louisiana, Michigan, New York, Ohio, and Texas.

Processing

After rock salt is mined and solar salt is harvested, the material undergoes some basic mechanical processing that usually consists of crushing and screening to reduce and separate the particles into different marketable size fractions. Rock salt mines have underground stations consisting of a combination of primary crusher and feeder units that load the salt onto conveyor belts for transport to secondary crushers elsewhere in the mine. Some mines have underground screening equipment to size the fragments; other operations conduct the screening at the surface. After screening, the salt is shipped to either underground or surface storage bins, each containing a different size fraction. From this point, the salt is ready for packaging and shipping or loading as bulk salt into railcars, trucks, barges, or ships.

Solar salt processing consists of hauling the salt to wash plants or directly to a stockpile. There are different variations of wash plants, but they should be designed to fit the local conditions and quality requirements. After solar salt is dumped into a pit at a typical wash plant, the salt is fed to a vibrating feeder or screw conveyor where it gets washed with saturated salt brine to minimize dissolving the salt crystals. Depending on the amount of surface insolubles or occluded dirt and debris, the use of seawater or dilute brine is often implemented. The washed salt goes to a classifier and then on for dewatering before being conveyed to a storage site. Some solar salt operations dry the salt in rotary dryers and screen the salt before

sending it to the stock pile. Others do some wet screening but allow the wet salt to drain in large windrows for periods not less than 2 weeks but up to several months before shipping.

Vacuum-pan process salt is produced by heating salt brine in large vertical evaporators. This processing method is usually applied to green brines formed from the solution mining method. Three to five evaporators are placed in series with each one in line under a greater vacuum than the preceding one. A unit consisting of three evaporators is also known as a triple-effect evaporator system. When pressure is lowered in an evaporator, the temperature at which water will boil also is reduced. Steam is fed to the first pan causing the brine to boil. The steam liberated by the boiling brine is used to heat the brine in the second pan. The pressure in the second pan is less, thereby allowing the steam made by the boiling action in the first pan to boil the brine in the second evaporator. The pressure continues to be reduced in each succeeding evaporator. Although the boiling process could be done using only one vacuum pan, more salt can be made per pound of steam using several pans in a row, and this multiple-effect process saves energy.

Brine processing can also consist of removing the majority of dissolved impurities from the salt in the solution. Calcium and magnesium are two common ions associated with salt that are precipitated and removed during brine purification treatment. Soda ash, also known as sodium carbonate, is used to remove calcium ions, which precipitates as calcium carbonate. Magnesium ions are precipitated and removed by adding caustic soda or lime. The resulting precipitates—magnesium hydroxide or magnesium carbonate—finally settle out along with the calcium carbonate. Barium carbonate is used to remove calcium sulfate from brines by forming insoluble barium sulfate. Sometimes hydrogen sulfide is dissolved in the brine but can be eliminated by reacting it with sulfuric acid to produce the gaseous oxides of sulfur and neutralizing the acid with lime. Once the salt has been purified, bringing the purity level above 99.9% sodium chloride, the salt is dried in either a rotary dryer or a fluid-bed dryer to keep the salt from caking during the drying process. If anticaking agents such as yellow prussiate of soda are added, they are added before drying. Free-flowing additives or other additives are added to the dry salt in mixing conveyors before storage or packaging.

A similar type of process called a recrystallizer process has been applied to solid salts, such as solar and rock, but is not as energy efficient and thus has lost popularity with processors. Solid salt requires dissolving before applying the recrystallization process.

Product Forms

Salt is marketed and shipped in various forms, the most common being bulk. Most large chemical and industrial salt consumers buy in bulk quantities to reduce costs. Bulk salt purchasers should have adequate storage space to accommodate the volume of material purchased. Bulk shipping costs are usually less than those for packaged salt.

Packaged salt consists of salt sold in round cans, boxes, shakers, single-serve packets, kraft paper bags with polyethylene film liners, or plastic bags. Big bags or super sacks, holding up to a ton of salt, are used as a means of shipping a small bulk quantity. These bags can be palletized for easy handling by forklift. Many purchasers use these containers to deliver pre-weighed quantities of bulk salt to their batch processes. Whatever the container size, most packaged products are sold and shipped as unitized pallet quantities. Most vacuum pan salt for human consumption is packaged in one or more type of container. Because of the packaging and handling costs, the unit price is higher than for bulk salt. The majority of packaged salt is sold through grocery, food service, institutional, and related outlets, or to food processors or manufacturers.

Pressed blocks include large salt bricks, spools, smaller bricks, pellets or “pillows,” and other compressed forms used by the water conditioning and agricultural sectors. Fifty-pound blocks are the most common pressed block sold. Very high hydraulic pressures are used to press the salt blocks. Blocks sold for animal nutrition often have trace minerals added to them, based on veterinary advice, to supplement what is missing from the normal diet of the animal. Because of an animal’s natural craving for salt, this method of nutrient supplementation works well to deliver just the right amount without overfeeding.

Pellets and pillows are briquetted e-shaped pieces of salt that have been compressed for ease of handling, reduced mashing, and slower dissolution rate. Most compressed salt products are for water softening applications. Although no longer commonplace, salt tablets were sold as compressed pellets and used to replace lost minerals during excessive fluid loss such as sweating and for canning applications.

Additives

Temperature and moisture (even as humidity) affect salt in storage or in use. For these reasons, free-flowing agents are added to help the salt pour freely. The agent should have very good adsorptive, covering, and adhesion properties; be food grade and nontoxic, odorless, colorless, dustless, tasteless, inexpensive, and soluble enough or fine enough to show no sediment in brine (Kaufmann 1960). For example, the agent also should not cover the salt grain so completely as to slow up the recognition of the salt taste when preparing food, and it should keep deicing salt, used for melting ice and snow, free flowing.

Between 0.5% to 1.0% of free-flowing additives are normally added to table salt. The agents could include sodium silicoaluminate, magnesium carbonate, calcium silicate, di- or tricalcium phosphate, and calcium carbonate.

Salt is an excellent carrier of potassium iodide or potassium iodate, which are used to prevent iodine deficiency disorders (IDD) in humans. Nearly one billion people are at risk of contracting IDD throughout the world, mainly in the underdeveloped nations. IDD includes several abnormalities, such as goiters, mental retardation, deaf mutism, squint, difficulty standing and walking, and stunted limbs. Without treating the population by simply using iodized salt, the social and economic progress of countries becomes adversely affected. The cost to prevent IDD is \$0.05 per person per year. The International Council for Control of Iodine Deficiency Disorders, the United Nations Children’s Fund, the Micronutrient Initiative, and the Salt Institute have joined together as the Network for the Sustained Elimination of Iodine Deficiency, the umbrella group coordinating the global effort to overcome this international, treatable problem. In developed countries, iodized salt contains 0.01% potassium iodide, with 0.2% of a stabilizing mixture of sodium thiosulfate and calcium hydrate or dextrose and sodium bicarbonate. Where iodine stability may be an issue, potassium iodate is used globally for both animals and for humans.

Specifications

Salt is sold to various end-use markets with specific chemical and physical specifications formulated by reputable scientific agencies and/or medical organizations, or on niche specifications established for particular branded products by the producing companies. The specifications are important to ensure that consumers are obtaining a safe, consistent, and reliable grade of salt for their requirements. The specifications of salt for human consumption are different than those for highway deicing. The purity and quality of salt also varies

Table 3. Specifications applying to the salt industry

Type Specification	Title	Designation	Jurisdiction
Analysis	Standard Methods for Chemical Analysis of Sodium Chloride	ASTM-E-534-98 (2003)	American Society for Testing and Materials
Food	Sodium Chloride	Food Chemicals Codex (FCC), 5th ed.	Institute of Medicine, National Academies
	Salt	AOAC 925.55	AOAC International, Official Methods of Analysis
Highway	Standard Specification for Sodium Chloride	ASTM-D-632-01	American Society for Testing and Materials
	Standard Specification for Sodium Chloride	AASHTO-M-143	American Association of State Highway Transportation Officials
	Handbook of Test Methods for Evaluating Chemical Deicers	SHRP-H-332	Strategic Highway Research Program
Medical	Official Monograph on Sodium Chloride	United States Pharmacopeia–National Formulary, 2005	U.S. Pharmacopeia Convention
Reagent	Sodium Chloride	Reagent Chemicals, 9th ed.	American Chemical Society
Soil stabilization	Standard Test Methods for Water-Soluble Chlorides Present as Admixes in Graded Aggregate Road Mixes	ASTM-D-1411-99	American Society for Testing and Materials
Table salt	Salt, Table, Iodized	A-A 20041B	U.S. Department of Agriculture
Water	Federal Specification Commercial Item, Description, Sodium Chloride, Technical (Water Conditioning Grade)	A-AZ-694	General Services Administration
	AWWA Standard for Sodium Chloride	ANSI/AWWA-B200-03	American National Standards Institute/ American Water Works Association

Adapted from the Salt Institute 2005.

depending on the type of salt; rock salt is generally less pure than more refined vacuum pan salt. Table 3 lists the specifications that apply to salt sold in the United States.

USES

World salt use is equal to world salt production, assuming that inventories on a global basis are discounted. Therefore, the total quantity of salt used in the world in 2002 was 210 Mt.

The pattern of end-use markets is very similar among developed nations in the world with the chemical industry as the largest international consumer of salt. Most markets are mature and show minimal growth rates for salt usage. Less developed countries tend to use more salt for human and agricultural applications. Table 4 lists the trends of the top 10 salt-producing countries of the world since 1990. Salt use in general in the United States has increased during the past 200 years. Various events have affected domestic per capita salt usage. Before the beginnings of the chemical industry in the United States in about 1884, most of the salt used was for food and animal hide preservation and in refrigeration.

New chemicals made from salt and new applications using salt contributed to a significant increase in salt use during the early twentieth century. It should be noted that the chemical and highway deicing sectors were responsible for the greatest increases in salt usage.

There are more than 14,000 direct and indirect uses of salt—it would be virtually impossible to collect data for all of them. The U.S. Geological Survey and the Salt Institute, the trade association of the North American salt industry, survey end-use consumption information on 28 individual uses in eight major categories that include chemical, food processing, general industrial, agricultural, water treatment, ice control, distributors, and miscellaneous. These industries are the first-tier consumers of salt; information on most of the other downstream customers (such as who the distributors sell salt to) is unavailable. Changes in the quantity of salt consumed by the chemical industry and for highway deicing changed substantially during the twentieth century. Highway deicing salt usage has

Table 4. World salt production (1990–2002), kt

Country	1990	1995	2000	2002 [*]
Australia	7,227	8,148	8,778	9,887
Canada	11,097	2,980	12,164	12,313
China	20,000	10,957	31,280	32,835
France	6,450	7,539	7,000	7,000
Germany	13,258	10,800	15,700	15,700
India	9,503	9,500	14,453	14,503
Mexico	7,135	7,670	8,884	8,500
The Netherlands	3,650	3,500	5,000	5,000
United Kingdom	6,434	6,650	5,800	5,800
United States	36,794	42,200	45,600	40,300
Other	71,945	82,056	57,341	58,162
World Totals	193,493	192,000	212,000	210,000

Source: U.S. Geological Survey 2004.

* Estimated value.

been controlled mainly through “Sensible Salting” techniques recommended by the Salt Institute, and training seminars that educate workers to spread highway salt judiciously and effectively. The result is achieving dry pavement using the least amount of salt per storm, thus protecting the environment from excess salt brine runoff and cost-effectiveness.

Chemical Industry

The U.S. chemical industry is the largest consumer of salt, representing 45% of reported consumption in 2002. This category is distinguished by two important categories: the chloralkali industry and other chemical manufacturers.

Chloralkali

The chloralkali industry is the largest segment of the chemical sector that uses salt. Traditionally, this end use included salt consumed for chlorine, coproduct sodium hydroxide (also known as caustic soda and lye), and synthetic soda ash; however, since 1986, no synthetic soda ash has been manufactured in the United States. Outside the United States, many manufacturers continue to use salt for synthetic soda ash production.

Salt is used as the primary raw material in chlorine manufacture because it is the chief source of chlorine ions. For sodium hydroxide production, salt is the main source of sodium ions. Approximately 98% of domestic chlorine and sodium hydroxide produced are obtained from the electrolysis of salt brine feedstock using three different cell technologies: (1) diaphragm, 78%; (2) mercury, 14%; and (3) membrane, 6%. It takes about 1.59 t of salt to make 0.9 t of chlorine and 1 t of coproduct caustic soda. The electrolytic process splits sodium chloride into ions that selectively pass through special membranes. Chlorine gas forms at the anode while sodium ions migrate through the membranes toward the cathode where sodium hydroxide forms and hydrogen gas evolves. In 2002, 10.3 Mt of chlorine and 8.2 Mt of caustic soda were produced in the United States.

Making synthetic soda ash had been the primary method for obtaining soda ash in the United States until 1971, when natural soda ash production exceeded that of synthetic. The main process for making soda ash was the Solvay process, developed in the early 1860s. Today, it is still the main technique used by the rest of the world. Carbon dioxide gas is percolated through a carbonation tower containing nearly saturated salt brine to which ammonia has been added. Ammonium bicarbonate forms, which reacts with the brine to form sodium bicarbonate and ammonium chloride. The sodium bicarbonate precipitate is collected, filtered, and calcined into soda ash. Residual sodium chloride is discharged as plant effluent. The chloralkali subsector is classified under Standard Industrial Classification (SIC) code 2812 and since 1997, under the North American Industry Classification System (NAICS) code 325181.

Other Chemicals

The other subsector that uses salt includes chemical establishments that make sodium chlorate, metallic sodium, and other downstream chemical operations that use salt as a feedstock. In powdered soaps and detergents, salt is used as a bulking agent, and as a coagulant for colloidal dispersion after saponification. In pharmaceuticals, salt is a chemical reagent, and it is used as the electrolyte in saline solutions. Additionally, it is the base ingredient for hemodialysis fluids and is used as a polishing agent for pharmaceutical tablets and caplets. Salt is used as a cofeedstock with sulfuric acid to produce sodium sulfate and hydrochloric acid. This subsector is relatively small, comprising only 10% of domestic salt sales for the entire chemical sector and only 4% of total domestic salt consumption. These chemicals are classified under SIC 2899 (NAICS 3251998), excluding SIC 2812 (NAICS 325181)—alkalis and chlorine.

Food Processing Industry

Although every person uses some quantity of salt in their food, the entire category only represented 4% of reported usage in 2002. Salt is added to food as a flavor enhancer, preservative, binder, fermentation control additive, texture aid, and color developer. This major category is subdivided into six subsectors, in descending order of salt consumption: meat packers, canning, other food processing, baking, dairy, and grain mill products. Additional salt for human consumption is also included in grocery wholesalers. It is estimated that about

75% of the grocery store category is salt for food processing; the remainder is for other household applications.

Meat Packers

Salt added to processed meats promotes the color development in bacon, ham, and other processed meat products. As a preservative, salt inhibits the growth of bacteria, which would lead to product spoilage. Salt acts as a binder in sausages, forming a binding gel comprised of meat, fat, and moisture. Salt also acts as a flavor enhancer and a tenderizer. This subsector is engaged in slaughtering and processing meat and poultry products and in sausage and other prepared meat manufacturing. It includes SIC codes 2011, 2013, and 2016, with their corresponding NAICS codes, 311611, 311612, and 311615.

Canning

Salt is primarily added to the canning process as a flavor enhancer and preservative. It also is used as a dehydrating agent, tenderizer, enzyme inhibitor, and as a carrier for other ingredients. Establishments that can vegetables, vegetable juices, jams, jellies, pickled fruits, and specialty products such as baby foods and seafood are in this category. It includes SIC 2032, 2033, 2034, 2035, and 2091. The NAICS codes for these products are 311422, 311999, 311421, and 311941.

Other Food Processing

Salt is used mainly as a seasoning agent, adding flavor to food in this end use. Other food processing includes miscellaneous manufacturers that make food for human consumption (i.e., potato chips, pretzels, and other snack food items) and domestic pet consumption (i.e., dog and cat food). They are included in SIC 206, 207, 208, 2047, 2099, and any other food category not included in the aforementioned SIC codes. NAICS codes correspond with 311111, 111998, 31134, 311911, 311423, 311991, 31183, 311823, and 311999.

Baking

Salt is added to control the rate of fermentation in bread dough. Additionally, it is used to strengthen the gluten (the elastic protein-water complex in certain doughs) and as a flavor enhancer, such as a topping on baked goods. This subsector includes companies making bread, cakes, cookies, and other perishable bakery products. It includes SIC codes 205, 2051, and 2052. The NAICS equivalents are 311812, 311821, and 311919.

Dairy

Salt is added to cheese as a fermentation control agent and as a color and texture control agent. The dairy subsector includes companies that manufacture creamery butter, natural and processed cheese, condensed and evaporated milk, ice cream, frozen desserts, and specialty dairy products. It incorporates SIC codes 202, 2021, 2022, 2023, 2024, and 2026. NAICS codes are 311512, 311513, 31152, 311514, and 311511.

Grain Mill Products

This group includes establishments engaged in milling flour and rice, and manufacturing cereal breakfast foods, and blended or prepared flour. SIC codes are 204 (excluding 2047), 2041, 2043, 2044, and 2045. NAICS codes are 311211, 31192, 31123, 311212, and 311822.

General Industrial

The industrial uses of salt are diverse. This major sector of salt consumption includes, in descending order of salt usage: oil and gas exploration where salt is used in the drilling process, metal

processing, other industrial, pulp and paper, textiles and dyeing, tanning and leather treatment, and rubber manufacture. General industrial applications accounted for 6% of 2002's total reported salt usage. The numbers are in decline in the United States because many of these manufacturing industries are moving overseas.

Oil and Gas Exploration

Salt is an important component of drilling fluids used in well drilling. It is used as a flocculent and as a compound to increase drilling fluid density to overcome high down-well gas pressures. Whenever drilling activities encounter salt formations, salt is added to the drilling fluid to saturate the solution and minimize the dissolution within the salt strata. Salt is also used to increase the set rate of concrete in cement casings. This SIC category includes companies engaged in oil, gas, crude petroleum, and refining and compounding lubricating oil. It includes SIC major groups 13 and 29. NAICS codes are 211111, 213112, and 336611.

Metal Processing

Salt is used in concentrating uranium ore into uranium oxide, or yellow cake. It is also used in processing aluminum, beryllium, copper, steel, and vanadium. Establishments engaged in the smelting, refining, and fabrication of ferrous and nonferrous metals represent this category, which includes SIC 33, 34, 35, and 37. NAICS equivalents are 422690, 333994, and 213114.

Other Industrial

This subsector is represented by any group not included in any of the general industrial groups in this major category.

Pulp and Paper

Salt is used to bleach wood pulp. It also is used to make sodium chlorate, which is added with sulfuric acid and water to manufacture chlorine dioxide—an excellent oxygen-based bleaching chemical. Although the chlorine dioxide process originated in Germany after World War I, it has become more popular because of environmental pressures to reduce or eliminate chlorinated bleaching compounds. Companies that manufacture wood pulp, cellulose fibers, pulp from rags, paper and paperboard, and paper and paperboard converted products are included in this subgroup, which includes SIC group 24 and NAICS groups 322121, 322130, and 322122.

Textiles and Dyeing

In commercial dye manufacture, salt is used as a brine rinse to separate organic contaminants, promote “salting out” of dyestuff precipitates, and blending with dyes to standardize concentrated dyes. One main role for sodium chloride is to act as a mordant (color fixer); that is, to provide the positive ion charge to promote the absorption of negatively charged dye ions. The textile and dyeing industry includes businesses involved in fiber preparation and subsequent yarn and woven fabrics manufacturing, and fiber dyeing and finishing. This includes SIC group 22 and also NAICS 313311.

Tanning and Leather Treatment

Salt is added to animal hides to inhibit bacterial decomposition on the underside of the hides, to remove some of the moisture in the hides, and to remove some of the blood. This process is called “curing” (Kaufmann 1960). This subsector includes establishments that cure and/or tan animal hides. It includes SIC 311 or NAICS 316110.

Rubber Manufacture

Salt is used to make neoprene rubber, white rubber, and Buna rubber. Salt brine and sulfuric acid are used to coagulate emulsified latex made from chlorinated butadiene. Businesses that make rubber

and rubber products, such as synthetic rubber, tires and inner tubes, rubber and plastic footwear, reclaimed rubber, rubber and plastic hose and belting, and other fabricated rubber products, comprise this category. It includes SIC codes 282, 2, 30 (excluding 3079), 3011, 3021, 3031, 3041, and 3069. The NAICS corresponding numbers are 325212, 326211, 316211, and 31332.

Agricultural Industry

Since prehistoric times, humans have noticed that animals satisfied their salt hunger by locating salt springs, salt licks, or playa lake salt crusts. Barnyard and grazing livestock need supplementary salt rations to maintain proper nutrition. Veterinarians have advocated adding salt in commercially mixed feeds or in block forms, which are sold to farmers and ranchers. Salt also acts as an excellent carrier for trace elements not found in the vegetation consumed by grazing livestock. Sulfur, selenium, and other essential elements are commonly added to salt licks, or salt blocks, for free-choice feeding.

The agricultural end-use sector contains three subgroups—feed retailers and/or dealers and mixers, feed manufacturers, and direct buying end users. The entire category represents 4% of total reported usage in 2002, even when including agricultural distribution (contained under “distributors”).

Feed Retailers/Dealers/Retailers-Mixers

Establishments engaged in the retail distribution of animal feeds, fertilizers, agricultural chemicals, pesticides, seeds, and other farm supplies represent this subgroup. It incorporates feed retailers who mix on-site some or all of the feed they sell and whose primary customers are feed end users, not other feed retailers. There are no suitable SIC classifications for this subsector, but the NAICS codes are 311111 and 311119.

Feed Manufacturers

This subcategory includes establishments engaged in preparing feeds and feed ingredients and adjuncts for animals and fowl, including poultry and livestock feed and feed ingredients such as feed supplements and concentrates and premixes. It does not include the local dealer-mixer, whose primary business is reselling prepackaged feed and feed ingredients to end users, but who does a moderate amount of custom mixing secondarily. The end use includes SIC 2048 and NAICS 311611.

Direct-Buying End Users

Salt used in this subsector is for consumption by farms, ranches, dairies, feed lots, and so forth, buying on a direct basis from salt producers. It includes SIC major group 2. Also, this would include NAICS 112000 series.

Agricultural Distribution

This subcategory of “distributors” is a secondary, or second-tier, consumer of salt, and includes companies involved in the wholesale distribution of animal feed products, fertilizers, agricultural chemicals, pesticides, seeds, and other farm supplies to retail feed dealers and some large end users who buy on a wholesale basis. It includes co-op (except mixing operations) and independent wholesalers/distributors. SIC 5159 is the category classification. The corresponding NAICS code is 42259.

Water Treatment

Approximately 1.2 trillion L (0.3 trillion gal) of water are used daily in the United States for residential and commercial use. Many areas of the United States have “hard” water, containing

excessive calcium and magnesium that contribute to buildup of a scale or film of alkaline mineral deposits in household and industrial equipment. Commercial and residential water softening units use salt to regenerate inactive sites on ion-exchange resin beds that work to soften water by removing the ions causing water hardness. Typical hardness ions, calcium and magnesium, are removed from water sources by passing the water supply through an ion-exchange resin bed where they exchange places with sodium ions that reside within the resin. Once depleted, flushing with salt brine recharges the resin bed. The sodium ions from the brine are exchanged for calcium and magnesium that have been in sites on the resin bed. In 2003, water treatment represented 4% of total domestic reported usage. During the past 10 years, potassium chloride has become increasingly popular for regenerating home water softener systems. Sodium chloride, however, is still the most popular regenerant on the market.

Since the turn of the twenty-first century, some municipalities have begun to restrict the use of water softeners claiming that the discharge from home softeners increases the total dissolved solids that impact municipal water treatment systems. This restriction has been most prevalent in some areas of Southern California where water reclamation is of considerable concern.

Government and commercial water treatment are the primary subgroupings of water treatment; and water treatment distribution is the secondary subgroup, which is the second-tier market for salt sales.

Government

This subsector includes local, state, and federal customers purchasing directly from salt producers for water treatment usage. It includes SIC 2899 and the corresponding NAICS code, 422690.

Commercial

All commercial establishments that purchase salt primarily for water treatment, and not classified elsewhere, are in this category. It includes car washes, laundries, and utilities. It is included in SIC 2899 and NAICS code 421720.

Water Treatment Distributors

Water-conditioning salt-route operators and distributors whose exclusive or dominant business is distributing water conditioning products to home or industry represent this subcategory. It is included in SIC 7399 or NAICS 221310.

Ice Control and Road Stabilization

The second largest end use of salt in North America and Europe is for highway deicing. Salt has been used to melt snow and ice on roadways for the past 60 years. Gabriel Daniel Fahrenheit, the developer of the Fahrenheit temperature scale, discovered that salt mixed with ice (at a temperature below the freezing point) creates a solution with a lower freezing point than water itself. When salt is applied to an ice-covered road, it bores through the ice, melting as it proceeds, and forms brine as it mixes with the melted liquid from the ice. The brine collects below the surface of the ice and snow and prevents the water from refreezing into ice and bonding to the road surface. The phase diagram (see Figure 5) for sodium chloride demonstrates the freezing point depression of brine, as opposed to plain water, along with the different phases of solid and liquid brine. The manner in which brine freezes depends on the initial strength of the brine. It is sometimes mistakenly assumed that the stronger the brine, the lower the temperature at which freezing begins. This is true only for brine strengths up to 23.31% by weight of sodium chloride. These issues are critical to the proper use of Sensible Salting techniques recommended by the Salt Institute.

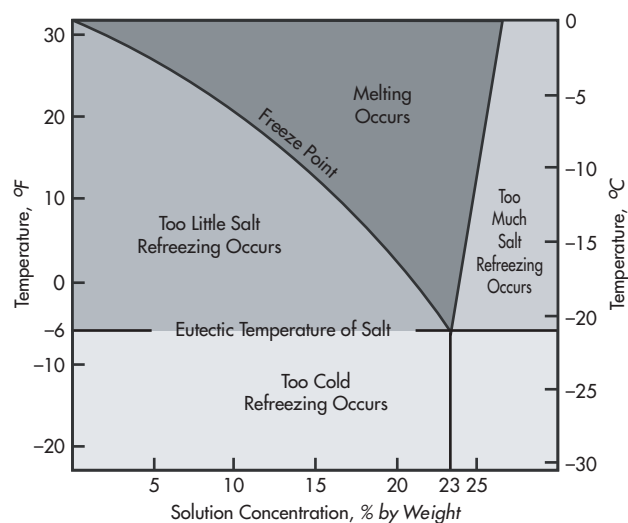


Figure 5. Phase diagram for sodium chloride water freezing point depression

Table 5. Economic impact of a 1-day shutdown—economic impact in \$ million

State/Province*	Wages/Salaries	State/Local Taxes	Federal Taxes	Retail Sales	Total
Illinois	220.66	10.79	19.64	98.48	349.57
Indiana	88.23	4.59	6.35	41.18	140.35
Iowa	38.25	1.99	2.52	19.91	62.67
Michigan	165.33	8.75	12.90	71.50	258.48
Minnesota	95.79	5.69	7.66	40.32	149.46
Missouri	90.70	4.01	6.44	39.05	140.19
New Jersey	174.44	8.68	17.09	80.66	280.87
New York	381.63	22.50	31.68	161.76	597.57
Ohio	179.29	10.23	12.91	79.07	281.50
Pennsylvania	214.17	12.02	17.35	93.17	336.70
Virginia	130.39	6.43	11.21	56.95	204.98
Wisconsin	84.82	4.40	6.36	38.78	134.36
Ontario	272.02	17.36	34.43	33.33	357.14
Quebec	142.77	14.39	13.62	19.23	190.01

Adapted from the Salt Institute 2004.

* Links to the methodology and downloadable one-page summaries for each state and province are found at <http://www.saltinstitute.org/30.html>.

The public in a dynamic society demands that governments keep commerce mobile by keeping traffic arteries open during winter snowfalls. A 2004 study by the economic consulting firm Global Insight Inc. (Waltham, Massachusetts) found enormous costs associated with blizzards that might shut down various states and provinces. The results of the study are shown in Table 5. The public also expects traffic accidents to be minimized. Salt is an inexpensive, widely available, and effective ice control agent to meet the demands. It does, however, become less effective as the temperature decreases below -21.2°C (-6.0°F). At lower temperatures, more salt would have to be applied to maintain higher brine concentrations to provide the same degree of melting. Most winter snowstorms and ice storms occur between -6°C (20°F) and 0°C (32°F), a range in which salt is most effective.

Table 6. Length of corrosion perforation warranties on model year 2000 automobiles sold in the United States

Make	Length of Warranty		Make	Length of Warranty	
	Years	Miles		Years	Miles
Acura	5	Unlimited	Lincoln	5	Unlimited
Audi	12	Unlimited	Mazda	5	Unlimited
BMW	6	Unlimited	Mercedes-Benz	4	50,000
Buick	6	100,000	Mercury	6	Unlimited
Cadillac	6	100,000	Mitsubishi	7	100,000
Chevrolet	6	100,000	Nissan	5	Unlimited
Daewoo	5	Unlimited	Oldsmobile	6	100,000
Dodge	5	100,000	Plymouth	5	100,000
Ford	5	Unlimited	Pontiac	6	100,000
GMC	6	100,000	Porsche	10	Unlimited
Honda	5	Unlimited	Saab	6	Unlimited
Hyundai	5	Unlimited	Saturn	6	100,000
Infiniti	7	Unlimited	Subaru	5	Unlimited
Isuzu	6	100,000	Suzuki	3	100,000
Jaguar	6	100,000	Toyota	5	Unlimited
Kia	5	100,000	Volkswagen	6	Unlimited
Land Rover	6	100,000	Volvo	8	Unlimited
Lexus	6	Unlimited			

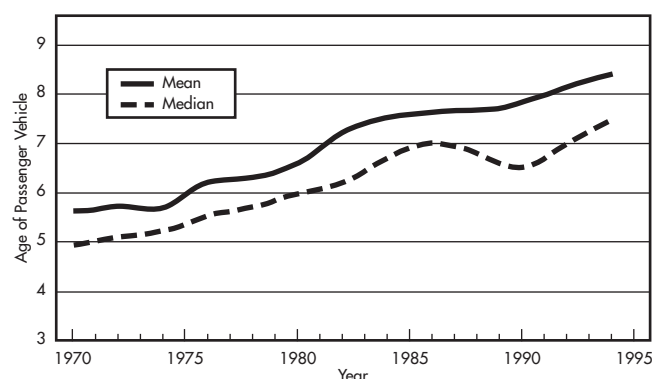
Source: Johnson 2000.

Since about 1994, there has been increasing use of pre-wetted salt and anti-icing techniques to improve the ability to gain a “bare pavement” road condition as quickly, safely, and as cost-effectively as possible, while still meeting the needs of the affected communities. Studies have documented the vital economic role of clearing ice and snow from roadways. Ice and snow also cause higher fuel costs as cars lose traction because of lower tire friction and spin their wheels to travel a given distance. A car that under normal weather conditions gets 25 mpg may get only 15 mpg on a slippery road (Hanalby 1994).

In addition, salt is added to stabilize the soil and provide firmness on which highways are built. The salt acts to minimize the effects of shifting brought about by changes in humidity and traffic load in the subsurface.

In highway deicing, salt has been associated with corrosion of motor vehicles, bridge decks, unprotected steel structures, and reinforcement bar and wire used in road construction. The automobile industry has made great strides in reducing the most costly impact from using deicing salt. Manufacturers have been successful in engineering corrosion resistance into their vehicles through better design and use of noncorrosive materials, such as fiberglass and plastics. The use of noncorrosive materials has lowered corrosion perforations significantly. The ages of passenger vehicles on the road has shown an upward trend for the past 20 to 25 years. This has allowed vehicle manufacturers to provide corrosion perforation warranties of up to 12 years for some model vehicles (see Table 6 and Figure 6). According to Rendahl (1998), “...some models nearly manage to avoid corrosion completely, by a combination of improved construction and materials, together with a careful application of anti-rust agent and adhesives, penetrating and covering crevice surfaces.”

Surface runoff, vehicle spraying, and windblown actions can also affect roadside vegetation, soil, and local surface and groundwater supplies. Although there is evidence of some environmental salt loading during peak usage, the spring rains and thaws usually



Source: Johnson 2000.

Figure 6. Average mean and median ages of passenger vehicles from 1970 to 1994

provide sufficient water to dilute the concentrations of sodium in the area. Adverse environmental action can also be controlled and minimized by effective spreading techniques recommended by the National Local Technical Assistance Program Association and by the Salt Institute.

The deicing category includes government (state, federal, and local) and commercial subsectors of consumption. Approximately 31% of total reported consumption was used in this category during 2002.

Government Deicing

More than 95% of this major category is for usage by separate local, state, and federal agencies to ensure safe and navigable roads during adverse climatic conditions.

Commercial Deicing

This subsector includes companies that purchase salt for ice control, such as transportation companies, shopping centers, ice control service contractors, and so forth. It includes any distributors whose primary or exclusive business is the distribution of salt for ice control purposes to business and/or government. It does not include institutional purchasers. There are no suitable SIC/NAICS codes for this section.

Other Uses of Salt

The other uses of salt include any consumer that is not included in any of the aforementioned categories. It also includes sales by distributors, excluding those by agricultural and water conditioning distributors that are included as subgroups under agriculture and water treatment. It includes part of grocery wholesale and retail, institutional whole sale distributors, U.S. government resale, and other wholesalers/retailers.

Institutional Wholesale Distributors

This subcategory includes companies engaged in the distribution of food and other salt products to restaurants, hospitals, schools, and other institutional establishments. These are included in SIC groups 58 and 70 and correspondingly, NAICS 722 series.

U.S. Government Resale

Included in this category are government units such as military commissaries that purchase salt for resale to armed forces personnel and dependents at the retail level. It also includes purchases by the government of food-grade salt used by armed forces/government food-services facilities, as well as all other government salt purchases not classified elsewhere. SIC 9199 or NAICS 92119 pertains to this subgroup.

Other Wholesale and Retail

This subsector includes wholesalers, not included elsewhere, primarily engaged in distributing merchandise for personal and household consumption to retailers, such as hardware stores, home centers, filling stations, and discount centers. It also includes all retail outlets that sell merchandise for personal or household consumption that purchase directly from salt producers. The SIC category is 5251, while the NAICS number is 44413.

ECONOMIC FACTORS

Prices

The price of salt depends on the type of salt, production location, product form, and nature of sale. Salt brine is the least expensive type of salt because it is not expensive to produce and processing is minimal. Vacuum pan salt is the most expensive because of the energy input and degree of final-product purity. The price of salt also can vary because of regional differences in labor rates, energy costs, packaging, transportation, and other operating factors. Large consumers of salt generally prefer to purchase salt in bulk quantities. When salt is packaged in bags, cylinders, or single-serve packets, or sold in compressed pellets or pressed blocks, the sales price increases compared with the bulk price. The price of salt can also vary if the consumer is buying based on bid contracts or spot purchases.

Foreign Trade

Salt is one of the largest internationally traded mineral commodities in the world. The estimated total world salt trade in 2002 is about 15% of total world salt production. Because salt is a low-valued material, it is uneconomic to transport long distances, particularly

over land. Overland transportation rates often are more expensive than ocean freight rates; therefore, some countries tend to import salt to certain regions where rail or truck rates from domestic salt production sites are cost-prohibitive.

Imports

Some countries import salt to satisfy demand requirements when indigenous salt resources are minimal or production capacity is inadequate. Japan is an example of a nation that imports the majority of its salt because it does not have any rock salt deposits. Climate and lack of available coastal land are not favorable for solar salt production. Other countries import salt because of economics. Although the United States is the largest salt producer in the world, it imported almost twelve times what it exported in 2002. Less expensive labor costs, transportation costs, and currency exchange rates are the main cost considerations for importing large quantities of salt into the United States. Most salt imported into the United States comes from Canada, Chile, the Caribbean, and Mexico. This salt is mainly consumed by the chemical industry or as deicing salt in areas of the country where there are no local salt deposits, such as the Pacific Northwest and the Southeast. The majority of salt imports are in bulk form, but there is also some imported product packaged in bags, sacks, barrels, and other forms. Before 1989, all imported salt was classified under the Tariff Schedule of the United States (TSUS), Annotated. The TSUS codes for salt in brine, bulk salt, and other salt were numbers 4209200, 4209400, and 4209600, respectively. Beginning in 1989, after the passage of the Omnibus Trade and Competitiveness Act of 1988, the United States adopted the internationally used Harmonized Tariff System (HTS) that aggregated the three classifications into one named "Salt (including table and denatured salt) and pure sodium chloride, whether or not in aqueous solution, sea water." This HTS code number is 2501.00.0000. Table 7 lists some of the recent U.S. import statistics.

Exports

Canadian exports to the United States make up the majority of foreign salt imports; however, the majority of U.S. salt exports are to the Canadian provinces of Ontario and Quebec. Canada represents about 87% of total U.S. exports. The remainder of export sales is small shipments mainly to other countries in the Western Hemisphere. Table 7 lists the trend in U.S. salt exports since 1970 (USGS 2004).

Transportation and Storage

Overland and waterborne transportation rates of salt are important economic factors to salt consumers. Transportation charges generally are always higher than the sales price of the salt being carried. Rock salt, solar salt, and vacuum pan salt are shipped in bulk or in some packaged form, such as shrink-wrapped bags on pallets, and 1-t "big bags." Because salt brine is a solution, it is transported through underground or surface pipelines.

Overland

Overland movements include salt moved by rail, truck, and pipeline from salt production localities to regional consumers. Because overland transportation rates are more costly than the salt, it is typically not economical to ship salt overland farther than about a 500-km (311-mi) radius from the production site. Competition from other salt producers is usually encountered at distances beyond that radius.

Rail Movement. Boxcars are used to convey packaged salt loaded on pallets. Forklifts and conveyor belts assist the loading of the salt into the boxcars. The majority of all railcars used to transport bulk salt are covered hopper cars. The protected cars prevent

Table 7. U.S. imports and exports of salt, kt

Year	Primary Production	Imports	Exports	Apparent Usage	Unit Value, \$/t	Unit Value, 98\$/t	World Production
1990	36,900	5,970	2,270	40,600	22.39	27.93	183,000
1991	35,900	190	1,780	40,300	22.32	26.71	202,000
1992	34,800	5,390	992	39,200	23.07	26.80	185,000
1993	38,200	5,870	688	43,400	23.66	26.70	187,000
1994	39,700	9,630	742	48,600	24.94	27.43	191,000
1995	40,800	7,090	670	47,200	24.51	26.22	199,000
1996	42,900	10,600	869	52,600	24.71	25.68	204,000
1997	40,600	9,160	748	49,000	24.46	24.84	221,000
1998	40,800	8,770	731	48,800	24.17	24.17	200,000
1999	44,400	8,870	892	52,400	25.00	24.46	210,000
2000	43,300	8,960	642	51,600	24.02	22.74	212,000
2001	42,200	12,900	1,120	54,000	26.30	24.21	217,000
2002	37,700	8,160	689	45,000	26.79	24.27	210,000

Source: U.S. Geological Survey 2004.

inclement weather from affecting the salt. To avoid caking resulting from moisture and humidity, deicing salt is treated with 40–60 ppm of ferric ferrocyanide (known as Prussian Blue) or sodium ferrocyanide (yellow prussiate of soda, or YPS).

To reduce freight rates, most producers ship in unit trains that contain up to 12 railcars. The loading and unloading of covered hopper cars includes pneumatic equipment using flexible hoses and pipes. Many cars are equipped with bottom-dump doors or gates that allow faster unloading. Conveyors beneath the railcars take the salt to truck-transfer stations or to warehouses or stockpiles.

Truck Movement. Trucks are used in shorter hauls from production sites to customers' locations, or from distribution centers and warehouses to consumers. Bulk salt is carried in dump trucks or specially built pneumatic and tank trucks. Dump trucks can drop their loads directly into hoppers or onto a surface pad so that the salt can be picked up by front-end loaders. Open trucks should be covered properly with tarps to prevent caking or salt losses from being blown or shaken off the vehicle. Dump trucks can also unload into pits, which are convenient for companies that convert dry salt into brine.

Pipeline. Some salt brine is transported by pipeline between production sites and consumers' locations. The chemical industry is the largest consumer of brine, but some chloralkali operations are not located adjacent to salt deposits that could be solution mined. Several chemical companies in Louisiana and New York rely on brine supply companies to provide a continual supply of brine feedstock. Some of the pipelines are only a couple of kilometers in length; however, others can be up to 100.0 km (62.1 mi) long or more.

Waterborne

Waterborne movements of salt include salt shipped in barges and freighters. This type of transportation is the most economical method to move salt great distances. Although rock salt and solar salt are the two major types of salt shipped on the water, bulk vacuum pan salt from the Netherlands is also shipped on water to various locations, including the southeastern United States.

Barge. The Erie Canal and the Chesapeake & Ohio Canal owe part of their origin to the early salt industry of the eastern United States. Barges were the easiest way to transport salt and other goods to customers far away. Barges are used today in shipping salt along the Intracoastal Waterway of the Gulf Coast, up the Mississippi River to other rivers, such as the Ohio, and to the Great Lake ports, the Florida coast, and inland waterways. They are also

used to transport salt across the Great Lakes to and from Canada, and from Mexico to the Pacific Northwest. Several barges are linked together and towed inexpensively to distant locations. When freezing winter conditions in the Midwest affect the major rivers and their tributaries, salt movements by barge cease until the ice is broken or thaws. Low water levels on the Mississippi River have, on occasion, halted barge traffic for weeks at a time.

Salt is usually loaded onto barges using conveyor belts with moveable swing arms to evenly distribute the salt in the hold. A conveyor system is also found in the bottom holds of many barges to unload the salt at the final destination. Barge-mounted or shore-mounted cranes with clamshell buckets are also used to unload salt.

Freighter. Bulk freighters are the dominant method of transporting waterborne salt throughout the world. Salt may represent a partial cargo or the entire cargo on a ship. When the Jamestown and Plymouth colonial settlers arrived in the New World, imported salt was carried as ballast in the hulls of sailing ships arriving from England. Today, modern bulk freighters may range in size from 6 to more than 90.7 kt (100 thousand st).

Some freighters have self-unloading equipment to discharge the salt from the cargo hold. The most common method of unloading bulk salt is by clamshell bucket and crane. The ship is brought alongside the dock and the salt is transferred to a dockside storage site or to a transportation system.

Storage

Bulk salt may be stored outside on specially engineered pads that reduce the amount of runoff that threatens surface and groundwater. The storage sites are usually located near areas accessible by water, rail, or truck. Salt is stored in conical-shaped piles or long windrows. Plastic, canvass, or burlap covers are often used to protect the salt from the wind and rain. These tarps are secured by adding weights or heavy tires to keep them from blowing off.

Inside storage bins, silos, and warehouses are also used to store bulk salt. For convenience, the site is usually located near the rail, truck, or ship loading facilities. Packaged salt is often stored in warehouses adjacent to where the salt is bagged or containerized. Some manufacturers will lease warehouse space near active markets that are located at some distance from their plants.

ENVIRONMENTAL AND HEALTH CONSIDERATIONS

Since the early 1970s, people throughout the world have become more conscious about the environmental effects of pollution caused

by industrialized societies. In pursuit of better living conditions and longer life spans, many people have changed their lifestyles based on advice found in literature and publicized in the media. These topics have a bearing on salt consumption, and therefore, salt demand.

The national energy crisis that began in 1973 adversely affected several energy-intensive industries, one being the synthetic soda ash industry that used tremendous quantities of salt. Higher energy costs, environmental problems pertaining to discharges of sodium chloride and calcium chloride to groundwater supplies, and competition from natural soda ash sources contributed to the closure by 1979 of seven of the eight synthetic soda ash plants that operated during the 1970s. The last plant closed in 1986, which ironically was the first plant constructed in 1881 and commenced production in 1884. The demise of this sector of the domestic chemical industry resulted in the significant loss of salt production.

In the highway-salt marketplace, the U.S. salt industry, through its membership in the Salt Institute, initiated a Sensible Salting Program in 1972 to educate transportation departments on proper ways to store, handle, and apply deicing salt to protect the environment while maintaining winter mobility and safety. The practice of knowing when to use salt, what alternative ice control agents to use, and how much salt to apply has contributed to improved environmental protection from overuse of salt. Deicing salt is the fastest, least expensive, and most effective agent to control the hazards associated with ice and snow. Without salt, there would be significant increases in the number of traffic accidents, loss of life, and productivity.

Population increases have caused increases in municipal waste treatment, resulting in elevated salinities in waterways. As individuals consume salt in their diets and in household activities, sodium and chloride are discharged to the environment through municipal sewage systems. The cities with growing populations are experiencing these increases. Although runoff from irrigated agriculture influences salinity, especially in the western United States, chloride trends are not appreciably correlated with changes in irrigated acreage nationwide.

In the late 1960s and early 1970s, health authorities attributed salt as one of the alleged causes of hypertension, or high blood pressure. People began restricting their salt intake and measuring the sodium levels in ingested food. It was not until the mid-1980s that other medical research suggested that other factors beside salt contributed to hypertension. In 1988, the U.S. Environmental Protection Agency (EPA) issued the National Primary Drinking Water Regulations that eliminated sodium as a regulated drinking water contaminant. The EPA rationale was that evidence was building that salt did not “cause” hypertension, and that the quantity of sodium in drinking water was very low compared with what is contained in food and other beverages.

Most ingested sodium comes from food, not beverages. Salt intake influences many bodily functions, the most discussed of which is blood pressure. For 4,000 years science has known that salt intakes can affect blood pressure through signals to the muscles of blood vessels trying to maintain blood pressure within a proper range. It is also accepted that a minority of the population can lower their blood pressure by restricting dietary salt. Elevated blood pressure, “hypertension,” is a well-documented risk factor for cardiovascular events such as heart attacks and strokes. It has been suggested that because salt intakes are related to blood pressure, and because cardiovascular risks are also related to blood pressure, that, surely, salt intake levels are related to cardiovascular risk. This is the “salt hypothesis” or “sodium hypothesis.” Data are needed to

confirm or reject this hypothesis. Until the 1990s, scientists had never tested the “salt hypothesis” by documenting whether reducing dietary salt actually reduces a person’s chances of having a heart attack or a stroke. As of 2004, there are ten “health outcomes” studies of sodium reduction. Not a single study has found an association in the general population between low-sodium diets and reduced incidence of cardiovascular events like stroke or heart attack. See www.saltinstitute.org/27.html for a list of the studies. It is also accepted that a minority of the population can lower blood pressure by restricting dietary salt.

Canada advises that only a minority of its population—those with high blood pressure or “high risk of developing high blood pressure” need concern themselves about the intake of sodium in their diet.

Official policy in the United States is for virtually everyone to reduce dietary salt. But conflicting recommendations exist even in the United States. The U.S. Preventive Services Task Force (2004, p. 634) states, for example:

There is insufficient evidence that, for the general population, reducing dietary sodium intake or increasing dietary intake of iron, beta-carotene, or other antioxidants results in improved health outcomes (“C” recommendation); recommendations to reduce sodium intake may be made on other grounds, including potential beneficial effects on blood pressure in salt sensitive persons.

The debate has confused the public, but there is a clear downward trend in consumer concern about dietary salt—tracking the new science. The International Food Information Council reported in early 2004 that only 5% of consumers are trying to avoid salt in their diets.

It is likely that new studies using the higher standards of evidence-based medicine will reduce the ongoing controversy, better inform public policy, and reduce consumer confusion.

FUTURE TRENDS

Despite the environmental concerns regarding deicing salt, rock salt will continue as the deicing agent of choice. Further improvements in technology for weather forecasting and instrumentation will allow calibrating technical application to actual ice-melting needs in ways not possible earlier. This will allow safer roads with less product usage. Other deicing products, such as calcium magnesium acetate, are commercially available but are more expensive, and more must be used to have the same effect as salt.

Human salt intakes are a function of population (intake levels are unchanged over the past century); thus continuing global increases are expected for the next 15 years. Because most markets for salt are mature, domestic and world consumption will grow proportional to the rise of population and the gross domestic product of countries.

The United States will remain the largest salt-producing nation in the world for years to come, though the rapid industrial growth in China may change its relative position in the coming decades. Since the middle of the twentieth century, the U.S. salt industry has restructured itself through acquisitions, name changes, and consolidations to become a more integrated North American industry competing in the Western Hemisphere.

The world will continue to mine, harvest, process, transport, and sell salt among neighboring countries. New deposits will be developed in the future that will probably compete with existing facilities. The facilities having the lowest production costs, offering a high-quality product, and having low transportation costs will be the leaders of the world salt industry.

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Industrial Sand and Sandstone

Steven Herron

Industrial sand is a term normally applied to high-purity silica sand products with closely controlled sizing. It is a more precise product than common concrete sand and asphalt gravels. Although deposits of common construction sand and gravel are wide spread, industrial sand deposits are limited. The special properties of industrial sands—purity, grain size, color, inertness, hardness, and resistance to high temperatures—make them often irreplaceable in a variety of industrial applications. Their higher silica content allows for more specialized, higher margin applications than construction sand and gravel.

Industrial sand is found in many forms, colors, and grades. In general terms, the mineral quartz (SiO_2) is the predominant component of industrial sand. Although most industrial sand deposits contain a high percentage of quartz (95% plus), using industrial sands with lower quartz content is becoming more common as demand for industrial sand outpaces production in certain markets, particularly in the western United States.

Silica is found in most rock types of every geologic age and virtually everywhere in the world. Silica can be found in products that are used daily. From fiber-optic cables to beverage containers and insulation, it is difficult to imagine a world without silica-derived products.

The crystal structure of silicon dioxide consists of one atom of silicon bonded to four surrounding atoms of oxygen to form a three-dimensional network of SiO_4 tetrahedra. Approximately 64% of the crust of the earth (Klein and Hurlbut 1999) is composed of minerals built around a three-dimensional framework of linked SiO_4 tetrahedra. These minerals belong to the tectosilicate class in which all the oxygen ions in each SiO_4 tetrahedron are shared with neighboring tetrahedral. This results in a stable, strongly bonded structure in which the Si:O ratio is 1:2.

There are at least nine known polymorphs of SiO_2 , one of which is synthetic. Each polymorph has its own space group, cell dimensions, characteristic morphology, and lattice energy. The principal naturally occurring SiO_2 polymorphs fall into three structural categories: low quartz, low tridymite, and low cristobalite. This chapter focuses on industrial sands containing the low-quartz polymorph.

Quartz is characterized by its glassy luster, conchoidal fracture, and crystal form. A great many different types of quartz exist, to which varietal names have been given. Although the mineral quartz is common, deposits of high-quality industrial sand and

sandstone are rare. Most industrial sands that consumers prefer are products with a high percentage of pure quartz and corresponding low percentages of “contaminants” (e.g., accessory minerals). However, many consumers sacrifice quartz grade for other considerations such as color, price, and availability. A number of consumers evaluate competing products and accept lower grade industrial sand products.

USES AND SPECIFICATIONS

Industrial sand that is mined and beneficiated for industrial uses must meet or exceed specifications derived by the product end users. Specifications are as varied as the users, and often consider freight and availability. In the United States, the glass industry consumes approximately 40% (Dolley 2003) of all industrial sand production. Other relevant markets include foundry (approximately 20%), ground silica (PV), abrasives (approximately 5%), proppants (approximately 5%), filtration products, and recreation and building materials (including stuccos, thin sets, and grouts).

Glass and Ceramic Sand

Quartz is the principal glass-forming compound in a glass batch. Glass manufacturers enjoy some flexibility in chemical specifications; therefore, most specifications are indexed to the chemistry of certain deposits. These specifications (Tables 1 and 2) define the limits and ranges for chemical properties and size distribution that can be permitted in a specific furnace. Some specifications such as heavy mineral content or total iron oxide content (Mills 1983) are critical to a glass manufacturer and require stringent limits. Iron oxide is present in almost every raw material used in a glass batch and must be strictly controlled so that a consistent color is maintained in the finished product. Heavy minerals must also be strictly controlled. Because of the refractory nature of many heavy minerals (e.g., corundum, zircon, and ilmenite), they do not fully melt in the furnace, which results in stones or “feathers” in the finished products.

Glass-grade industrial sand can be sold into several markets within the glass market segment. Sand is used in the production of flat, container, fiber, and specialty glass products. Specialty glass consists of many products. The largest portion of the specialty glass business is laboratory and lighting glass (incandescent and fluorescent light bulbs). Specialty glass also includes components in the electronics industry such as optical fiber and semiconductors.

Table 1. Glass sand specifications for flat glass

Chemical	
SiO ₂	99.5% minimum
Fe ₂ O ₃	0.04% maximum
Al ₂ O ₃	0.030% maximum
TiO ₂	0.1% maximum
Cr ₂ O ₃	2 ppm maximum
MnO ₂	0.002 ppm maximum
H ₂ O	0.05% maximum
Physical	
Size, mm	Cumulative Retained, %
1.18	0.0
0.85	0.01 maximum
0.425	0.10 maximum
0.106	92.0 minimum
0.075	99.5 minimum

Source: Zdunczyk and Linkous 1994.

Table 2. Glass sand specifications for flint container glass

Chemical	
SiO ₂	98.5% minimum
Fe ₂ O ₃	0.035% maximum
Al ₂ O ₃	0.5% maximum
CaO + MgO	0.2% maximum
TiO ₂	0.03% maximum
ZrO ₂	0.01% maximum
H ₂ O	0.1% maximum
Cr ₂ O ₃	0.05% maximum
Physical	
Size, mm	Cumulative Retained, %
1.18	0.0
0.850	0.0
0.600	4 maximum
0.425	25 minimum
0.106	95 minimum

Source: Zdunczyk and Linkous 1994.

Glass-grade, whole-grain industrial sand is also sold into the ceramics market. Up to 32% of the ceramic body of sanitary ware (toilets, sinks, etc.) is composed of whole-grain industrial sand.

It is difficult for industrial sand producers to tightly control the chemistry of a deposit. Therefore, most consumers work closely with producers to develop a specification that can be acceptable to both parties. In general terms, the consumers of industrial sand are most concerned about consistency, which allows for more efficient furnace operation and consistent products.

Foundry Sand

In terms of volume, foundry sand consumers are the second highest consumers of industrial sand. The American Foundry Society (AFS) estimates that there are 2,950 foundries in all 50 states of the United States, and nearly 60% of them are in Illinois, Indiana, Michigan, Ohio, and Wisconsin. Foundry sand must generally exceed 98% SiO₂ in purity, and limits are placed on the amounts of CaO and MgO. Specifications for some foundries, however, can vary greatly, depending on price and availability. Much like glass

consumers, foundry consumers are most concerned about consistency of the sand.

The properties important for commercial foundry sand are grain shape, size distribution, base permeability, sintering point, clay content, and mineralogical composition (Dietert 1966). Foundries use industrial sand in the manufacture of molds and cores for casting metals such as steel, ductile iron, gray iron, and aluminum- and copper-based alloys (Wilborg and Henderson 1983). A casting is a metal part formed by pouring molten metal into a sand mold or metal die. The mold comprises two halves that, when mated, form a cavity into which the molten metal is poured (Whitlatch 1939). If an internal cavity is required in the casting, a core is placed inside the mold cavity. In molds, fine- to medium-grained sand is generally preferred, and coarser sands are preferred for cores.

Specialty sands such as chromite, olivine, fused silica, and zircon are increasingly displacing quartz sand in foundry applications. However, quartz-rich industrial sand still holds the predominant market share in foundry applications (Hoyt 1987) because of its abundance, which translates into cost savings for the end user. The use of specialty sand and industrial sand blends is increasing. Blends cost less than specialty sands and can create a superior mold by increasing permeability.

The effect of grain size on the permeability of foundry sand cannot be understated. After ramming, the permeability of the sand must remain high enough to allow gases to escape. Even a small amount of fine sand (– 0.106 mm) will greatly reduce the performance of foundry sand (Dietert 1966). The AFS grain fineness number is used in describing the results of a sieve analysis and is also a means of calculating the mean diameter of sand particles. The AFS grain fineness number is approximately the number of openings per inch corresponding to a sieve that would just pass a sand sample if its grains were of uniform size. It is approximately proportional to the surface area per unit weight of sand exclusive of any clay binder or matrix (Anon. 1978). To further characterize the size profile of a sand grain, the number of adjacent screens having 10% or more of the material retained on them can be noted (Hoyt 1987).

In addition to size, the shape of sand grains also affects the porosity of the mold (Zdunczyk and Linkous 1994). High porosity promotes high green strength and allows use of less binder in a mold. The more angular the sand grain, the lower the porosity and green strength of a mold. Angular grains also tend to resist compaction; therefore, the mold densities are 8% to 10% lower than for round grains (Zdunczyk and Linkous 1994).

Ground Silica

Ground silica (PV) is used as a functional filler and extender in many industrial applications, including paints and coatings, caulks, epoxy-based compounds, sealants, precision castings, and synthetic rubber. It is also the major batch component in the production of fiberglass. PV is an essential component of the glaze and body formulations of all types of ceramic products, including tableware, sanitary ware, and floor and wall tile. In the ceramic body, silica is the skeletal structure on which clays and flux components attach. The SiO₂ contribution is used to modify thermal expansion, regulate drying and shrinkage, and improve structural integrity and appearance. PV products are also used as the primary aggregate in both shape and monolithic-type refractories to provide high-temperature resistance to acidic attack in industrial furnaces.

The term PV contains two primary subsets of products: silica flour and ground silica. Silica flour generally is sold into lower value markets, and ground silica is generally sold into higher value markets. Table 3 presents typical chemical and physical specifications for PV products.

Surface-modified PV (chemically treated) and uncoated PV are conventionally used as a functional filler to modify the physical properties of a product (e.g., altering its thermal characteristics). In paint, PV is used in a range of products to increase durability, to improve weatherability, and as a pigment extender. Pigment extenders can provide significant value to consumers of PV, because a high-quality PV can reduce the need for high-priced pigments such as titanium dioxide (Guillet and Kriens 1984). Paint formulators select micron-sized products to improve the appearance and durability of architectural and industrial paint and coatings. High-purity silica contributes critical performance properties such as brightness and reflectance, color consistency, and oil absorption. In architectural paints, silica fillers improve tint retention, durability, and resistance to dirt, mildew, cracking, and weathering. Low oil absorption allows increased pigment loading for improved finish color. In marine and maintenance coatings, the durability of silica imparts abrasion and corrosion resistance. In plastics, PV provides dielectric properties and enhances the strength of the final product. PV is also valued for its stable chemistry, and it is used as an inert filler.

PV is also used in the production of chemicals. Silicon-based chemicals are the foundation of thousands of everyday applications, ranging from food processing to soap and dye production. PV is the main component in the production of sodium silicate, silicon tetrachloride, and silicon gels. These chemicals are used in household and industrial cleaners, to manufacture fiber-optic materials, and to remove impurities from cooking oil and brewed beverages.

Abrasives

Industrial sand enjoys significant market share as an abrasive. It is used to clean surfaces and is valued for its relatively low price, cutting capability, blasting profile, and availability. High-quality abrasive sand must be free of impurities such as carbonates or caliche, organics, and aluminum silicate minerals. Impurities greatly affect performance by reducing the cutting ability of the sand, creating a nonuniform blasting profile, or creating dust. Most consumers prefer angular sand.

Abrasive grades or sizes are indexed to application. Coarse grades are primarily used for large-scale blasting of iron or steel structures, and for removing thick coatings of unwanted material from a surface. Conversely, fine grades of sand are used for polishing surfaces and cleaning softer alloys such as brass and aluminum. Silica sand is also used in the apparel industry for "stone washing" denim products.

The abrasives market is highly competitive, and consumers are generally price conscious and often will compromise quality for price. In addition, health concerns regarding respirable silica have been a major factor in the abrasives market. Industrial sand also competes with many other abrasive products such as slag, garnet, fused alumina, and walnut shells, which do not contain crystalline silica. Although respirable dust can be mitigated by treating the surface of blasting-grade industrial sand with a chemical dust surfactant, producers can never fully mitigate the concerns surrounding respirable silica.

Proppant Sand

Known commonly as *proppant*, or *frac sand*, industrial sand is pumped down holes in deep well applications to "prop" open rock fissures and increase the flow rate of natural gas or oil. Proppant sands are generally added to the "pay zone" of an oil or gas well to increase the conductivity of the well. The conductivity of the well is the sum of the permeability of the proppant multiplied by the propped width of the fissure. Proppant sands are first categorized

Table 3. Specifications for PV

Chemical	
Fe ₂ O ₃	0.10% maximum
Al ₂ O ₃	0.38% maximum
Na ₂ O ₃	0.10% maximum
K ₂ O	0.10% maximum
Physical	
Size, mm	Cumulative Retained, %
0.250	0.0
0.075	1 maximum
0.045	3 maximum

Source: Zdunczyk and Linkous 1994.

Table 4. Proppant stress range

Proppant	Stress Range, psig
Class C sands	0–4,000
Class D sands	0–5,000
Class E sands	2,000–6,000
Surface modified sands (resin)	4,000–12,000
Ceramics	10,000–16,000

by the stress range that they can support (Table 4), and then by the mesh or sieve size. Mesh size is important to performance because sizing is a relative measure of strength. The smaller the porosity in proppants (smaller mesh sands), the more contact area available to support stress. Therefore, all larger mesh size sands exhibit less strength compared to smaller mesh size sands. The final method of categorizing proppant sand is the American Petroleum Institute's (API) specifications. The API testing procedure is known as RP-56.

The sand can be surface modified (resin coated) or nonmodified. The highest valued sands are clean, relatively dust-free, and round, and exhibit better permeability at higher well closure stresses. Under the same stress values, larger mesh sands are more permeable than smaller meshed sands. The hardness and overall structural integrity of silica sand combine to deliver the required crush resistance of the high pressures present in wells up to 2,450 m deep. Its relative chemical nonreactivity is required to resist chemical attack in the corrosive environments found downhole.

Nonmodified proppant markets primarily use two sands—"brown sand" and "white sand." Brown sand is primarily from the Hickory Sandstone of Texas and the eolian sand deposits of southern Colorado. The API recognizes the Hickory sand as a Class D sand and the Colorado sands as Class C sand. White sand is mostly produced from the St. Peter Sandstone near the Ottawa, Illinois, area, and is recognized by the API as Class E. In general terms, the brown sand is used in shallow well applications and the white sand is used in deep wells. The primary differences between the Class E and Class D sands are roundness, acid solubility, and crush strength. Class C sands contain feldspar, which significantly affects the performance of the material at depth. However, Class C sands can demonstrate superior performance compared to Class D and E sands in wells with lower closure levels. This is due to the angularity of the sand. Under higher stress loading (>4,000 psig), angular silica and feldspar particles crush and lodge in the pore throats of the sand pack; however, under low-stress environments, the Class C sands actually increase the permeability of the sand pack. Table 5 illustrates typical proppant grades. Each grade is used for a specific

Table 5. Typical proppant grades (sizes)

Metric, mm	U.S. Mesh Size
2.36 × 1.18	8 × 16
1.70 × 0.850	12 × 20
1.18 × 0.60	16 × 30
0.850 × 0.425	20 × 40
0.600 × 0.300	30 × 50
0.425 × 0.212	40 × 70

application. For each grade, 90% of the product should be within the size range specified.

Filtration Sand

Industrial sand is used in filtration of drinking water, processing of wastewater, and production of water from wells. Uniform grain shapes and grain size distributions produce efficient filtration bed operation to remove contaminants in both potable water and wastewater. Chemically inert, silica will not degrade or react when it comes in contact with acids, contaminants, volatile organics, or solvents. Silica gravel is used as packing material in deep-water wells to increase yield from the aquifer by expanding the permeable zone around the well screen and preventing the infiltration of fine particles from the formation.

The American Water Works Association (AWWA) and NSF International largely govern sand specifications used in filtration. No specifications strictly govern the shape of the sand grains; in general, both round and angular grains perform well. Round grains are valued for their flow characteristics, and angular grains are valued for their ability to trap solids. However, if the grains are too angular, they can lock and inhibit flow in a filter media. It is critical that the sand be uniform, be clean, and have a low effective size and a low uniformity coefficient. The effective size is the size of a sieve opening that will pass 10% by weight of a representative sample. For example, if the size distribution of a sand is such that 10% by weight is finer than 0.45 mm, the sand has an effective size of 0.45 mm (Anon. 1989). The uniformity coefficient of a filter sand is a ratio calculated by dividing the size of a sieve opening that will pass 60% of a representative sample of the sand by the size of a sieve opening that will pass 10% of the sample (the effective size) (Anon. 1989). In general terms, if the sand has a low uniformity coefficient, the sand will perform better as a filter media. Excess fines tend to retard flow, and excess coarse material does not offer sufficient filtering. Table 6 illustrates typical commercial filtration sand specifications.

Recreation and Building Materials

Industrial sand is used for golf course bunkers and greens and the construction of natural or synthetic athletic fields. Bunker sand is frequently blasted from greenside bunkers onto putting greens; therefore, an ideal bunker sand should contain less than 3% gravel (2 to 4 mm) and 7% coarse sand (0.25 to 1.0 mm). Further, an ideal bunker should contain 65% or more particles in the 0.25 to 1.0 mm range and 25% or less in the 0.05 to 0.25 mm range. Bunker sands should also be clean and contain low carbonates. Sands high in carbonates tend to exhibit crusting and setup. Crusting is the formation of a thin hard shell on the surface, and setup is the formation of a thick crust that extends as deep as water penetrates. Crusting and setup increase operating costs by requiring more maintenance to keep the bunker in a playable condition.

In golf and sports turf applications, industrial sand is the structural component of an inert, uncontaminated, growing media. Industrial sand is also used to repair greens and to facilitate everyday maintenance like roto aeration and fertilization. The natural

Table 6. Typical chemical composition and grain size of filtration sand*

Chemical	
SiO ₂	99.39
Fe ₂ O ₃	0.24
Al ₂ O ₃	0.19
TiO ₂	0.12
CaO	0.01
MgO	0.004
Loss on ignition (LOI)	0.046
Physical	
Size Range, mm	Cumulative Retained, %
0.40–0.50	1.60 maximum
0.50–0.60	1.60 maximum
0.60–0.70	1.60 maximum
0.70–0.80	1.60 maximum
0.80–1.00	1.65 maximum
1.00–1.50	1.70 maximum

Source: Zdunczyk and Linkous 1994.

* Acid solubility (1:1 HCl) 0.08%–0.11%. Specific gravity 2.64–2.66.

grain shape and controlled particle-size distribution of silica sand provide the required permeability and compaction properties for drainage, healthy plant growth, and stability. The United States Golf Association (USGA) typically controls the specifications for recreation sand grades used in golf bunkers and in green mixes. Typically, root-zone sand should contain no more than 3% particles ranging from 2 to 4 mm. Sands free of gravel are preferred. Sands containing more than 3% gravel are likely to damage mower blades and bed knives. An ideal root-zone sand should contain 60% or more particles in the 0.25 to 1.0 mm range, and no more than 10% of the particles in the 1.0 to 2.0 mm range, with an additional 5% or less in the 0.05 to 0.15 mm range.

Surface-modified industrial sand has also been recently introduced into recreation markets. The sand is coated with a dye to create a product that has many colors (blue, orange, black, red, purple, etc.). The colored sand is used primarily as play sand product.

Industrial sand is also the primary structural component in a wide variety of building and construction products. Because of its inert nature and wear strength, industrial sand has significant value in the building materials industry. Whole grain silica is used in flooring compounds, mortars, specialty cements, stucco, roofing shingles, skid-resistant surfaces, and asphalt mixtures to provide packing density and flexural strength without adversely affecting the chemical properties of the binding system. The building materials product lines of industrial sand producers have enjoyed significant growth during the 1990s, and demand continues to grow. Although industrial sand has significant competition from other industrial minerals (e.g., limestone), industrial sand tends to be more durable than competing materials, and thus more suitable for use in building materials applications.

GEOLOGY AND DISTRIBUTION OF MAJOR DEPOSIT TYPES IN THE UNITED STATES AND CANADA

The industrial sand deposits mined in the United States vary greatly in chemistry, location, and physical characteristics. In general terms, the highest quality industrial sand deposits are located in the Midwest. The deposits usually contain less than 20% deleterious materials (Pettijohn, Potter, and Siever 1987), and are contained within the mid-continent marine quartz arenites. Table 7

Table 7. Typical processed chemistry of the St. Peter Sandstone

Element or Oxide	Result (% , unless otherwise noted)
Na	<0.05
Mg	<0.05
SiO ₂	99.6
P ₂ O ₅	<0.05
S	<0.05
Cl	<0.05
K ₂ O	0.02
Ca ₂ O	<0.01
TiO ₂	0.03
MnO	<0.01
BaO	<0.01
Cr	<10 ppm
Zr	40 ppm
Pb	<10 ppm

Table 8. Typical chemistry of the Santiago Formation

Analyte	Result, %
SiO ₂	80.98
Al ₂ O ₃	9.96
Fe ₂ O ₃	0.34
CaO	1.69
MgO	0.05
Na ₂ O	1.93
K ₂ O	3.35
Cr ₂ O ₃	<0.01
TiO ₂	0.52
MnO	0.02
P ₂ O ₅	0.02
SrO	0.03
BaO	0.12
LOI	0.64

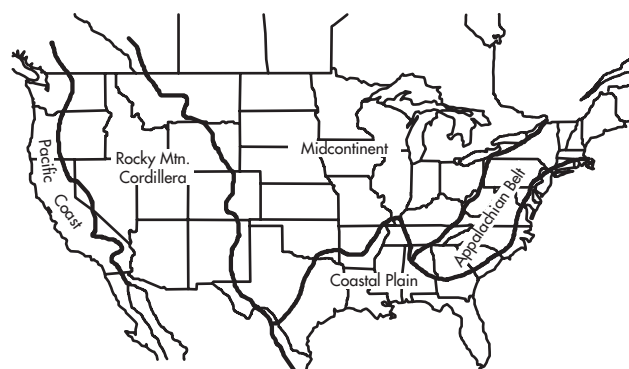
shows typical chemistry of a high-quality midcontinent sand, from the St. Peter Sandstone.

Industrial sand deposits in the western and southwestern United States are generally of lower quality than the industrial sands produced in the Midwest. The western and southwestern deposits have not undergone as many cycles of erosion and weathering; therefore, these sands tend to be less rounded and contain more deleterious material. In some cases, feldspar content exceeds 25%. Table 8 depicts the chemistry of a typical Pacific Coast sand, from the Santiago Formation.

Industrial sand deposits in the continental United States occur in five geologic provinces (Heinrich 1981): Pacific Coast, Rocky Mountain Cordillera, Midcontinent, Coastal Plain, and Appalachian Belt (Figure 1). Each province yields industrial sand products that are unique and directly related to the local geologic conditions. The geologic history of the deposit directly influences its size distribution, grain shape, and chemistry. The separable parameters then directly influence the markets and commercial value of the deposit.

Pacific Coast

Production from California dominates the Pacific Coast province. Minor industrial sand deposits are used for local markets in Oregon



Adapted from Adapted from Zdunczyk and Linkous 1994.

Figure 1. Geologic provinces of industrial sand deposits in the United States

and Washington; the majority of commercial production, however, comes from California. Pacific Coast province production is primarily from immature, feldspathic, clayey sands of Pliocene to Pleistocene/Pleistocene age. Commercial production also takes place in central California where hydraulic gold tailings are reprocessed to yield industrial-grade and filtration products.

Santiago Formation

Sand is extracted from the Eocene Santiago Formation in Orange County, California, and sold into the industrial/building materials markets. The medium-grained sandstone consists of approximately 70% quartz, and the remainder of nearly equal percentages of clay and feldspar (Silva 1985). Table 8 shows the typical chemistry of Santiago Formation industrial sand. The sand crops out for several miles to the north and south of the developed deposit near San Juan Capistrano. The formation contains evidence of several local sea-level transgressions on the basis of sand gradation and the presence of unpredictable clay/shale banding. Three mappable members of the Santiago Formation are recognized: the lower, middle, and upper members represent an overall transgressive sequence of non-marine to estuarine to shallow marine sandstone, siltstone, and mudstone. The deposit is more than 400 m thick, and faulting of regional and local nature is common. The deposit has a gradational contact with the underlying Silverado Formation, the source deposit of past industrial sand production near Corona.

Saugus Formation

Five miles north of Santa Susana in Ventura County, California, sand is extracted from the Pleistocene Saugus Formation and sold into industrial/building material markets. The formation is typical of deltaic deposits, consisting of conglomerate, sandstone, and siltstone. The mining area is in the Soledad Basin, a depression that was cut off from the sea until subsidence during the Miocene allowed marine transgression into its western extension. The Saugus Formation represents the resumption of fresh water deposition after the sea regressed at the end of the Pliocene (Norris and Webb 1990).

Recent Beach Deposits

Beach sands have been commercially developed in Monterey County, California. The sand is harvested using dredges and sold into filtration and industrial/building materials markets. The sands are of Holocene age and are regenerated annually by storm events.

The sand is coarse grained and characterized by high feldspar content and iron staining.

Fluvial Sands and Gravel

In the Marysville and Yuba City area of north-central California, hydraulic mining tails are reprocessed to produce filtration and industrial/building materials products. The deposits are the result of historical hydraulic gold mining in which vast quantities of quartzose Tertiary sand and gravel flowed into streams draining into the Yuba and American rivers. They are typically high in feldspar and other accessory minerals. The sands are a low-grade product; because of the location and market demands, however, they have a high commercial value.

Ione Formation

Sand is extracted from the Eocene Ione Formation in Amador County, California. The sand is mined from a site south of the town of Ione and is used in glass production. The deposit is composed of quartz sand and clay in an approximately 60-40 mix (Silva 1985). The Ione Formation is locally exposed from Oroville in Butte County to the north to Knights Ferry in Stanislaus County to the south. The source of the Ione sediments was deeply weathered granitic and metamorphic rocks of the ancestral Sierra Nevada that were uplifted in the Late Jurassic during the Nevadan Orogeny. The sediments were deposited in lagoons and shallow basins along a broad, swampy coastal plain bordering the Eocene sea. The sediments were altered by chemical weathering, covered by volcanic material in the Miocene and Pliocene (Anon. 1956; Zdunczyk and Linkous 1994), and eventually exposed by renewed uplift and erosion.

Oro Grande Quartzite

Western San Bernardino County has been the principal source of manufactured industrial sands for Southern California. The deposits are located east of the town of Oro Grande and north of Victorville. Massively bedded quartzite (thought to be of the Carboniferous) Oro Grande and Hodge Series occur in extensive bodies as much as 100 m thick (Silva 1985) with typical silica content of 98% to 99%. Although the quartzite is relatively pure, it has not been used extensively in industrial markets. The material is used primarily in the ceramic and filler markets.

Puget Group Sands

A commercial deposit of industrial sand in King County, Washington, is mined for feldspathic sand used in the local glass and recreation markets. The sands are derived from glacial outwash sediments from the last ice age—part of the Fraser Glaciation. The sands are not high quality and are used in local markets because of freight advantages.

Rocky Mountain Cordillera

The Rocky Mountain Cordillera is not a major source of industrial sand production. Commercial deposits exist in Colorado, Idaho, Nevada, and eastern Washington. The commercial Colorado deposits are Quaternary dune deposits. The Idaho deposit is a lacustrine Pliocene-Pleistocene deposit. The Nevada deposits are tectonically crushed quartzite and reworked sandstone. Washington industrial sand is a manufactured industrial sand from weathered quartzite.

Quaternary Eolian Dunes

The Colorado Piedmont offers some opportunities for industrial sand exploration and production. The Colorado Piedmont is a broad erosional trench that separates the southern Rocky Mountains from

the High Plains. Structurally, the site lies along the western flank of the Denver Basin. Relatively flat uplands and broad valleys characterize the present-day topography of the Colorado Piedmont in this region. In El Paso County, Colorado, Quaternary eolian dunes and other surficial deposits are mined for proppant, filtration, industrial, and recreation sands. The eolian sand deposits are coarse to medium sand derived mainly from stream alluvium and distributed east of the source area by wind. The source rock appears to be the Pikes Peak Granite. The sand is subrounded to subangular, frosted, and contains approximately 90% to 95% quartz and 5% to 10% feldspar. The eolian dunes range in thickness from 1 to 10 m. Other surficial deposits have been commercially viable and are considered to be typical eolian and fluvial transported sands and gravels. These deposits also range in thickness from 1 to 10 m.

Idaho Group

The Emmett feldspathic sand operation is located in and near the town of Emmett in Gem County, Idaho. The deposit is mined for a wide range of products, which are sold into the glass, foundry, building materials, and golf course industries. The feldspathic sand is marketed on the basis of product chemistry and physical specifications (W.A. Bratney, personal communication).

Within the structural graben represented by the Late Miocene to Early Pliocene rift that developed along the present-day course of the Snake River, volcanic eruptive events associated with the Columbia River basalts blocked the natural stream drainages. Historical Lake Idaho developed as a freshwater lake into which Pliocene-Pleistocene sediments were deposited. Sedimentation is interpreted to have occurred in many lakes interconnected at times by a river system that was present in the newly formed rift environment. This assemblage, collectively known as the Idaho Group, is divided into a number of recognized formations, including, from oldest to youngest, the Poison Creek, Banbury Basalt, Chalk Hills, and Glenns Ferry formations. Many of the Idaho Group sediments are covered by basalt flows and sediments deposited in recent times. Coarse-grained sand and gravel detritus from the tonalites and quartz diorites of the Idaho Batholith eroded rapidly into Lake Idaho during a period of active regional uplift and formed a coarse fluvio-deltaic wedge in the finer grained lacustrine deposits near the top of the Idaho Group. Mining takes place at or near the contact of the Chalk Hills with the overlying Glenns Ferry Formation. The stratigraphic section here is approximately 30 m thick (W.A. Bratney, personal communication). Mine exposures exhibit prominent cross-bedding, scour channels, and extreme variability in sediment size. The mine has fine clay horizons at the top and bottom of the developed zone. Mining is accomplished with a front-end wheel loader that fills over-the-road trucks.

The ore horizon consists of quartz clasts present in amounts up to 80% (W.A. Bratney, personal communication). Feldspars are the principal accessory minerals. Microcline occurs in amounts ranging from 16% to 19% by weight. Oligoclase is very abundant and can range between 45% and 55% by weight (W.A. Bratney, personal communication). Muscovite and, to a lesser extent, biotite are abundant in the finer grained lenses frequently observed in the deposit. The micaceous minerals have not been quantified, but they are estimated at less than 5% of the mineral assemblage. Trace amounts of magnetite, ilmenite, rutile, and garnet also occur.

Baseline Formation

The Cretaceous Baseline Formation is mined for glass, foundry, industrial, ceramic, and filler applications near Overtown, Clark County, Nevada. The Baseline Formation is relatively limited in outcrop and currently hosts only one commercial operation. The

Baseline is interpreted to be reworked Jurassic age Aztec Sandstone. It is white to buff and is weakly cemented by clay, calcium carbonate, and minor to moderate iron oxide. The sand is mined by scrapers, washed in the open pit, and slurried to a screening plant at Overton. Unprocessed sand contains approximately 97% SiO₂, and washed product contains approximately 99% SiO₂ (S. Castor, personal communication).

Eureka Quartzite

The Eureka Quartzite is mined near Mercury, Nevada. The deposit produces limited quantities of industrial- and recreation-grade manufactured sands for local and regional markets. It consists of a limited east-west zone of intensely fractured quartzite. The deposit is unique in that it has undergone intense cataclastic brecciation, most likely caused by local and regional faulting. The deposit is estimated to be more than 50 m thick; it is overlain, however, by thick limestone/dolomite overburden. The Eureka Quartzite is widespread throughout Utah and Nevada, but most deposits are not close enough to transportation or markets to be commercially viable.

Addy Quartzite

The Addy Quartzite, mined in Stevens County, Washington, for use in the glass industry, varies from unconsolidated sand to competent quartzite. The deposit has been described as tabular in nature, 60 to 90 m thick, and 5 km long (Zdunczyk and Linkous 1994). Where mined, the material has been leached to a highly friable condition. It is buff to white (Reed 1974), and grain shapes vary from angular to subangular.

Midcontinent

Zdunczyk and Linkous (1994) described the industrial sand resources of the Midcontinent Area in detail, and the distribution of deposits in this area has changed little since that publication, from which the following text borrows heavily.

These Midwest sands are mature to supermature, multicycle sheet sands that are Early Paleozoic in age, flat lying, and moderately consolidated. The quality of the deposits has been greatly enhanced by multiple cycles of erosion, winnowing, and redeposition.

St. Peter Sandstone

The Ordovician St. Peter Sandstone is the type deposit for multi-use, high-quality industrial sands. The formation is uniform, widespread, quartz arenite sheet sand. It is exposed in southeastern Minnesota and crops out across the southern margin of the Wisconsin Dome into eastern Iowa. Exposures extend south into Illinois, and across the flanks of the Ozark Dome in eastern Missouri and northern Arkansas (Bates 1960). The St. Peter has also been discovered in the subsurface in South Dakota, where it joins with basal clastics of the Winnipeg Formation (Bunker et al. 1989).

The St. Peter is generally interpreted as having a marine origin. It is a multicycled sand whose source is inferred to have been Precambrian quartzites of the Canadian Shield and Cambrian and Early Ordovician sandstones (Lamar 1927). Studies have shown the St. Peter to be a transgressive sheet sand of reworked beach deposits formed along the edge of a northwestward advancing sea (Bates 1960). The St. Peter is valued for its well-rounded, homogeneous, and inclusion-free sand grains. Sand chemistry usually exceeds 97% silica, with minor amounts of clay and feldspar (Harben and Bates 1990). Table 7 gives the typical chemistry of processed St. Peter Sandstone. The material is white to buff and is typically referred to in the industry as white sand.

In the Ottawa District of Illinois, the best known commercial mining area for St. Peter Sandstone, the formation was deposited on

an erosional surface of underlying Shakopee Dolomite and is up to 130 m thick (Bates 1960). Postdepositional erosion has reduced the deposit to approximately 70 m thick. Most production occurs in the upper portion of the deposit because the deposit typically becomes finer with depth, and feldspar, clay, and iron also increase. Because of the nature of the deposit, mining costs are low and recovery is high. Although the St. Peter Sandstone is, arguably, the most valued industrial sand on the market, the selling prices are some of the lowest on the market. This is due to its wide distribution and market saturation. More than six major operations exist within a 60-km radius, and a large volume of high-quality sand is available. Because of low production costs, Ottawa District sands can be economically transported to western United States for glass, filtration, proppant, and industrial markets.

Hickory Sandstone

The Hickory Sandstone member of the Cambrian Riley Formation is mined near Brady, Texas. The Hickory is as much as 167 m thick (Cornish 1975), but mining thicknesses generally average 30 to 40 m. The Hickory yields products used in the proppant, filtration, and foundry markets. It is often referred to in the industry as a brown sand. The Hickory outcrops along northeast-trending fault blocks of the Llano uplift area of central Texas and dips away from the uplift in all directions. It lies unconformably on the irregular surface of the Precambrian Texas craton. The contrasting and variable thickening and thinning of the Hickory suggest topographic control during deposition.

The Hickory is one of many lower Paleozoic cratonic sandstones of North America. The depositional environment was largely transgressive. The Hickory can be divided into the lower, middle, and upper facies (Pettigrew 1988). The lower facies is a fine- to coarse-grained, poorly sorted sand with rounded to subrounded grains and minor to moderate amounts of siltstone and shale. The lower facies can be most easily recognized by the planar and festoon crossbeds with large-scale foresets (Cornish 1975). It contains minor to moderate amounts of feldspar. The middle facies interfingers with the lower facies and is composed of layers of coarse- to medium-grained sand interbedded with fine-grained sand, silt, and shale. The middle Hickory can be most easily identified by the massive bedding of the coarse sand zones, and the planar to wavy laminations in the fine-grained zones. The upper facies is medium to coarse grained, well rounded, and hematitic (Cornish 1975). The upper facies has not been commercially mined. To date, all commercial activities take place in the lower and middle facies.

Black Hand Sandstone

The Mississippian-age Black Hand Sandstone Member of the Cuyahoga Formation is up to 60 m thick and consists almost entirely of nonmarine, cross-bedded, coarse-grained, conglomeratic sandstone (Kammer 2002). The Black Hand has been interpreted as braided river sediments filling incised-valleys within finer-grained marine sediments of the Cuyahoga. The Black Hand has been mined for more than 100 years as a source of glass sand, PV, and recreational sand for local and regional markets of the Knox County, Ohio, area. The sands vary from buff to dark brown, and subangular to angular.

Massillon Sandstone

The Massillon Sandstone Member of the Pennsylvanian-age Pottsville Formation has been a source for glass and recreation sand for more than 100 years. The commercial deposit in Perry County, Ohio, produces industrial sand for local and regional markets. The sand is white to buff, medium to coarse grained, and subangular to

angular. The deposit averages approximately 15 m thick, with upper and lower 1-m borders containing moderate to high amounts of iron oxide or iron sulfide or both.

Sylvania Formation

The Sylvania Formation is found in southern Michigan and northern Ohio. It is recognized as a high-quality glass sand. The sand was interpreted by Bates (1960) as a basal-blanket quartz arenite of Middle Devonian age, and is the lowermost unit of the Detroit River Group. The deposit, which dips gently to the northwest, has been structurally influenced by the Michigan Basin and by the Findlay Arch in Ohio, where the Sylvania rests on the northwestern flank. Heinrich (1977) suggested that the source for the Sylvania is the St. Peter Formation, which outcrops to the north. The Sylvania is believed to be a littoral eolian sand that was deposited in a near-shore environment. It is friable, pure, and often weakly cemented by carbonates. The sand is fairly well sorted; significant variations, however, can occur along strike. The larger grains of the deposit are well rounded; small size fractions can be angular, however, because of secondary silica overgrowths, which make the rock resistant to weathering (Heinrich 1977).

Oil Creek and McLish Formations

The Oil Creek and McLish formations of southwestern Oklahoma yield high-quality glass, ceramic, and PV-grade sand. The deposits are generally poorly consolidated and contain minor amounts of clay. The grains tend to be well rounded and frosted, and the gradation trends toward a fine sand. Because of the relatively fine-grained nature of the deposits, they tend to have more value in PV applications than as a glass sand. The deposits are part of the Ordovician Simpson Group, which consists of 300 to 700 m of sandstone and limestone with interbedded green shales (Buttram 1913). The Oil Creek and McLish formations within this group have been considered lithologically equivalent to, and of the same age as, the St. Peter Sandstone (Ham 1945).

Jordan Sandstone

The Jordan Sandstone consists of three distinct members: (1) the Norwalk Member, a fine-grained, silty, yellow quartzose sandstone; (2) the Van Osse Member, a coarse- to medium-grained, white or yellow orthoquartzite that is mined for proppant and foundry sands; and (3) the Sunset Point Member, a dolomitic and argillaceous quartz sandstone containing pebble-size clasts of dolomitic sandstone (Ojakangas and Matsch 1982). During the Late Cambrian, most of the central Midcontinent Area was covered by an epicontinental sea characterized by carbonate deposition. The regression of this sea was followed by the prograding of sandstone units eroding from the Wisconsin Dome across much of present-day Minnesota, Iowa, and northeastern Missouri. These Upper Cambrian sandstone units included the Lower Jordan Sandstone in Minnesota (Bunker et al. 1989; Zdunczyk and Linkous 1994). The Jordan is primarily mined in Minnesota for proppant and foundry applications.

Appalachian Belt

Zdunczyk and Linkous (1994) described the Appalachian Belt area in detail. The distribution of deposits there has changed little since 1994. Therefore, this section borrows heavily from their work. The area produces some high-quality industrial sands for regional markets. Although the sands are more than adequate for regional markets, they lack the preferred physical and chemical characteristics of the Midwest sands. The sands were deposited in thick wedges of nonmarine clastic sediments during the Taconic Orogeny in Late Ordovician time. As erosional unloading occurred following

large-scale tectonic events, terrigenous material shed from the fold-thrust mountain belt was deposited westward into an adjacent foreland basin. Following the orogenic events—the Silurian and Early Devonian—were periods of relative quiescence. When erosion and subsidence slowed, the siliclastic sediments that accumulated in the foreland basin were reworked into high quartz sandstones (Smosna 1992).

Clinch Formation

The Clinch Formation is mined near Rogersville, Tennessee, for glass, PV, recreation, and building materials. The sand grains are subrounded to subangular. The geologic history of the deposit is complex and includes alluvial fan, coastal plain, and tidal river environments, and near-shore shelf sand wave complexes (De Witt and Milici 1989). The Clinch is interpreted to be the stratigraphic equivalent of the Tuscarora Formation to the north.

Oriskany Group

The Lower Devonian Oriskany is actually the Ridgeley Member of the Old Port Formation. The deposit, however, has typically been referred to as the Oriskany. The Oriskany has been a significant source of high-quality industrial sands used in glass, foundry, PV, and building materials markets. The commercial portion of the Oriskany is a hard, white to bluish-gray, clean marine quartz arenite that extends from New York into Virginia. Current mining is limited to a folded belt of the Central Appalachians in the Virginia, West Virginia, and Pennsylvania tristate area. In this area, the Oriskany is well sorted and averages 90 m thick. Fracturing and jointing have allowed groundwater to leach out the calcareous matrix, resulting in a friable to loose sandstone (Harben and Bates 1990). South of New York, the source of the Oriskany sand was most likely the Silurian and Cambrian quartzites in southeastern Pennsylvania (Berkheiser 1985). The predominance of marine fossils and conglomerate lenses suggests that it was deposited under tectonically stable, near-shore, shallow water conditions (Bates 1960).

Coastal Plain

Along the Atlantic coastal plain, unconsolidated, nearly horizontal sediments of Late Cretaceous to Holocene age are mined for many industrial applications. The distribution of deposits in the Coastal Plain Area has changed little since 1994. This section borrows heavily from Zdunczyk and Linkous (1994).

Cohansey Formation

In the coastal plain of southern New Jersey, sand of the Miocene Cohansey Formation is mined for use in glass, ceramics, PV, foundry, filtration, building materials, and recreation markets. The formation consists of a 30- to 70-m-thick section of poorly sorted, subangular, fine- to medium-grained sand containing minor clay (Zdunczyk and Linkous 1994). Tertiary sediments that make up the New Jersey Coastal Plain are inferred to have been deposited in an environment that ranged from continental to midshelf or outer-shelf marine. The sources of these sediments appear to be the Piedmont Lowland, Valley, and Ridge; the New Jersey highlands provinces; and Cretaceous and Tertiary beach sands. The sediments were carried and deposited on a submerged coastal shelf by southeastward-flowing streams and were then reworked and upgraded by marine action (Wolfe 1977).

Pinehurst Formation

The Late Miocene to Early Pliocene Pinehurst Formation of central South Carolina and south-central North Carolina is a valuable source of high-quality industrial sand. The Pinehurst ranges from a

thin veneer to more than 10 m thick and contains angular to subrounded sand that is generally poorly sorted and medium to very coarse in grain size (Zdunczyk and Linkous 1994). The sand varies from nearly white to yellow-orange and averages about 90% quartz. The Pinehurst is inferred to be of eolian origin based on the presence of well-defined dune topography, in verse grading in some cross beds, and the lack of clay, silt, or fossils (Nyström, Wiloughby, and Price 1991).

McNairy Sand

The McNairy Sand is a source of industrial sand in western Tennessee. The McNairy is part of the Gulf Coastal Plain—Upper Mississippi Embayment. The McNairy was considered by Russell and Parks (1975) to have been deposited in a cyclic, near-shore geologic environment. The outcrop belt parallels the Tennessee River and varies from approximately 19 km wide in McNairy County to approximately 13 km wide in Benton County. Zdunczyk and Linkous (1994) describe the McNairy section as (1) a regressive, near-shore basal sand that is fine grained and contains heavy minerals; (2) a middle wedge of coarser-grained sand that appears to be fluvial, deltaic, and partly estuarine in origin; and (3) an upper transgressive marine sand, which is present only in southwestern McNairy County.

Florida

Industrial sands are produced throughout Florida for local and regional markets. Glass-grade sand is produced near Davenport, Plant, and Edgar. Zdunczyk and Linkous (1994) described the Citronelle Formation as a fluvial blanket deposit of highly cross-bedded sand, clays, and gravel extending across western Florida, Alabama, and Mississippi. It attains a maximum thickness of approximately 50 m in western Alabama. It is inferred that the Citronelle sediments were deposited as coalescing deltas by several rivers that emptied into the Gulf of Mexico (MacNeil 1950). Closely associated with the Citronelle Formation are the Pleistocene marine terraces near Davenport, Plant City, and Edgar (Olson 1970). Four marine shorelines have been recognized in the Gulf Coast terraces, representing the inland limits of transgressive seas. These marine terraces consist of fine- to medium-grained, well-sorted, unconsolidated sand. The quartz grains are generally clear to milky, and iron staining and organic materials are not uncommon (Cathcart 1963).

Canada

Industrial sand production takes place across Canada. The provinces of Quebec, Ontario, and Alberta are the primary producers of industrial sand, followed by Saskatchewan, British Columbia, and Nova Scotia (Dumont 2001).

In Newfoundland and Labrador, the Roy's Knob quartzite deposit is mined for use in silicon metal. New Brunswick has two active operations where material is mined and processed for use in blasting, foundry, filtration, recreation, and flux markets. Quebec has several active operations where quartzite is mined near Saint-Donat-de-Montcalm, north of La Mabaie, and from sandstone deposits at Saint-Canut, Sainte-Clotilde-de-Chateauguay, and Saint-Remi-d'Amherst. Unconsolidated deposits are mined for mixed uses at Saint-Joseph-du-Lac, Ormstown, and Saint-Bruno-de-Guigues. Ontario has the largest production with sources at Badgley Island, Elgin Quarry, Fripp Quarry, and the Ellis Quarry. Industrial sand is produced in Saskatchewan in the Amisk Lake area, northeast of the village of Hudson Bay, and Prince Albert. Sand dunes are mined in Alberta in the Bruderheim Area. Industrial sand is also produced in Peace River. In the Golden Area of British Columbia, industrial sand is mined for varied industrial applications.

Mt. Wilson Formation

In the Rocky Mountains near Golden, British Columbia, a zone of friable quartzite within the Ordovician Mt. Wilson Formation is mined for mixed industrial uses. The rock is fine grained, white, and massive (Zdunczyk and Linkous 1994). The quartz grains are well rounded and average 0.25 to 1 mm in diameter. The friable zone that is mined lies along the crest of an anticline at the northwestern exposure of the formation (Zdunczyk and Linkous 1994).

Potsdam Formation

Near St. Canut, Quebec, the Cambrian Potsdam Formation is mined for high-purity industrial sand. In southeastern Ontario, the Potsdam is the lowermost Paleozoic formation present, and it is assumed to be the stratigraphic equivalent to the Potsdam in New York (Keith 1949). Both deep-water and near-shore facies have been identified. The near-shore facies appear to contain the purest sandstone (Guillet and Kriens 1984).

The Potsdam can vary from white to red, depending on whether the matrix is primarily ferruginous, calcareous, or siliceous (Zdunczyk and Linkous 1994). Where mined, the material is a white, massive, saccharoidal sandstone with a siliceous cement (Keith 1949). When crushed, the sandstone easily breaks into angular to subrounded grains, more than 80% of which are between 0.60 and 0.15 mm.

Bar River Formation

On Badgley Island, the Precambrian Bar River Formation is mined for varied industrial applications. According to Guillet and Kriens (1984), the Bar River is the youngest and purest of a series of three quartzite units at the top of the Cobalt Group in the Huronian Supergroup of middle to late Precambrian age. The Bar River is typically light gray to white (Zdunczyk and Linkous 1994). Where completely recrystallized by metamorphism, it consists of interlocking grains of quartz, which caused the rock to be extremely hard and to break across grains with a conchoidal fracture (Hewitt 1963). Where metamorphism was less intense, it is easier to see that the Bar River was originally made up of intergradational units of well-sorted and -rounded, fine- to medium-size sand grains (Guillet and Kriens 1984).

GEOLOGY AND DISTRIBUTION OF MAJOR DEPOSITS OUTSIDE NORTH AMERICA

Little has been published on deposits of industrial sand outside North America. Harben and Bates (1990) briefly described some European deposits, and information is available on some Australian deposits. Industrial sand deposits in China and India, however, which may become important in the near future, are not described in the literature.

Europe

The industrial sand deposits mined in Europe vary greatly in chemistry, location, and physical characteristics. The primary markets are glass, foundry, and building materials. The author could not find information in English-language literature on deposits in many of the important producing countries in Europe, such as Germany, Austria, France, and Spain.

Industrial sand is produced in the Mol, Maasmechelen, and Charleroi districts of Belgium, and in the "silversand" area near Heerlen, the Netherlands (Harben and Bates 1990). According to Harben and Bates (1990), the deposits are Pliocene sands that are valued for their low iron content (less than 0.01% Fe₂O₃). The high-grade, low-iron sands are used in the production of crystal glass, and the lower-quality sands are used in the production of

sheet glass, ceramics, silica flour, and silica carbide, and in building materials. The combined production of Belgium and the Netherlands is estimated to be greater than 20 Mtpy.

Scandinavia and Portugal produce high-quality industrial sands as a by-product of feldspar production from quartz-rich pegmatites. The silica sands produced from these sources contain 99.6% to 99.75% SiO₂, 0.03% to 0.06% Al₂O₃, and 0.2% to 0.5% Fe₂O₃ (Harben and Bates 1990).

In the United Kingdom, industrial sand deposits range in age from Carboniferous to Recent (Harben and Bates 1990). More than 50% of the production comes from Pleistocene to Holocene deposits of fluvioglacial, in terstadial, and eolian origin. Cheshire and Lancashire are important areas of production for glass, ceramics, and foundry sands. Approximately one third of the production is derived from Cretaceous beds south of London.

Australia

Australia produces industrial sands for local and regional markets. The primary markets are in glass and foundry applications. In the New South Wales area, container glass deposits are concentrated near the "inner barrier" dune deposits on the Tilligerry Peninsula near Tanilba Bay. The primary source for high-iron sand used in amber glass is the Salt Ash mine at Williamstown and a deposit at Londonerry, near Penrith. The New South Wales area is also a major producer of foundry sand from the "outer barrier" dunes of Stockton Bight.

In South Australia, industrial sand for foundry markets is mined from Holocene dunes near Sandy Creek, Tailem Bend, and Balaklava. Other significant industrial sand sources are the Glenshera sand pit near Mount Compass, 50 km south of Adelaide (Pain, Shaw, and Valentine 1999), and the 23-Mile lump silica deposit near Whyalla.

The Glenshera deposit contains Permian fluvioglacial sand, and portions of the deposit were reworked during the Tertiary. Up to 10 m of high-iron sand overlies approximately 80 m of low-iron sand. The low-iron sand is processed for container glass markets, and the high-iron sand is processed for amber glass and foundry markets (Valentine 1989).

Industrial sand is mined at the 23-Mile deposit for use as an additive in blast furnaces (Valentine 1989). The deposit was described by Valentine (1989) as a north-south trending quartz reef. The deposit is approximately 8 km long within dark gray volcanoclastic grit and sandstone of the Proterozoic Moonabie Formation.

TECHNOLOGY

Exploration

Like most industrial minerals, exploration for industrial sand begins with transportation and marketing studies. Understanding the location of competitors and distance to markets allows a potential producer to determine if a project warrants further investigation. For example, many potential high-grade manufactured sand sources exist in Idaho, Utah, and Nevada; the deposits have never been commercially viable, however, because of their distance from markets. Nonetheless, the complexification of industrial sand exploration has been changing in the last 10 years. Most deposits are well known, but the increase in demand in the western United States and emigration of population to that area have created a shift in industrial sand exploration. Consumers are now willing to consider local, more cost-effective sources of industrial sand rather than pay high freight premiums. This is particularly true in the building materials and recreation markets.

Although conventional exploration methods still apply, progressive industrial sand suppliers must now consider whether or not

a deposit can be permitted before investing significant capital into an exploration program. Planning, land use, zoning, and general regulatory requirements are as important as the chemical and physical properties for any potential deposit. Industrial sand exploration has become increasingly computerized, and computer processing allows rapid integration with marketing and regulatory concerns. With the advent of affordable geographic information software (GIS) and global positioning system (GPS) technology, industrial sand suppliers can quickly and efficiently review and catalog deposits. Transportation networks can be easily integrated into the model, and the company can quickly determine haul rates and commercial viability. Likewise, where available, county zoning maps and wildlife habitat, floodplain, wetland, and population density overlays can be placed on the model to determine if the deposit can be permitted.

Exploration targets can cover entire physiographic regions or can be limited to a certain "haul distance" from a given consumer. After determining what markets the supplier desires to serve, the supplier then begins the process of exploration. This will involve detailed literature searches. Many states and counties have readily available information that will assist the potential producer in determining if a location warrants further review. Once a site is identified, the company should conduct a detailed regulatory and land status review to determine if the deposit can be permitted within the allotted time and at a reasonable cost. Once the company determines that the deposit can be permitted, physical evaluation can be initiated.

Depending on location, exploration permitting can be a lengthy process. If the deposit is located on public land, community involvement and participation will take place. It is in the best interest of the company to develop relationships with all stakeholders and conduct business in a transparent and responsible manner. In the current regulatory environment, it is critical to develop relationships with all stakeholders: neighbors, elected officials, regulators, and environmental groups. Although additional costs and delays may occur because of the relationship-building phase of the exploration project, the company will quickly learn if the public will "allow" a site to be permitted.

During exploration, it is important to collect clean, unoxidized samples. The type of laboratory analysis that is required is contingent on the projected markets to be served. Roundness, gradation, chemistry, and sphericity must be analyzed for proppant, foundry, and filtration markets, whereas a stucco consumer may be concerned with only gradation and iron content. Furthermore, end market considerations vary by region. Colorado stucco sand consumers prefer round sand and California stucco consumers prefer angular sand. It is important that the company fully understand aesthetic and chemical requirements for their prospective markets.

As population centers continue to shift, deposits that have had no commercial value are garnering the attention of major producers. Several small start-up operators tried to develop deposits in the 1990s, but most were unsuccessful. This trend appeared related to the drop in gold prices in the 1990s and subsequent migration of small gold exploration companies into industrial minerals, and a rapid increase in the industrial sand demand in California. Most startups are unsuccessful; this generally is related to the complexities of the market and a general lack of understanding of freight costs.

Economic industrial sand deposits are market driven; therefore, deposits are developed in a wide variety of geologic regions. Physical exploration techniques are varied and depend on the site conditions. In unconsolidated deposits where the water table is high (Gulf Coast deposits), a rotary drill rig with a split-spoon sampler

or a vibrocore rig is recommended. In this type of exploration, contamination from the sides of the hole is common. If contamination is a concern, care must be taken to stabilize the walls of the hole. Bentonite-based drilling mud can be used, but clay-based mud can lead to erroneous chemical results and inflated clay matrix values.

Auger and suction drilling can also be used in unconsolidated deposits. Auger and suction drilling is recommended only in unconsolidated deposits where the water table is not a concern. Auger and suction drilling should be used only where contamination (sloughing and mixing) is not a major concern. When using an auger, the flights are either driven into the deposit by hand or rotated mechanically. In suction drilling, a polyvinyl chloride (PVC) pipe is driven into the deposit and connected to a suction device. Both methods will yield quick and inexpensive results; the sample integrity, however, is not as good as split-spoon sampling.

In consolidated deposits, reverse circulation can be used for quick and inexpensive (compared to core) results. Reverse circulation drilling, though, may mix samples and is likely to add clay from the drilling fluid to the sample matrix. Reverse circulation is an excellent tool when used with core drilling.

Core drilling yields the best data for geologic modeling. A drill rig equipped with NX size (54.9-mm diameter) wireline coring capability is generally adequate to obtain samples. If the rock is fractured or friable, the geologist should consider using a larger diameter core.

Percussion drilling can also be used. Percussion drilling is not a preferred method but can yield meaningful data if the deposit is well understood. The cuttings generated by percussion rigs are valuable as a “quick and dirty” assessment or for infilling data holes. Percussion drilling should not be used as an exclusive exploration tool.

If the deposit permits, trenching can also be a valuable tool. However, care must be given to sampling methods and the safety of the sampling team. Trenches can yield invaluable information and should not be discounted as a tool when conditions permit.

Once samples are collected, it is imperative that the field geologist work closely with the production team to ensure that the samples are thoroughly described and prepared for analysis. The geologist should include the type of iron minerals present and severity of iron staining in sample descriptions. Matrix material and cement, refractory minerals, and mineral inclusions within the quartz are also important characteristics to note. Grain size, particle distribution, and grain shape are also market-critical concerns that the geologist must consider.

Once all of the data are collected, reserve estimates must be calculated. There are many definitions for reporting reserves, but if the company is publicly traded, they must comply with the Security and Exchange Commission's (SEC's) industry guide (SEC 2005). If the company is not publicly traded, then the company can use their discretion as to how to report reserves. Nonetheless, an industry-recognized standard should be selected such that the results of the modeling are credible. Computerized reserve calculation models are an invaluable tool, and most operators now use computer-assisted modeling. Most geology departments are understaffed, and computer modeling allows a company to develop a quick and accurate model. The model is only as accurate as the data; therefore, the use of models must be based on a reasonable understanding of the geology and proper laboratory procedures.

Laboratory Testing

The type of laboratory testing required is directly related to the market served. In general terms, all deposits should be analyzed for a full suite of oxides and elements. Samples should also be washed,

dried, and sieved. If the proposed market is proppant sand, then acid solubility, crush strength, and conductivity tests must occur. If the filtration market is being considered, then leach tests must be performed to ensure that the material will not exceed drinking water standards. In general terms, a company should consider conducting as many tests as possible. Many consumers require analytical data, and market penetration should not be limited by lack of product testing.

In today's market, it is imperative that all industrial sand producers have an internal quality assurance and quality control program. Each load shipped should be sampled, and each load should be correlated to a “lot number.” Outside quality control laboratories generally specialize only in conducting product samples and are not equipped to provide data on mine run and processing stream samples. Therefore, industrial sand producers must have bench-scale capabilities. At a minimum, a producer should have an x-ray fluorescence (or equivalent) machine and sieving, washing, drying, and crushing facilities for sample preparation. Depending on processing techniques and markets served, internal laboratory equipment may need to include flotation, attrition scrubbing, and heavy mineral separation.

Mining

Industrial sand mining methods are contingent on deposit type. Unconsolidated deposits such as those in Colorado are mined using front-end loaders, scrapers, or bulldozers. Material is dug, excavated, and pushed to a central point. The ore-grade material is then loaded onto a truck using standard earth-moving equipment, where it then reports to a stockpile or a plant. Other unconsolidated deposits, like those found in the Atlantic Coastal Plain and on or near fluvial channels in Northern California, are mined with dredges or draglines. A hydraulic dredge uses a suction pipe to excavate the sand, which is pumped through a pipeline to surge piles or directly to a processing plant. Although draglines can be more expensive than hydraulic dredges, they are still used along the American and Yuba rivers in Northern California. The channel or tailings deposit is excavated, scalped, and placed in a stockpile. The ore-grade material is loaded into haul trucks for transportation to a processing plant.

Loosely consolidated material such as the St. Peter Sandstone can be mined using a high-pressure hydraulic monitor. Sand washed from the working face is collected in a sump, from which it is usually pumped to a dewatering/surge pile, where the material is allowed to free drain. Once drained, the sand reports to a plant.

At well-consolidated deposits such as the Hickory Sandstone, conventional drill-and-blast methods are used. Once blasted, the sandstone is “muck ed” using a front-end loader, placed into haul trucks, and transported to a primary crusher. Following crushing, the material may report to a secondary or tertiary crushing plant. The sized material is then transported to a processing plant, usually by a conveyance system.

Although uncommon, underground mining can also be used to extract competent, well-lithified sandstone or quartzite, which is extracted using conventional drill-and-blast methods. The material is then loaded by power equipment and hauled or conveyed to a plant or surge pile. In general terms, underground mining is the most expensive method, and because of the modest selling prices for industrial sand, it is usually cost-prohibitive.

Processing

Processing is what distinguishes industrial sand from common construction sand. The type of processing or beneficiation is directly related to the relative purity of the deposit and which markets the

Table 9. Historical industrial sand production in the United States and world production, t

Year	Primary Production	Imports	Exports	Apparent Consumption	Unit Value, \$/t	Unit Value, \$98/t	World Production
1985	26,700,000	73,500	786,000	26,000,000	13.58	20.58	115,000,000
1986	24,900,000	79,800	770,000	24,200,000	14.06	20.91	113,000,000
1987	25,400,000	94,300	688,000	24,800,000	13.86	19.88	113,000,000
1988	25,800,000	39,000	962,000	24,900,000	14.41	19.86	120,000,000
1989	26,500,000	31,800	1,870,000	24,700,000	13.55	17.81	118,000,000
1990	25,800,000	66,200	1,050,000	24,800,000	14.32	17.86	110,000,000
1991	23,200,000	82,600	1,490,000	21,800,000	13.07	15.64	111,000,000
1992	25,200,000	164,000	1,340,000	24,000,000	14.03	16.30	112,000,000
1993	26,200,000	44,000	1,750,000	24,500,000	14.12	15.92	104,000,000
1994	27,300,000	24,000	1,880,000	25,400,000	13.75	15.12	117,000,000
1995	28,200,000	59,000	1,870,000	26,400,000	13.90	14.87	121,000,000
1996	27,800,000	7,000	1,430,000	26,400,000	13.32	13.84	106,000,000
1997	28,500,000	39,000	980,000	27,600,000	12.38	12.58	94,600,000
1998	28,200,000	44,000	2,400,000	25,800,000	14.23	14.23	93,900,000
1999	28,900,000	211,000	1,670,000	27,400,000	14.96	14.64	95,700,000
2000	28,400,000	247,000	1,660,000	27,400,000	14.41	13.64	96,000,000
2001	27,900,000	172,000	1,540,000	26,500,000	15.98	14.71	96,400,000
2002	27,300,000	250,000	1,410,000	26,100,000	16.70	15.13	94,900,000

Source: Kelly et al. 2004.

supplier desires to serve. Regardless of markets, sands are, at a minimum, washed, dried, and screened. A typical process circuit would include washing to remove clay and other deleterious material. At this point, some processes may require that the material report to a rod or ball mill. After leaving the wash-and-mill circuit, a sand-water slurry is pumped to a desliming circuit in which hydrocyclones remove the slimes, which report as tailings to a thickener circuit or directly to settling ponds. The washed sand is then subjected to a coarse separation cut by hydrosizing or wet screening. The sand is further dewatered by reporting to surge piles or cyclones. Once the sand contains approximately 70% solids, it reports to attrition scrubbing, which is performed in tanks equipped with propeller-type blades. Attrition scrubbing removes clays, iron oxides, and other materials that may be on the surface of the sand grains. It also creates a fresh surface on nonquartz minerals to enhance reagent attachment, if flotation is used during further processing. Flotation is used only when high-purity quartz is required for the market. Many deposits that service filtration, oppant, abrasives, building materials, and recreation markets do not require flotation. If flotation is required, there are two types: cationic and anionic.

Some customers will accept nondried material, but all value-added markets require dry sand. Once washing and flotation (if required) is completed, the sand is dried. If a producer makes finer grade products, then those products generally report to a fluid bed dryer, whereas coarser grades generally report to a rotary dryer. Once dry, the sand is processed by dry screening. Once sized, the product reports to silos for bulk shipments, or to packaging, where the material is placed in bags or "super sacks."

ECONOMIC FACTORS

Market Trends

Industrial sand production in the United States from 1995 to 2002 remained relatively flat (Table 9), averaging 28.1 Mt (Dolley 2002). World production in 2002 was approximately 95 Mt (Dolley 2002). The United States was the leading producer, followed by Germany, Austria, France, Spain, Australia, and the United Kingdom. The

market forecast for industrial sand suggests an increase over the next several years; however, the increases are likely to be minor (1% to 3% per annum). The United States is the largest producer of industrial sand and is capable of meeting approximately 99% of the market requirements (Dolley 2002). The most significant market threats come from Mexico, Canada, China, and India.

Glass sand sales are expected to increase slightly, but sales are expected to vary from market segment to market segment. Market growth is expected in the flat glass and specialty glass markets; this growth, however, is likely to be offset by declines in fiberglass and container glass markets. Currently, a market shift to areas west of the Mississippi River is occurring in the glass industry. One major flat glass plant was recently commissioned in Oklahoma, and another plant is scheduled to be built in Washington. A large producer of container glass is also planning a significant new facility in northern Colorado.

Recycling laws enacted in many areas have affected the container glass market by increasing the supply of post-consumer cullet. To reduce costs, container glass producers have turned to cullet as a feedstock, displacing raw glass sand. Significant competition in the container glass segment has come from plastic, aluminum, and cardboard. Overcapacity in the glass-grade sand industry and the threat from packaging substitutes are likely to affect the price and sales of container glass sands. Nonetheless, since the early- to mid-1990s, container glass has experienced some growth in sales because of the increase in sales of designer alcoholic beverages.

Foundry sand demand is directly linked with automobile production. Another important factor is the amount of recycling. In the 1990s, several foundries moved to Mexico and new, state-of-the-art foundries were built there. Although some foundry sand sales were affected by the move, the high-quality sands produced in the United States are still quite competitive in Mexican markets. Foundry sand sales are also experiencing a significant threat from China. Increasing market presence in the United States of steel from Chinese foundries has displaced foundry sands produced in the United States. At the same time, it appears as though recycling of foundry

sand has increased. The overall trend in foundry sales is likely to decrease over the next decade.

Proppant sand sales are directly related to oil and gas drilling, and so the proppant market is highly cyclical. For instance, in the early 1980s the market was depressed owing to a lack of well development. The late 1990s through 2003 witnessed steady production and sales in this market—particularly in deep-gas well applications. Canada, Wyoming, and the western slope of the Rocky Mountains have seen considerable growth in gas well production. Surfaced-modified sand and white sand sales have benefited from the increase in natural gas wells, which is related to the construction of natural gas-fired power plants. Currently, there is not enough gas production to meet demand, and the major industrial sand producers are aggressively selling proppant-grade products into the gas and oil fields. Industrial sand producers are likely to continue to produce significant tons for the proppant markets. This high level of production will create production imbalances and is likely to lower pricing for glass, foundry, and abrasives applications.

The industrial sand industry has experienced consolidation, and very few new operations have come online in the last 10 years. Currently, there are 4 major producers of industrial sand, and 10 producers control 76% of the U.S. market (Dolley 2002). Additional market consolidation is likely because of the dominance of one producer. Two of the four leading producers of industrial sand are suffering from serious debt issues related to acquisitions and tort litigation due to silicosis lawsuits.

The location of production facilities will continue to drive exploration and expansions. As markets move west, deposits that were usually thought to have no market value are being revisited. However, because of low production costs and high quality, producers in the Midwest can be competitive in western markets. A significant increase in demand for industrial sand products is likely within the next 10 years in California, where two of the major producers may soon close because of the effects of urbanization and resource depletion. Therefore, it is more than likely that the western United States will be the focus of intense exploration for industrial sand.

The use of substitute materials for cast metals could have an effect on the foundry market; however, this effect could be offset by increases in the production of PV, which is used in the production of replacements for foundry sands. Because of recycling and substitution, the overall demand for industrial sand may decrease, but the value of the production may increase because of higher selling prices for value-added products such as PV.

Concerns regarding silicosis are likely to have the most significant effect on the industrial sand business. Regulatory agencies such as the Occupational Safety and Health Administration (OSHA) are working to lower the personal exposure limit (PEL) for respirable silica. If that effort is successful, consumers will consider substitution products. This will have a significant effect on the building materials and recreation market segments, where limestone could replace industrial sand. In the absence of tort reform at the federal level, silicosis claims and fears will have a significant and material effect on the industrial sand business.

Transportation

The primary methods of transportation for industrial sand products are truck, rail, barge, and ship. Of the industrial sand produced in 2002 in the United States, 64% was transported by truck from the plant to the site of first sale or use, up 2% from 2001; 34% was transported by rail, down from 35% in 2001; and 2% was transported by waterway (Dolley 2002). The availability of efficient transportation is critical to the success of any operation. Most

highly successful operations have access to both rail and truck. If production costs are low, producers can be competitive over long distances by rail. Given the uncertainties of dealing with railroads, many operators use lease cars, which limits the shipper's exposure to car availability and demurrage costs. Truck transportation is generally more reliable than rail; however, it is also more expensive. Freight contracts with guaranteed tonnages can help lower shipping costs. Many companies also treat freight as a profit center. Although there is risk in arranging and "marking up" freight, producers can make reasonable profits and can provide a service to their customers.

Production and Pricing

Industrial sand production from 1994 to 2003 has been relatively static. Total production in the United States decreased by 3.7% from 2001 to 2002. Positive or negative variations of less than 5% are the norm for this industry. Table 9 shows historical production for industrial sand. In 2002, the Midwest led the United States in production of industrial sand, with approximately 41% of the 27.3 Mt of production from this geographic area (Dolley 2002). The leading producing states, in descending order, were Illinois, Michigan, California, Wisconsin, Texas, New Jersey, Oklahoma, and North Carolina (Table 10). The combined production in these states accounted for 59% of the total U.S. production in 2002 (Dolley 2002).

In 2002, approximately 82% of the total industrial sand production was produced by 50 operations, each with production of more than 200,000 Mtpy (Table 11). Compared to 1981, the total number of producers decreased by 24 to 67. This change is likely the result of industry consolidation. The five leading producers of industrial sand, in descending order, are Unimin Corp., U.S. Silica Co., Fairmont Minerals Ltd., Oglebay Norton Industrial Sands Inc., and Badger Mining Corp.

In 2002, the average selling price for industrial sand products in the United States for all grades of industrial sand was \$20.96/Mt, up slightly from 2001 (Dolley 2002). By comparison with 1990 prices, the average selling price for combined markets increased 36.5% overall, or 3% per year. The 3% increase is approximately equal to the increase in the producer price index over that same time period. This statistic is an average and does not necessarily reflect the dynamic nature of some market segments. For example, from 1998 through 2001, certain building materials consumers in Southern California were absorbing 10% to 14% price increases per annum.

In 2002, the average price ranged from \$11.67/t for metallurgical flux to \$82.87/t for PV. Producer prices for industrial sand range from several dollars per ton to more than \$40/t, depending on the amount of processing and markets served. For some highly specialized uses, production costs can exceed \$1,000/t (Dolley 2002). In the United States, PV for use in paint, putty, and rubber had the highest average value (\$82.87/t), followed by PV for use in foundry moldings and core (\$82.43/t), swimming pool filters (\$77.07/t), well packing (\$64.63/t), municipal water filtration (\$41.83/t), PV used in fiberglass (\$40.87/t), proppants (\$40.08/t), and abrasives (\$36.86/t).

By geographic region in 2002, the average value of industrial sand was highest in the South (\$23.09/t), followed by the West (\$22.74/t), the Northeast (\$21.85/t), and the Midwest (\$18.20/t) (Dolley 2002). By comparison, in 1994 the following prices applied: the West (\$19.89/t), the South (\$19.08/t), the Northeast (\$18.57/t), and the Midwest (\$16.22/t) (Bolen 1996). Western markets command higher prices because of lack of supply and high demand. Conversely, midwestern markets garner lower prices because of overcapacity.

Table 10. Industrial sand production by state*

State	2001		2002	
	Quantity, kt	Value, US\$1,000	Quantity, kt	Value, US\$1,000
Alabama	743	9,420	722	8,990
Arizona	W†	W	W	W
Arkansas	W	W	W	W
California	1,840	47,700	1,800	48,000
Colorado	W	W	61	W
Florida	598	7,520	645	8,640
Georgia	W	W	606	12,200
Idaho	W	W	W	W
Illinois	4,460	72,100	4,510	72,800
Indiana	W	W	W	W
Iowa	35	1,590	W	W
Kansas	W	W	W	W
Louisiana	637	11,900	672	13,100
Maryland	W	W	W	W
Michigan	2,530	30,000	2,210	31,000
Minnesota	W	W	W	W
Mississippi	W	W	W	W
Missouri	W	W	W	W
Nebraska	W	W	W	W
Nevada	609	W	615	11,000
New Jersey	1,580	34,800	1,420	32,700
New Mexico	W	W	W	W
New York	W	W	W	W
North Carolina	1,300	26,000	1,320	25,600
North Dakota	W	W	W	W
Ohio	1,120	30,700	1,000	28,900
Oklahoma	1,360	28,200	1,320	28,400
Pennsylvania	W	W	W	W
Rhode Island	138	W	157	W
South Carolina	694	15,900	831	16,400
Tennessee	W	22,900	1,070	25,700
Texas	1,850	70,000	1,670	62,200
Virginia	W	W	W	W
Washington	W	W	W	W
West Virginia	W	W	W	W
Wisconsin	1,710	W	1,740	32,700
Other	6,720	167,000	4,960	115,000
Total	27,900	576,000	27,300	573,000

Source: Dolley 2002.

* Data are rounded to no more than three significant digits; may not add to totals shown.

† W = Withheld to avoid disclosing company proprietary data; included with "Other."

Foreign Trade

From 1993 to 1994, exports of industrial sand from the United States increased 7% to 1,880,000 t, whereas the value increased 12%. According to Bolen (1996), exports of industrial sand were as follows: 79% to Canada, 8% to Mexico, and the balance to numerous countries throughout the world. Based on U.S. Census data for 2002, industrial sand exports decreased 8.4% to 1,410,000 t, whereas the value decreased by 11%. Most of the decrease in

Table 11. Industrial sand production in 2002 by size of operation*

Size Range, Mtpy	Number of Operations	Percentage of Total Operations	Quantity, kt	Percentage of Total Quantity
Less than 25,000	18	14	207	1
25,000 to 49,999	18	15	619	2
50,000 to 99,999	22	17	1,440	5
100,000 to 199,999	19	15	2,570	10
200,000 to 299,999	14	12	3,040	12
300,000 to 399,999	6	5	1,990	7
400,000 to 499,999	11	8	4,510	16
500,000 to 599,999	7	5	3,480	12
600,000 to 699,999	4	3	2,340	9
700,000 and more	8	6	7,150	26
Total	127	100	27,300	100

Source: Dolley 2002.

* Data are rounded to no more than three significant digits; may not add to totals shown.

exports is attributable to the sharp declines in shipments to Asia and Europe (Dolley 2002). Export distribution in 2002 for industrial sand produced in the United States was as follows: 39% to Canada, 35% to Mexico, 12% to Japan, 4% to Europe, and the remainder to South America and other destinations. According to Dolley (2002), the average price of exports decreased to \$103/t in 2002 from \$106/t in 2001. Export prices vary widely by region, with higher grade prices of exported material to Europe averaging \$585/t and the rest of the world averaging \$81/t.

Imports for industrial sand, from 1993 to 1994 data, dropped by 50% to 22,000 t, valued at \$1.8 million. Conversely, imports in 2002 rose to 250,000 t, which was an increase of 45% compared to imports in 2001 (Dolley 2002). Industrial sand imports vary greatly from year to year, and are, as a whole, insignificant in relation to total U.S. consumption. The variations are generally related to the emphasis of importers on niche markets. For example, in 2002, several thousand tons of filtration-grade and proppant-grade Chinese sand was imported for use in the Bakersfield and Sacramento areas of California. Because of quality issues, the sand was rejected for use; therefore, Chinese sands were not imported in 2003. In 2002, Mexico supplied 72% of the industrial sand imports, which averaged \$6.66/t.

World Review

World production of industrial sand in 1994 was estimated to be approximately 111 Mt, up nearly 5% over 1993 data (Bolen 1996). The United States was the leading world producer (and consumer) of industrial sand, followed in descending order by the Netherlands, Germany, Austria, and France (Table 12). In 2003, world production was estimated to be 94 Mt (Dolley 2002). The United States continued to be the leading producer (and consumer), followed by Germany, Austria, France, Spain, Australia, and the United Kingdom, in descending order. Most countries in the world produce

Table 12. World mine production, kt

Country	2002	2003
Australia	4,500	4,500
Austria	6,800	6,800
Belgium	1,800	1,800
Brazil	1,600	1,600
Canada	1,600	1,600
France	6,500	5,500
Germany	8,500	8,500
India	1,400	1,450
Iran	1,700	1,700
Italy	3,000	3,000
Japan	2,200	1,900
Mexico	1,700	1,800
Norway	1,400	1,400
South Africa	2,300	2,300
Spain	6,500	6,500
Turkey	1,400	1,300
United Kingdom	4,500	4,000
United States	27,300	28,300
Other countries	10,300	10,300
World total (rounded)	95,000	94,000

Source: Dolley 2004.

some industrial sand because of requirements for foundry and glass applications. World production continues to be difficult to track. Many countries report grades differently; therefore, obtaining reliable data is problematic.

China and India continue to pose a significant threat to U.S. producers. Currently, limited amounts of industrial sand are imported to the United States from India and China. This is due primarily to the relatively low price for industrial sand and quality issues that have plagued Chinese sand.

Government Controls and Restrictions

Silicosis and Regulatory Restrictions

The most significant challenges presented to the industrial sand business in the United States are tort litigation related to silicosis claims and continued attempts by state and federal regulatory agencies to reduce PELs of respirable silica. In 1986, the International Agency for Research on Cancer (IARC) classified respirable crystalline silica as Group 2A, Probably Carcinogenic to Humans (IARC 1987). In 1996, IARC reviewed additional data and recommended that quartz and cristobalite be listed as Group 1, Carcinogenic to Humans. Following the publication of the IARC data in 1997, several state and federal regulatory agencies began attempts to closely regulate respirable silica.

OSHA has established 0.1% of a suspected carcinogen as the maximum amount any product may contain before its sale must be accompanied by a health hazard warning (Hazard Communication Standard). To comply with the Hazard Communication Standard, and other state (e.g., California Proposition 65) and federal regulations, products must be evaluated for crystalline silica content at a threshold of 0.1%. Several analytical methods have been developed to determine crystalline silica in a variety of products. However, accurately quantifying small amounts of crystalline silica in a mixture of accessory minerals and unknown states is difficult. Of all of the analytical techniques, x-ray diffraction (XRD) has the greatest

potential for accurately identifying the polymorphs of crystalline silica and determining each at the 0.1% threshold (Miles 1999). XRD techniques are nondestructive, thus allowing analyzed samples to be preserved. XRD is neither inexpensive nor routine, however, and care must be taken to identify the crystalline silica polymorphs with certainty. The most significant issue is spectral overlap with other minerals. It is important to employ quality laboratories with specific experience in identifying crystalline silica. It is not uncommon for a laboratory that lacks crystalline silica experience to inaccurately identify silica polymorphs. This leads to a significant concern with respect to the regulation of crystalline silica.

For a number of years, inhalation of crystalline silica for extended periods has been known to cause, in some workers, a potentially disabling and sometimes fatal respiratory disease known as silicosis. Silicosis is a preventable occupational illness with a specific diagnosis. Outside the occupational setting, there is no scientific evidence that exposures of the general population to crystalline silica in the ambient air have caused (or would be expected to cause) silicosis. The number of new silicosis cases in the United States has fallen dramatically over the years. The Centers for Disease Control and Prevention (CDC) data suggest that silica-related mortality declined by an order of magnitude since 1969, from 1,800 related cases to fewer than 180 cases in 2000. This can be attributed to improved ventilation and the use of proper personal protective equipment (PPE). Moreover, because there is a significant lag period following exposure, new cases of chronic silicosis that are diagnosed today most likely are attributable to exceedances of the PEL that occurred 10 to 20 years ago or more. While exposures to crystalline silica have been reduced in recent decades, data collected by OSHA, the National Institute for Occupational Safety and Health (NIOSH), and the Mine Safety and Health Administration (MSHA) indicate that overexposures continue to occur in the occupational setting. For example, 37.8% of the samples collected for respirable quartz testing by OSHA in manufacturing exceeded the PEL in 1998, and 38.3% exceeded the PEL in 1999. The comparable exceedances for metal/nonmetal mining were 6.7% in 1998 and 8.0% in 1999 (NIOSH 2002).

The current OSHA/MSHA PEL for quartz (the most abundant mineral in industrial sand) equates to 0.1 mg/m³ as an 8-hr time-weighted average. In March 2004, the California Office of Environmental Health Hazard Assessment in association with the California Environmental Protection Agency (EPA) Science Review Board began considering recommending a Chronic Inhalation Reference Exposure Level (REL) for crystalline silica of 3 µg/m³, along with a Chronic Toxicity Summary document in which the recommended REL is derived. Although the proposed REL was not scientifically derived, California is still considering regulating crystalline silica at levels that, in many localities, are below the ambient crystalline silica levels.

For a variety of industry sectors, including industrial sand producers, it is unlikely that a PEL below the current permitted regulatory limits would be technologically or economically feasible. This is particularly true given that PELs are enforced on a single-shift basis, even if long-term average exposure on multiple shifts is significantly below the PEL. This approach to enforcement effectively requires producers to maintain the workplace environment at a fraction of the PEL to ensure that a single-shift measurement does not result in a citation.

If regulatory agencies are successful in lowering the PEL or implementing a REL below ambient crystalline silica levels, then it would be technologically and feasibly impossible for industrial sand producers to comply. Further, lowering the PEL would create

serious and relevant concerns with respect to the accuracy and reliability of the data.

Crystalline silica was listed in the regulations for MSHA and OSHA in 2004. It is likely that industrial sand producers will continue to be the focus of ever-increasing regulation. In addition to increased regulation, industrial sand producers have been the focus of litigation regarding silicosis. One significant silica litigation risk issue is the regulations covering silica. Regulations establish requirements and create enforcement risks for the industry, but they also create assumed corporate knowledge of risk and standards of care that become evidence in tort liability cases. Industry monitoring groups estimated that 35,000 new silicosis claims would be filed by October 2004, with a focus on producers in Mississippi, Texas, Ohio, and Pennsylvania. Recent tort reform laws in Mississippi and Texas, and silica-specific legislation passed in Ohio, are expected to prompt acceleration in claims in those states and create a trend of litigation in other states. In the spring of 2004, the Minnesota Supreme Court issued a decision restricting the conventional "sophisticated user" defense used by industry. Therefore, it is reasonable to expect more silica-related claims in Minnesota and in other states where the sophisticated-user defense has been used by industry.

It is also important to note that several insurance providers to the industry are circulating "silica exclusions" for all new policies and renewals. Therefore, claims going forward from renewal will not be covered by insurance. In the absence of tort reform at the national level, it is likely that this trend will increase significantly. Defending silicosis litigation has the potential to be the most relevant financial concern for the industrial sands business.

Land Use and Environmental Restrictions

Urbanization continues to pose a material threat to current operations and exploration targets. High-density housing threatens existing operations all over the United States, and new homes are encroaching on or condemning known resources. This is a concern in the western United States, particularly California. High-density, high-value housing subdivisions are being developed close to the permit boundaries of the two largest producers of industrial sand in California.

The mineral extraction industry, for the most part, has poor relations with local communities, and it is becoming increasingly more difficult to permit operations on both public and private land. As development continues and environmental regulations become more stringent, operators will have to increase the transparency of their operations and work in partnership with community and environmental groups. Although operators are not likely to be successful in deregulating the industry, operators can increase their credibility in the community by operating clean, safe, and efficient operations. If practical, operators should create community advisory boards and meet with them regularly. It is also important to integrate community comments into the management of an operation. Many industrial sand plants and extraction sites are located close to population centers; therefore, working in partnership with stakeholders is the only way that producers can enjoy overall success in the current regulatory environment. As regulation increases, operators must identify issues and work with the community and the regulatory agencies to minimize risk to the environment, stakeholders, and their operations.

Since 1998, aboriginal land claims in the United States and Canada have increased. In general terms, Native Americans claim that their land was illegally taken from them, thus mineral extraction operations have committed trespass. As plaintiffs, the Native American tribe or pueblo generally requests compensation for loss of revenue and a return of the land. It is difficult to predict how the

courts will decide in these cases, but an unfavorable decision for the industry would create a judicial precedence that would be problematic for the industry as a whole. Any operation in the western United States that operates on patented land or public land is at risk. It is difficult to predict what, if any, overall effect aboriginal land claims will have on the industrial sands business. However, it is a risk that all operators should evaluate.

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High Pure and Ultra-High Pure Quartz

John W. Schlantz

INTRODUCTION

Quartz, or silica sand (SiO_2), has enjoyed a multitude of industrial uses, from low-end markets of construction material to mid-range markets of glass, ceramics, and fillers to high-end, high-tech uses such as electronics, optics, semiconductors, lighting, infrared, specialty glass, fiber optics, and the computer and communications industries. *Fused silica*, or *fused quartz*, is the common term that applies to silica in most of these high-tech markets.

In the first half of the 20th century, quartz for higher end markets was hand-cobbed from crystal or lump deposits. The most sought-after material came from the Lascus deposits in Brazil, which had such purity that it was considered a strategic supply for early communications (radio), especially during World Wars I and II. Later, advances in beneficiation technology enabled the mass production of quartz to various levels of purity, depending on the nature of a quartz deposit, the natural characteristics of the quartz, and the ultimate end use.

IMC Corp. began mass production of high pure and ultra-high pure quartz in the Mitchell County/Spruce Pine area of western North Carolina in the late 1950s. These quartz products were marketed under the trade names Quintas (high pure) and Iota (ultra-high pure quartz). Because of their success, the two grades are often referred to by these trade names in the industry. Over the years this operation changed hands several times, and Unimin Corporation now owns and operates it.

Because of advances in many high tech industries, and the relative scarcity of supply, the use and price of high pure and ultra-high pure grades have grown accordingly, creating a high level of interest in finding suitable deposits capable of producing equivalent raw materials or superior products.

MITCHELL COUNTY/SPRUCE PINE QUARTZ

The mass production of high pure and ultra-high quartz products in the Mitchell County/Spruce Pine district of western North Carolina by Unimin Corporation supplies the majority of the world market. The Feldspar Corporation (Zemex Corporation) also produced high-grade quartz, but on a limited basis. Feldspar Corporation entered the quartz market in the early 1980s and built the second quartz plant in Spruce Pine. Because of challenges in the development of markets, however, the operation never became profitable. Zemex sold the operation to Unimin in the early 1990s, giving Unimin an exceptionally strong position in the market, which they maintain today.

Feldspar and Mica Recovery

High pure and ultra-high pure quartz in North Carolina originally were by-products from the mining and recovery of mica and feldspar from the vast reserves of the granitic pegmatite referred to as alaskite. Initially, both Zemex and Unimin mined the same alaskite ore body, which has the approximate composition of 60% to 65% feldspar; 20% to 25% quartz; 5% to 10% mica; and 5% to 10% iron minerals (such as garnet and biotite). The process to recover feldspar and mica (Figure 1) has been used for more than 50 years.

The process begins with run-of-mine ore undergoing primary and secondary crushing (jaw and cone crushers, respectively) to approximately $-1/2$ in. The crushed ore is reduced further to 20 mesh by rod and ball milling in closed circuit. It then is washed through a series of cyclones to remove fines <200 mesh, providing a flotation feed of 20 × 200 mesh.

Flotation first recovers mica and consists of conditioning with amine-type collectors in an acid circuit. A rougher concentrate is produced that is subsequently cleaned to produce a concentrate at +90% mica content.

Tailings from the mica flotation report to another acid circuit with a petroleum sulfonate collector to remove the iron-bearing minerals, which, with the exception of the fines, is the only waste product generated. The clean pulp finally is floated with hydrofluoric acid and amine for feldspar concentration. The feldspar is filtered and dried, then sold directly to the glass industry or processed further with magnetic separation and fine grinding for the ceramic and filler industries.

Quartz Processing

Tailings from the feldspar flotation serve as feed to the quartz-processing plants. Producing the high pure grades of quartz from these tailings was a very attractive prospect to both companies, especially Feldspar Corporation. For many of the early years of these operations, Feldspar sold these tailings as low-grade construction products for a dollar or two per ton or disposed of them in tailings dumps. The companies actually were looking for ways to dispose of the tailings, and the potential to produce value-added products from "waste" is always compelling.

Because feldspar is the primary product and quartz is a by-product, the feldspar flotation leaves residual amounts of all minerals in the quartz tailings, and these must be thoroughly removed to produce the purity required for the high and ultra-high pure grades. These processes are considered proprietary and cannot be discussed

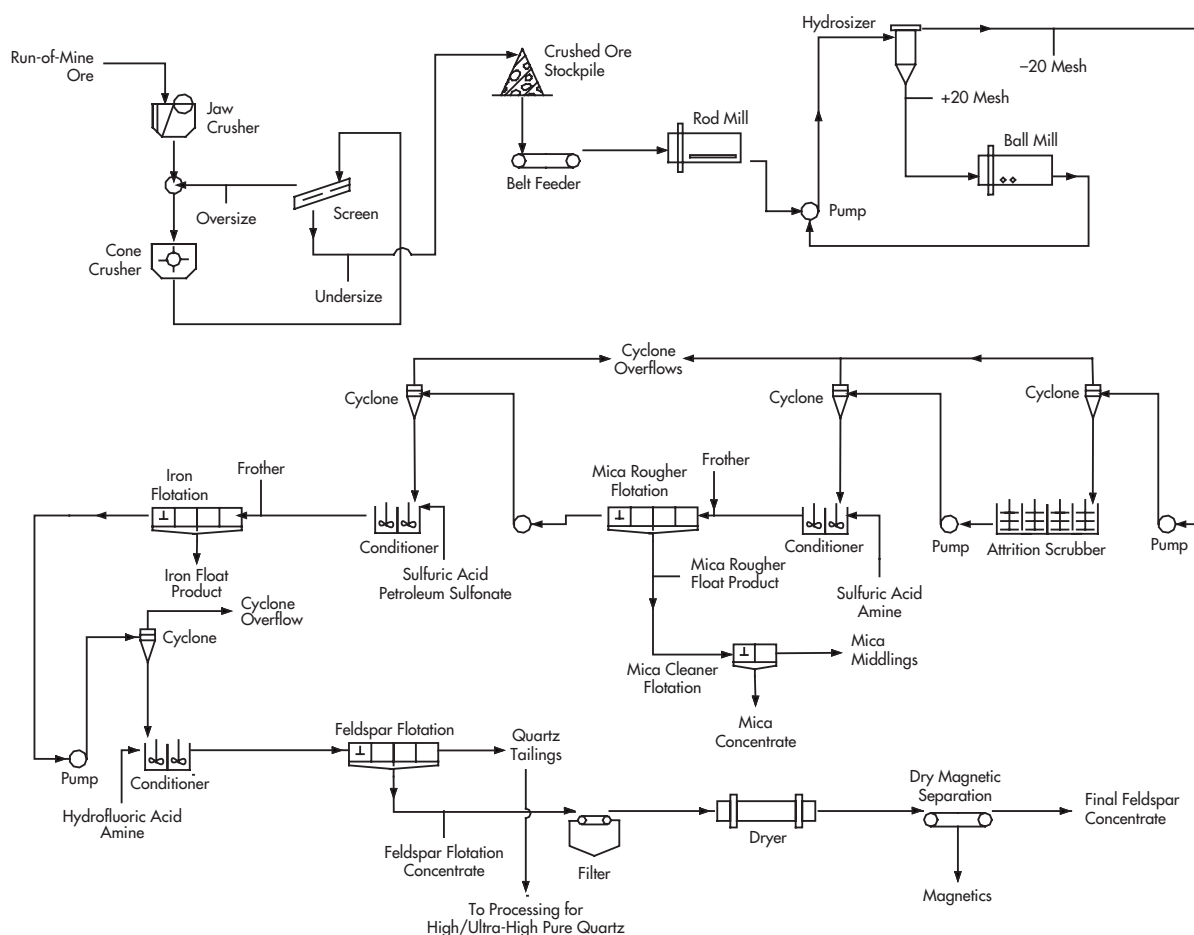


Figure 1. Schematic flowsheet of typical alaskite flotation (mica, iron, and feldspar flotation)

in this chapter; a general statement regarding the processing in to higher grades, however, would show that the high pure quartz, or Quintas grade, typically is produced through additional physical separations whereas the ultra-high pure, or Iota grade, will require additional chemical processing methods. The unit operations to which the final quartz is subjected can vary, depending on the degree of purity required for given markets.

The Unimin Corporation gained a significant advantage over the Feldspar Corporation in the late 1980s with the purchase of the old Harris Mining Company property. This operation mined and processed mica and kaolin for many years, and Unimin purchased the property for uses other than mining (i.e., water discharge permits). They soon discovered, however, that quartz in the soft or weathered Harris alaskite deposit could produce grades superior to those extracted from the hard alaskite ore.

Although Unimin continues to mine and process quartz from the alaskite ore, the development of the Harris deposit raised the standard of purity and led to the development of higher-grade Iota products. Even though this material goes only into highly specialized markets (i.e., computer chip manufacturing), this development was a factor in Feldspar Corporation's decision to abandon the quartz business.

Unimin today controls the majority of the world market for high pure and ultra-high pure quartz. Feldspar Corporation continues to supply small amounts, but only in the high pure form that is sold to a few select customers who process this quartz into higher-

grade products. Hand-cobbing operations in some developing countries such as India produce small amounts, but they do not represent significant competition to Unimin's Spruce Pine operations.

EXPLORATION AND DEVELOPMENT

Logically, exploration efforts tend to focus on similar alaskite deposits, but the geology of the pegmatite in the Spruce Pine area remains somewhat of a mystery with regard to the purity of the quartz. The author personally is aware of consulting geologists working exclusively in the quartz industry, and their ideas about where to look and what to look for change frequently. Quartz with high potential for development has been found in both pegmatite and vein deposits.

The author also has evaluated literally hundreds of samples from throughout the world. These samples were submitted by qualified geologists and, more often than not, the material was inferior in quality. In addition, extensive work was done comparing various chemical and elemental properties to find a correlation between quartz with high-grade properties and those defined as unsuitable, with inconclusive results.

Many theories and ideas have been offered over the years to explain the exceptional purity of the Spruce Pine quartz deposits. These range from extreme weathering conditions to remelting theories. The weathering theory received considerable attention: the belief is that such weathering leached out the majority of contaminants found in typical granitic pegmatites. Therefore, considerable

emphasis was placed on this type of weathered deposit for exploration. On the surface, this line of thought had some logic to it because the Harris deposit certainly underwent extreme weathering and it produces the purest quartz products. Given the type of “contaminants” that disqualify most quartz deposits, however, this theory cannot account for its total purity.

Contaminants found on the surfaces of quartz particles, or liberated from the quartz crystal, typically can be removed through a variety of processes; it is these contaminants that would be removed via the weathering process. Those contaminants found within the quartz crystal itself in trace amounts are those that current technology cannot remove. These are present either as interstitial cation impurities or as substitutions for the silicon atoms in the center of the tetrahedral crystal structure of the silica.

Commonly, quartz contains aluminum (Al^{+++}) and ferric iron (Fe^{+++}) substituting for silicon (Si^{++++}) in the tetrahedral site; balance is achieved by ions such as sodium (Na^+), potassium (K^+), lithium (Li^+), and hydrogen (H^+) in the interstitial positions. The dominant contaminants, or those most likely to enter the quartz structure, are not necessarily those with the highest affinity or structural fit but rather those that are the most abundant in the geological environment. Most quartz does not contain a large amount of such impurities except when compared to those found in Spruce Pine.

Impurities of another type occur as inclusions in the quartz grains, and these can be solid or liquid and/or gas inclusions. Common solid inclusions are rutile, mica, and garnet. Liquid and gas inclusions can contain CO_2 , N_2 , H_2O , ammonia (NH_3), SO_3^- , F_2 , Cl_2 , Na^+ , K^+ , and Li^+ .

Liquid and gas inclusions occur when solutions or gas become entrapped during the initial crystallization of quartz or later during secondary growth. Solid or mineral inclusions typically occur either by mechanical enclosure in quartz grains during initial crystal formation or by exsolution after crystal formation.

It is commonly believed that the Spruce Pine quartz is the purest in the world, and it is certainly superior to any other mass-produced quartz. Its purity comes primarily from its lack of trace impurities. It is well known that impurities and structural defects in quartz are typically greater in quartz formed at lower temperatures and pressures. One might postulate, therefore, that the Spruce Pine quartz was formed under high temperatures and high pressures. Because this quartz is classified as primary quartz, it also is theorized that the parent magma did not have an abundance of trace elements in its environment available for substitutions and was probably lacking in H_2O . Relatively high quantities of calcium and plagioclase feldspar found in the alaskite suggest evidence of such conditions. Atypical crystallization temperatures and pressures, magma water content, lack of contaminating elements in the enriched magma during quartz formation, and other factors are probably responsible for the high level of purity of these quartz deposits. These circumstances are responsible for classifying the Spruce Pine quartz as unique.

After evaluating numerous samples, and given the lack of intensive geological data on quartz deposits throughout the world, the author believes that finding a suitable raw material may be a simple case of “hit or miss” or “trial and error.” In fact, the quality of Spruce Pine quartz was “stumbled” on: neither company realized its potential for many years. Today many evaluations for these quartz products result from evaluating deposits for other mineral values; the quartz in samples from these deposits may show some initial potential for upgrading.

Given the unique example described, suggesting guidelines for high pure quartz exploration is, at the least, difficult. The best sug-

Table 1. Elemental limits—initial qualification, maximum ppm

Quartz Product	Fe	Al	K	Na	Ca	Li	Mg	Ti
High pure	20	250	80	100	50	2	30	5
Ultra-high pure	1.0	15.0	2.0	2.0	2.0	0.5	0.5	1.0

gestion is to search for quartz that has no inclusions and no contaminants substituting in the actual SiO_2 crystal matrix. To produce the purity required, all contaminants must be liberated from the quartz or from the surfaces of individual grains. The explorer, therefore, should investigate deposits that appear, on microscopic examination, relatively clean and clear. The deposits should then be compared with quartz from current operations with data indicating potential grades, if available. Unfortunately, the only way to determine conclusively the true quality of any quartz is large-scale testing.

Any final judgment on quartz purity based on feed analysis, or data generated from partially or unbeneficiated material, could lead to false conclusions. The Spruce Pine material is a good example. Because it contains high amounts of feldspar, mica, and other minerals in the ore, analysis of a Spruce Pine run-of-mine sample would not indicate the quartz potential. The same could be said for the actual quartz tailings from these operations that serve as feedstock for quartz processing, because these tailings typically contain up to 5% to 10% feldspar and residual mica, biotite, and garnet. Only after these had been removed completely did the true potential for quartz become apparent.

Development/Evaluation

After a suitable source of raw material has been found, its evaluation, although highly objective in the initial phases, can become rather complex and time consuming. Once the material has initially qualified and its performance has been determined, furnace trials must be conducted with potential customers to certify the material for their use.

Because end uses for quartz products vary, exact product specifications are ultimately defined by product performance as determined by a potential consumer. Some typical elemental contaminant limits, however, can be applied initially to evaluate the quartz or control the process.

Table 1 lists typical limits on contaminants. It does not include all the elements that would disqualify a quartz resource, but it serves as a basis for further evaluation. Although many describe quartz in terms of percent SiO_2 , this often is misleading, especially in the ultra-high pure grades. A quartz product could be described as 99.999% SiO_2 but still contain trace elements on a level measured in parts per million that could hinder the performance of quartz in its end use.

The typical evaluation process begins with bench-testing the raw material to produce relatively small samples of high pure and ultra-high pure products. (The ultra-high pure grades are produced only if the high pure product compares reasonably well with the elemental guidelines in Table 1.) If the chemistry is acceptable, the material is evaluated to see how it actually will perform; this defines its commercial viability. This phase of the evaluation is almost always market specific. A common method is to produce a fused quartz product (e.g., crucibles) and examine it for flaws.

Once chemistry and fusion are deemed satisfactory, furnace trials certify the quartz. This is done by the producer using the quartz products and requires the production of bulk concentrates (sometimes up to 10 st or more) on a pilot-plant scale under very tightly controlled and contamination-free conditions. Few commercial or academic research laboratories have the expertise and

Table 2. Typical product specifications, maximum ppm

Product	Fe	Al	K	Na	Ca	Li	Mg	Ti
High Pure Quartz								
Sample A	12	250	60	120	40	2	3	2
Sample B	50	230	30	40	30	na*	30	na
Sample C	15	250	60	120	40	2	3	2
Sample D	5	250	80	140	na	na	na	na
Ultra-High Pure Quartz								
Sample E	0.7	13.5	0.8	1.2	1.5	0.5	0.1	0.1
Sample F	0.4	17.0	0.8	1.0	0.7	0.5	0.1	1.0
Sample G	1.0	25.0	2.0	2.0	2.0	0.5	0.5	1.2
Sample H	1.0	20.0	1.5	2.0	1.5	0.5	0.2	1.2

* na = not available.

experience (e.g., North Carolina State University [NCSU] Minerals Research Laboratory, Asheville) to produce such bulk concentrates that have passed the strenuous qualifying process.

Although actual fusion performance is the ultimate evaluation factor, some researchers use the high standard set by Unimin's highest Iota grades to assess the quartz on an elemental basis. Iota grades contain exceptionally low aluminum (<7 ppm) and other elements are in the range of those listed in Table 1 and produced from the Spruce Pine alaskite. Disqualifying a material based on direct comparison to the Iota products may be a mistake, because relatively lower-grade products (10 to 15 ppm Al) can be introduced into the market with success. To support this, Table 2 lists some actual marketed products along with their chemistries. Though Iota 7 is used as a comparison tool, it should not be the only factor in the final evaluation process.

Evaluation Costs

It is difficult to place an exact cost on the evaluation process because all deposits and projects are unique; some estimates can be offered, however, based on experience. The initial bench evaluation can range from \$1,500 to \$5,000 per sample, which includes the production of a small amount of quartz, chemical analysis of the high pure quartz product, and possibly leaching, chlorination, and final chemical analysis of the ultra-high pure product.

The most cost-intensive items are the chemical analysis and leaching. Few laboratories can perform accurate chemical analysis on these products. An extensive search for suitable raw material can involve evaluating many samples, and the evaluation can become expensive, if not prohibitive.

Pilot-plant testing that produces bulk concentrates of high pure quartz costs \$40,000 to \$100,000, depending on the amount and type of processing required and the tonnage produced. Additional costs would be incurred should these bulk concentrates require processing to the ultra-high pure grades.

It is important to realize that noncontaminating conditions are critical during both bench scale and pilot-plant scale tests. The simple touch of a human hand or a cough can contaminate a sample and yield erroneous results regarding product grade.

MARKETING

In most industrial minerals ventures, a market study is key in determining the potential use of the product, size of the market, price of the commodity, transportation costs, profit estimations, potential by-products, and competition (not only from other suppliers but also from other materials). In the high pure quartz market, the specialization and anticipated profit margins ensure a high unit price,

so transportation is usually not a factor. Competition comes only from other suppliers, because there are no known substitutes.

A marketing strategy in the quartz industry is essential, as is a competent sales staff, which should be included in any operating costs. The sales and marketing staff should have a thorough understanding of the potential markets, and finding such a team may be a significant challenge because experienced people are not readily available.

A common mistake in the marketing strategy of high pure and ultra-high pure quartz is neglecting the wide variety of high pure quartz markets. Many promoters and developers focus their attention on producing the best quartz available, attempting to surpass the quality of Iota grades; the overall ultra-high pure quartz market, however, is relatively small (albeit with very large profit margins). Developing a high pure product with reduced production costs may be necessary to create volume sales from any proposed plant.

Even with the capability of developing a high pure product and its markets, total volume of production at the plant will be comparatively small. Any operation under serious consideration would be specifying a plant to produce 35,000 to 50,000 tpy of high pure quartz product, with perhaps 10,000 to 15,000 t earmarked for eventual ultra-high pure quartz production. This total yearly tonnage is equivalent to what some conventional mining operations process in a day.

The high pure markets would include applications in specialty glass, glass tubing, lighting, decorative glass, and opticals, among others. These niche markets are easier to penetrate than the markets for electronics, computer applications, and fiber optics. Therefore, a marketing approach should consider the high pure quartz products that conceivably can create a more immediate cash flow. The plant can survive financially on this volume while inroads are made in the harder-to-penetrate, ultra-high pure quartz markets.

These niche markets are small in terms of the volume required by individual consumers, but there are many of them, so the total volume (overall tonnage) of high pure quartz that can be moved into these niche markets can be significant. This is further justification for employing a well-trained sales staff.

Marketing the products should be done early in the evaluation process, especially for the ultra-high pure products. Relationships with potential consumers are critical given the rigorous certification process. Having one or two customers involved at the beginning is a tremendous advantage and can lead to timelier furnace trials, assistance in product development, additional expertise, and perhaps funding for the operation (i.e., joint ventures). The best-case scenario would be sales commitments from at least one high-end user once production begins.

It is important to understand that these high-end users stand to lose significant revenue if a batch of quartz fails to perform as expected. Therefore, customers are very cautious and reluctant to change suppliers, but they are seldom closed to the idea.

COSTS

Because of contamination concerns and the need for special materials of construction, a high pure quartz plant is costly to build, operate, and maintain compared to typical mineral processing plants. In the early 1980s, it is estimated that at Feldspar Corporation's quartz plant cost \$15 to \$20 million to construct and was designed to process 60,000 tpy of quartz with a projected production capacity of 35,000 tpy. A similar plant today would cost upward of \$50 million. Unit costs per ton of product would have to be high given the relatively low production volume.

Potential profit margins on the high pure and ultra-high pure quartz products can offset these capital costs with rapid return on investment. High pure quartz today is demanding \$500 to +\$1,000/t in the marketplace, whereas the ultra-high pure products sell for \$2,000/t to more than \$10,000/t (and some are rumored to be as much as \$15,000/t). The final sales price depends on end use and product quality. Again, the ultra-high pure market is considerably smaller, but with the high unit price of the high pure products, it is obvious why both markets need to be taken advantage of. For comparison, this is much more attractive than the \$1.50/t for silica sand as construction materials.

Production costs, which depend on process parameters and quartz recovery, are difficult to predict. High pure quartz, however,

could probably be produced for \$300 to \$600/t, whereas the ultra-high pure product would most certainly be double that at \$600 to \$1,200/t. Given the relatively high sales price, it is obvious that a high profit margin would exist. The pricing structure is due to today's market conditions, but additional suppliers could alter this; there is still, however, opportunity in the industry for competitors to enter the market and maintain a high profit margin.

These costs are estimates based on experience and should not be used to justify any quartz venture. A detailed economic evaluation is recommended and should be based on specific ore grades, process parameters, and a detailed market evaluation. It is important to realize that the Spruce Pine operations produce quartz as a by-product, and mica and feldspar production absorb a portion of the production cost (for example, mining and crushing costs), offering the producer a significant production cost advantage.

PRODUCTION AND FUTURE TRENDS

Given the highly secretive nature of the high pure quartz industry and the small number of producers active in the marketplace, no production figures are available and they are unlikely to ever be published. A select few companies enjoy an exceptionally strong position in the market and would certainly like to see it remain as such.

Future market conditions and technological advances may demand increased quantities and higher purity, which may bring synthetic silica into play; but thus far there is little or no evidence of such activity.

Specialty Silica Materials

Stanley T. Krukowski

Specialty silica materials, as defined in this chapter, are rocks that consist predominantly of silica (SiO_2) and are produced as chunks, round pebbles, and sawed or trimmed blocks and other shapes for nonconstruction applications. Rock types are quartzite, sandstone, novaculite, flint, chert, and vein quartz. Other terms used commercially include jasper, silix, lascas, and rock crystal.

In its *Minerals Yearbooks*, the U.S. Geological Survey (USGS) reports the production and consumption of some specialty silica materials under several headings. Quartzite, sandstone, and novaculite use in abrasives are covered by the USGS under Abrasive Materials. Lascas, a type of vein quartz used in growing synthetic quartz crystals and in fusing applications, is discussed under Quartz Crystal. Silica gravel used in manufacturing silicon metal and ferrosilicon, as metallurgical fluxstone and as a filtration medium, is covered under Industrial Sand and Gravel. This overview consolidates information on these and other specialty silica materials.

GEOLOGY

Sandstone

Sandstone is a sedimentary rock comprising predominantly quartz grains bound together by argillaceous, calcareous, ferruginous, or siliceous cements. Common detrital impurities are feldspar, mica, and a wide variety of heavy minerals such as ilmenite and kyanite. The purest quartz sandstones, also called quartz arenites, consist almost entirely (i.e., >95%) of fine to medium, well-sorted, and well-rounded quartz grains. They are more common in near-shore facies than in deepwater facies. The degree of induration varies from tightly cemented, hard, and tough sandstone to loosely consolidated, friable rock. Induration usually increases as grain size decreases. Color depends largely on the cementing material present. Most sandstones used in specialty applications in Canada, England, Germany, and the United States are Cambrian, Silurian, or Pennsylvanian (Carboniferous) in age and range from 3 to 85 m in thickness. Cambrian age sandstones usually rest unconformably on an eroded Precambrian surface.

Formations of medium- to coarse-grained sandstone mined for specialty applications contain lenses of round quartz pebbles or thicker beds of quartz pebble conglomerate. Pebbly zones commonly are found as long, narrow bands deposited in channels cut by streams into underlying rock. Pebbles range in diameter from 0.3 to 8 cm, and conglomeratic beds range in thickness from 15 to 90 m.

Quartzite

Quartzite is a metamorphic rock derived from sandstone and is distinguished from sandstone by its fracture. Sandstone breaks along grain boundaries, whereas quartzite is so well indurated that it breaks across constituent grains. Orthoquartzite, the metamorphic equivalent of quartz arenite, consists of quartz grains cemented by silica and commonly exhibits relict sedimentary textures (Murphy and Brown 1985). In metaquartzite, quartz grains no longer are discrete particles but have coalesced into a network of interlocking crystals as a result of recrystallization during metamorphism.

Quartzites range in thickness from 100 to >1,200 m and occur mostly in Precambrian- to Silurian-age formations. The rock can vary widely in texture, friability, color, and chemical purity depending on the type of cement, grain size, and mineral composition of the original sandstone, and the intensity of metamorphism. Quartzite derived from argillaceous sandstone often contains sericitic partings, which may raise its alumina and alkali content above acceptable limits, causing it to crush into undesirable slabby pieces. Fine- to medium-grained, massive quartzite containing little or no feldspar, mica, or carbonate mineral impurities tends to be dense, hard, and tough; it tends to crush into sharp, brittle, angular fragments. Its chemical purity can range from 96.0% to 99.8% SiO_2 . Coarse-grained quartzite tends to be less pure and more friable, particularly if the cement is argillaceous or calcareous. Colors range from white and gray-white to shades of red, pink, purple, blue, and orange. Compressive strength can vary from 1.52×10^5 to 4.96×10^5 kPa, and the specific gravity of most quartzites is between 2.65 and 2.70.

Novaculite

The term *novaculite* is derived from the Latin word *novacula*, meaning razor hone (Steuart, Holbrook, and Stone 1985). Novaculite is a very dense, hard, fine-grained, homogeneous, and highly siliceous sedimentary rock with Mohs hardness of 7 and specific gravity of 2.63 to 2.64. Its color varies from white to gray, light brown, bluish, or black; it is translucent on thin edges; and it breaks with an uneven conchoidal or subconchoidal fracture (Holbrook and Stone 1979). It resembles chert, although its fracture surfaces are finely granular or gritty in comparison to the smooth fracture surfaces of chert and flint (Sholes 1977). The luster of novaculite varies from waxy to dull, the latter resembling unglazed porcelain. Its chemical purity can exceed 99% SiO_2 in the form of microcrystalline or cryptocrystalline quartz.

Perhaps the most distinguishing characteristic of novaculite is its texture. Rock that has been little affected by thermal metamorphism is made up of anhedral quartz grains. By comparison, rock that underwent thermal metamorphism—for example, near Hot Springs, Arkansas, and Broken Bow, Oklahoma consists of coarser, polygonal or polyhedral, triple-point crystals or sharp-edged blocks of quartz 5 to 20 μm in diameter (Keller, Stone, and Hoersch 1984; Steuart, Holbrook, and Stone 1984). The porosity of novaculite from near Hot Springs ranges from 0.07% to 0.25% for the Hard Arkansas Stone variety, which has a waxy luster, and from 5% to 16% for the Washita Stone (Ouachita Stone, or Soft Arkansas) variety, which has a porcelanic appearance (Harben 1983). Washita Stone contains rhombic cavities from which calcite or other carbonate mineral were dissolved. Broken surfaces of Hard Arkansas Stone are smooth, whereas those of Washita Stone are rough. Beds of Washita Stone contain fewer joints and quartz veins; the stone becomes tougher (less easily fractured) when exposed to weathering.

The Arkansas Novaculite Formation lies conformably between the older Missouri Mountain Shale and the younger Stanley Shale. It attains a maximum thickness of 290 m and consists of upper and lower novaculite members interbedded with three units of chert and shale. The upper member is Mississippian in age and has a maximum thickness of 55 m. It is a white to light gray or blue-black massive calcareous rock that contains as much as 30% carbonate minerals where it is unweathered. It weathers to beds of soft, powdery tripoli that reach up to 12 m in thickness. The purer lower member ranges in thickness from 15 to 135 m, is Devonian in age, and is a white to light gray or light brown massive rock that is cut extensively by joints oriented normal to bedding. It is slightly calcareous near its base where dissolution of calcite rhombs produced a distinctive whetstone texture (Steuart, Holbrook, and Stone 1984).

Vein Quartz

Massive quartz for specialty applications is obtained from the central core of zoned pegmatites and from veins, dikes, and plugs within sedimentary, igneous, or metamorphic host rocks. Host rock formations usually range in age from Precambrian to Jurassic. It is believed that most deposits formed by hydrothermal processes, although not all are located near granitic intrusions. They occur as fissure and cavity fillings and, less commonly, as metasomatic replacement bodies.

Pegmatites associated with granitic intrusions generally yield very pure quartz, especially in the case of microcline pegmatites devoid of muscovite and rare-earth oxides; but they have a well-developed quartz core with druse cavities. Cores of such pegmatites commonly contain abundant fluid inclusions that render the quartz unsuitable for fusing into clear quartz glass. Massive quartz veins of hydrothermal or metasomatic origin may have a zoned structure consisting of several generations of quartz crystal growth. The oldest generation is coarse grained and usually contains abundant fluid inclusions; the younger generations are finer grained and purer; and the youngest generation consists of crystals in druse cavities. Wall rocks of such veins usually are leached, sericitized, or chloritized. The size of cavities containing quartz crystals is directly proportional to the intensity of wall rock alteration. In general, the more chlorite a vein contains, the purer the quartz within the vein. Hydrothermal veins that were metamorphosed, or segregated from country rocks during regional metamorphism, tend to be free of fluid inclusions and, therefore, tend to yield fusing-grade quartz (Kuzvart 1984).

Primary quartz deposits in Brazil occur in the form of veins, pipes, pockets, stockworks, and composite lodes confined to sili-

ceous host rocks. They are found mostly within crossbedded sandstone and quartzite of Late Precambrian age and along the contact between Precambrian granite and Silurian shale. Veins and pockets were emplaced in early Paleozoic, probably Silurian, time (Bates 1960). They are made up mostly of very large crystals of milky or gray bull quartz that grew inward from the walls of druse cavities to form a comb structure. Vugs are abundant; some are lined with well-formed quartz crystals and/or filled with clay. Some crystals, especially smaller ones weighing less than 250 g, are clear and make electronic grade; most piezoelectric-grade quartz, however, occurs as clear or translucent pyramidal terminations on milky bull quartz crystals that can exceed 1 t.

In Brazil, primary vein deposits in bedrock are overlain by a residual soil blanketing containing alluvial and colluvial deposits of clear, unworn quartz crystals. They also are associated with nearby alluvial placer deposits in present or former stream channels that contain rounded and frosted but usable crystal fragments. Some alluvial deposits consist of several beds of quartz gravel separated by lenses of clay. They are commonly enriched in high-quality quartz, because fractured or twinned crystals break down more readily during weathering and stream transportation. Alluvial placer deposits are elliptical with long axes parallel to the strike of the veins, whereas colluvial placers are fan-shaped (Kuzvart 1984).

Silica Pebble

In addition to the quartz pebble facies of sandstone formations, geologic resources that yield silica pebbles for specialty applications include sedimentary chalk and marl beds and fluvial deposits. These are generally much younger than other specialty silica rock resources. They usually range in age from Cretaceous to Holocene. The high-purity silica pebbles may be flint, quartzite, or massive, vein-sourced quartz.

DISTRIBUTION OF MAJOR DEPOSITS

Sandstone, quartzite, vein quartz, and other silica-rich rocks are common and distributed worldwide, but only at few locations does the rock have the physical and chemical properties required for specialty applications.

Sandstone

Canada

The Potsdam (Nepean) Sandstone has been quarried in eastern Ontario and southern Quebec. It is Late Cambrian to Early Ordovician in age, rests unconformably on an eroded Precambrian surface, and ranges in thickness from 20 to 85 m in Frontenac, Leeds, and Lanark counties in eastern Ontario. Where exposed between Kingston, Brockville, Perth, and Smiths Falls in Ontario, this sandstone consists of well-indurated grains of 75 to 850 μm (Guillet and Kriens 1984). At St. Canut north of Montreal, Quebec, the Potsdam (Nepean) is mined and processed and then sold for use in glassmaking and silicon carbide manufacturing.

The Medina Sandstone of Early Silurian age crops out in several counties west of the Niagara Escarpment in Ontario. Medina sandstone varies in color from gray to brown to red and is fine to medium grained. It has been quarried principally for dimension stone, but it also has been used for mill blocks and in ganister mixes for lining cupolas and ladles in the steel industry and as a source of silica for ferrosilicon and glass.

The Winnipeg Formation of Cambro-Ordovician age crops out on three islands and two promontories in Lake Winnipeg, Manitoba. It consists of nearly white, poorly consolidated, well-rounded sandstone and has been mined principally on the southeastern shore of Black Island. After washing and screening, the product was

barged 140 km south to a plant at Selkirk, Manitoba, for further processing (Guillet and Kriens 1984). The silica sand was used for foundry and filter-bed sand and for sandblasting. The plant at Selkirk, on the Red River 40 km north of Winnipeg, has a production capacity of 115,000 tpy. Although sandstone is no longer mined in Manitoba, the Selkirk plant still processes imported silica sand. East of Lake Winnipeg, 1 km southwest of Seymourville, exploration and development of Winnipeg Formation sandstone, which averages 99.6% SiO_2 , is under way.

Grindstones, millstones, and pulp stones have been produced from Carboniferous and Permian-Carboniferous sandstones in New Brunswick, Nova Scotia, and British Columbia.

Egypt

The El-Zaafarana sand in the Wadi El-Dakhi in the Eastern Desert of Egypt supplies silica sand from semi-isolated blocks of 100-m thickness. El-Zaafarana sand has the following average composition: 97.27% to 99.79% SiO_2 ; 0.04% to 0.11% Al_2O_3 ; 0.01% to 0.18% Fe_2O_3 ; 0.0001% to 0.0005% Cr_2O_3 ; 0.06% to 0.12% CaO ; 0.02% to 0.05% Na_2O ; and 0.02% to 0.04% K_2O . The sand is used mostly in glass manufacture, but beneficiation in the form of tabling and magnetic separation has opened new markets for export in Europe.

The Wadi Qena white sand deposit ranges in thickness from 50 to 100 m in the El-Naqus Formation (Ordovician-Silurian). Average chemical analysis is 95.79% SiO_2 , 4.0% Al_2O_3 , and 0.033% Fe_2O_3 . Sinai deposits also are in the El-Naqus at Gebel El-Gunnah. The alumina content is associated with kaolin clay, which is easily washed from the sand and provides a valuable by-product (Ibrahim 2002).

England

One of the principal sources of grindstones, pulpstones, and millstones in England has been the fine-grained Newcastle Stone quarried from Carboniferous sandstone associated with Coal Measures near Newcastle (Bateman 1959). Derbyshire (Peak) and Yorkshire stones also have been quarried for this purpose from the Millstone Grits, which yield some of the best pulpstones in the world.

Germany and Italy

Carboniferous sandstone for grindstones, millstones, and pulpstones has been quarried in Germany and Italy.

New Zealand

At Pebbly Hills, 50 km northeast of Invercargill on South Island, a quartz pebble conglomerate deposit contains more than 200 Mt of high-quality gravel suitable for silicon metal production. The +12-mm gravel averages more than 98.75% SiO_2 (Benbow 1990; Christie et al. 2000).

United States

The Pottsville Group of Lower Pennsylvanian age contains quartz pebble conglomerate facies in sandstones of the Sharon and Olean formations. These formations have been mined in New York, Ohio, Pennsylvania, and Tennessee as sources of ganister for refractory brick and as sources of metallurgical gravel for silicon metal and ferrosilicon production (Murphy and Brown 1985). The Sharon Conglomerate, the lowermost member of the Pottsville Group, varies in thickness from 15 m in the northeastern Ohio counties of Geauga, Portage, and Summit to 70 m in the southern Ohio counties of Pike and Jackson. It is friable, medium- to coarse-grained sandstone with 95% to 99% SiO_2 containing pebbly zones that occur as long, narrow, north-south-trending bands deposited in channels cut into underlying Mississippian rocks. Metallurgical-

grade quartz pebbles also have been mined in Franklin County on the Cumberland Plateau of east-central Tennessee, where the Sewanee Conglomerate Member of the Pennsylvanian Crab Orchard Formation contains 99% SiO_2 .

At Keck Center in Fulton County, New York, white, granular sandstone containing as much as 99% SiO_2 was mined years ago for use in ferrosilicon production. Sandstone from the Homewood Formation has been quarried for ganister near Upper Hillville and Foxburg, Pennsylvania. Cambrian sandstone has been quarried in Pennsylvania for whetstone manufacture near Allentown in Lehigh County; for ganister and millstone production in Lancaster County; and for ganister in Montgomery County. Fine-grained quartzites and quartzitic sandstones of the Pennsylvanian Stanley and Jackfork formations in the Ouachita Mountains of Oklahoma are suitable for fabricating millstones and buhrstones. In Montana, a sandstone quarry at Columbus in Stillwater County has produced grindstones, and another at Dillon in Beaverhead County has produced metallurgical fluxstone and refractory ganister. High-quality sandstone suitable for specialty applications has been quarried near Denison in Spokane County, Washington.

The Shawangunk Conglomerate outcrops occur in a belt that extends from near Kingston, New York, southwestward into New Jersey and Pennsylvania. It has been quarried extensively for millstones at Shawangunk Mountain and near Kyserike, St. Josen, Granite, and Kerhonkson in New York. It is light gray, well-cemented and hard, pebbly sandstone that ranges in thickness from 15 to 90 m. Tough, fine-grained sandstone near Rawlins in Carbon County and on Baldwin Creek near Lander in Fremont County, Wyoming, was once used for grindstones, as was the Dakota Sandstone northeast of Edgemont, Nebraska, near the South Dakota border. More recently, Dakota Sandstone has been mined in Colorado for use as ganister in refractory applications.

Pulpstones have been fabricated from sandstone quarried in Pierce, Wilkerson, and Skagit counties, Washington, and whetstones have been produced from a 2.5-m-thick bed of sandstone in Skamania County, Washington, between White Salmon and Stevenson. Good pulpstones, grindstones, and millstones also have been produced from the Dunkard and Berea sandstones in Michigan, Ohio, and West Virginia. Hard sandstone, such as the Hindostan Stone from Indiana and the Queen Creek Stone from Ohio, has been used as waterstones (Bateman 1959). Until 1989, sandstone quarried at Orleans in Orange County, Indiana, was fabricated into cuticle removers, sharpening stones, and table coasters.

One of the few remaining U.S. producers of sandstone for nonconstruction purposes is Cleveland Quarries, which extracts and saws the Berea Sandstone into refractory bricks and blocks at South Amherst in Lorain County, Ohio. In this part of northern Ohio, the Berea, which is part of the Waverly Series of Mississippian age, can exceed 68 m in thickness, although it is only 15 m thick elsewhere. Cleveland Quarries cuts Buckeye Silica Stone into beams measuring 1.6 to 3.2 cm^2 in cross-section and into slabs, which are normally 1.2 cm thick. These refractory firestone shapes are used in fabricating acid tanks, steel pickling tanks, acid wash trays, soaking pits, and ladle linings, and for related applications in the steel and chemical industries. The company also has produced grindstones, pulpstones, and deburring media as coproducts at its dimension stone operations.

Quartzite

Australia

In Western Australia, high-purity quartzite is quarried at 60,000 tpy at Picton Junction near Moora, 185 km north of Perth. It is hauled 350 km to a 34,000-tpy-capacity silicon metal plant at Kemerton,

Table 1. Typical composition of Precambrian quartzites in Ontario, Canada

Chemical	Bar River Formation		Lorrain Formation McGregor Point, %	Grenville Quartzite Alban, %
	Badgeley Island, %	Shequiandah, %		
SiO ₂	98.50	97.90	94.10	96.90
Al ₂ O ₃	0.80	0.80	3.46	0.68
Fe ₂ O ₃	0.04	0.08	0.02	0.22
MgO	0.03	0.07	0.13	0.03
CaO	0.00	0.04	0.01	0.00
Na ₂ O	0.01	0.10	0.13	0.01
K ₂ O	0.14	0.30	0.38	0.09
LOI	0.16	0.24	0.43	0.12
TiO ₂	0.02	0.05	0.06	0.06
P ₂ O ₅	0.01	0.03	0.01	0.01
MnO	0.00	0.01	0.00	0.00
Total	99.71	99.62	98.73	98.12

Source: Guillet and Kriens 1984.

20 km north of the port of Bunbury and 165 km south of Perth. The quarry has a capacity of 75,000 tpy, and the Kemerton plant produces about 26,000 tpy of chemical-grade silicon metal.

Canada

In eastern Canada, three quartzite formations constitute the top of the Cobalt Group of Middle to Late Precambrian (Middle Huronian) age. The purest is the Bar River Formation at the top of the series, which is underlain by the Gordon Lake Formation and then the Lorrain Formation. The Bar River high-purity quartzite is white, dense, and massive. It is composed of fine to medium, rounded, and well-sorted quartz grains cemented by secondary quartz (Guillet and Kriens 1984). It is at least 900 m thick and is exposed on a chain of islands in the North Channel of Georgian Bay (Lake Huron), including Pine Island north of Killarney, Ontario, and Badgeley, Centre, Partridge, and Heywood islands.

The Bar River Formation has been quarried at Shequiandah on Manitoulin Island south of Little Current, where lump quartzite was produced for ferrosilicon manufacturing. It is now being quarried on Badgeley Island, 6 km west of Killarney, where the beds dip nearly vertically and contain a few lenses of diabase and amphibolite. Crushed quartzite is shipped to ferrosilicon and silicon metal producers at Welland, Thorold, and Niagara Falls, Ontario; at Bécancour, Quebec; and at Niagara Falls, New York. Fine sand is shipped 190 km south to a plant at Midland, Ontario, for further processing. Production capacity is 1 Mtpy at Badgeley Island and 0.5 Mtpy at Midland. The chemical compositions of the Bar River Formation and Lorrain Formation quartzites in Table 1 illustrate their purities.

The Lorrain Formation approaches the purity of the Bar River Formation, but it contains more alumina. It is exposed along the northern shore of Lake Huron between Sault Ste. Marie and Killarney, Ontario. The Belle vue Quarry north of Sault Ste. Marie formerly supplied quartzite as ganister for refractory brick, and a quarry at Killarney produced lump quartzite for ferrosilicon. Some lump quartzite from the Bar River Formation has been shipped to the Sudbury Area in Ontario and the Noranda Area in Quebec for metallurgical fluxstone in smelting nickel and copper matte. The Lawson Quarry at Whitefish Falls, Ontario, was a captive operation that supplied silica fluxstone to nickel smelters at Sudbury (Guillet

and Kriens 1984). Quartzite also is supplied to a nickel smelter at Thompson, Manitoba.

A friable orthoquartzite of Grenville (Precambrian) age is quarried near St. Donat, Quebec. It is processed at St. Canut, Quebec, 80 km to the southeast, where the Potsdam (Nepean) Sandstone also is quarried. Several quartzite mines in Beauharnois County, Quebec, supply metallurgical-grade stone to local ferrosilicon manufacturers. Elsewhere in eastern Canada high-purity quartzite is found near Labrador City, Labrador. In Newfoundland, 100,000 tpy of quartzite have been quarried at Villa Marie on the Avalon Peninsula in Placentia Bay and shipped to Long Harbour for fluxstone for the electric furnace production of elemental phosphorus. In Nova Scotia, a fine-grained, brittle quartzite of George River (Precambrian) age has been quarried in Cape Breton County as ganister for the refractory brick linings of open-hearth steel furnaces at Sydney. The stone is highly fractured and contains serpentine and chlorite impurities.

In western Canada the Mount Wilson Formation of Ordovician age consists of white, massive, uniform, medium-grained orthoquartzite or silica-cemented quartz arenite. It ranges in thickness from more than 330 m near Golden, British Columbia, to as little as 20 m at Canal Flats, which is 110 km to the southeast. It is quarried at Nicholson, 11 km from Golden in southeastern British Columbia, from which 30,000 to 60,000 tpy are shipped as metallurgical lump for silicon metal and ferrosilicon production at Rock Island near Wenatchee, Washington. It has supplied lump for the manufacture of polycrystalline silicon at Moses Lake, Washington. The Mount Wilson quartzite grade is as high as 99.85% to 99.9% SiO₂ with only 0.10% Al₂O₃ and 0.04% Fe₂O₃ (Simandl, Jakobsen, and Fischl 1992). Reserves of lump silica at Nicholson are estimated at 3 Mt. At Mount Moberly, British Columbia, a friable variety of Mount Wilson quartzite is mined and used in conventional markets for industrial silica sand. It contains 99.67% SiO₂, 0.06% Al₂O₃, and 0.02% Fe₂O₃ (Simandl, Jakobsen, and Fischl 1992).

In the vicinity of Longworth, east of Prince George, British Columbia, the Nonda Quartzite of Silurian-age outcrops extend for a strike length of 2.5 km and may be as much as 250 m thick. It is reportedly even purer than the Mount Wilson stone at Golden (Hamilton and Hora 1987). Quartzite for ferrosilicon and silicon

carbide manufacture formerly was quarried near Oliver in south-central British Columbia near the U.S. border.

Czech Republic

In central Europe, quartzites of Early Tertiary age, especially freshwater quartzites, are used as ganister for refractories and in the manufacture of ferrosilicon and silicon metal (Kuzvart 1984). Since depletion of deposits in the Most District, acid refractories (*dinas*) in the Czech Republic have been made with fine-grained quartzite from the Lahost-Jeníkov deposit near Teplice in North Bohemia. This deposit is 20 m thick, and the stone contains less than 1% Al_2O_3 and more than 97% SiO_2 (Hruska 1991).

Italy

Lump quartzite has been produced at Valsinni in Matera for local steel and chemical markets (Robbins 1986).

Norway

At Tana in northern Norway, quartzite is quarried and used in manufacturing 50% ferrosilicon. Lump quartzite from Tana has been shipped to Iceland for use in a ferrosilicon plant near Reykjavik.

Pakistan

Lump quartzite for use as a steel mill flux has been produced in the Lasbela region of Baluchistan (Griffiths 1987a).

Republic of South Africa

South Africa produces lump quartzite at Donkerhoek, 20 km east of Pretoria, and uses the stone as blast furnace flux for steel mills at Vanderbijlpark and Newcastle. The stone contains more than 95% SiO_2 and less than 0.18% alkalis and 1.7% Al_2O_3 . At Delmas, 85 km from Johannesburg, quartzite is produced for use by domestic ferroalloys and refractories manufacturers. The –180+100, –100+76, and –20+12 mm grades average 98.8% SiO_2 , 0.5% Fe_2O_3 , and less than 0.5% Al_2O_3 , 0.04% S, and 0.01% P, respectively. Metallurgical-grade silica also is produced at Letaba, Bronkhorstspuit, and Lydenburg (Griffiths 1989).

Sweden

At Åmal in Dalsland, high-purity quartzite is quarried and used in ferrosilicon production, in the manufacture of monolithic refractories (Clarke 1987; Russell 1990), and in the manufacture of silicon metal.

United States

In the eastern United States, massive quartzite of the Lower Cambrian Erwin Formation is more than 100 m thick and is well exposed in an anticline in the Lick Mountain District, which is part of the Appalachian Valley in Virginia. It contains 97.63% to 99.37% SiO_2 and has been quarried as metallurgical-grade stone for silicon metal and ferrosilicon manufacture in Virginia (e.g., at Sand Mountain), West Virginia, and east-central Tennessee.

Belts of high-purity quartzite extend across central and southeastern Pennsylvania and across Calhoun, Talladega, Cherokee, Clay, and Cleburne counties in Alabama. Quartzite (actually quartzitic sandstone) from the Lower Silurian Tuscarora (Medina) Formation has been mined in Carbon, Bedford, Blair, and Huntingdon counties, Pennsylvania, for use as ganister in refractory bricks for furnace linings. It also has been quarried in Virginia and near Minnehaha Springs in Pocahontas County, West Virginia, for use as metallurgical stone. It is light gray to white and 120 to 180 m thick in central Pennsylvania (e.g., at Lock Mountain near Point View). In addition to the Tuscarora, quartzite from the Chickies Formation

in southeastern Pennsylvania has been used as refractory ganister and for tube-mill linings. In Cherokee County, Alabama, quartzite containing 97.75% to 98% SiO_2 can be obtained from the Lower Cambrian Weisner Formation.

In Cherokee County, North Carolina, the Tusquitee Quartzite is metallurgical quality. The hard, tough, Poughquag Quartzite near Highland, New York, is suitable for chemical use, for metallurgical stone, and for cutting into blocks for lining grinding mills. Buxton stone has been quarried from the Cambrian Cheshire Quartzite between Dalton and Washington in Berkshire County, Massachusetts, where the formation is nearly 55 m thick at Coltsville. The Carboniferous Quabbin Quartzite is a pure, white, sucrosic but locally flaggy rock that forms part of the Quabbin and Felton mountains in Rhode Island and Massachusetts. Many years ago near Stafford, Connecticut, it was quarried and sawed into hearthstone and firestone for iron ore smelting.

In the central United States, one of the most important sources of specialty silica stone is the Sioux Quartzite, also known as the Sioux Falls Granite, of Late Huronian (Middle Precambrian) age. A fine-grained quartzite that ranges in thickness from 460 to 1,220 m, the Sioux crops out in a belt more than 95 km wide that extends more than 15,540 km^2 from the junction of the Cottonwood and Minnesota rivers at Redstone, Minnesota, westward to Mitchell on the James River in South Dakota. This belt includes parts of the southwestern Minnesota counties of Nicollet, Pipestone, Cottonwood, Rock, and Watonwan; part of northwestern Iowa; and parts of the southeastern South Dakota counties of Turner, McCook, Hanson, and Minnehaha. Outcrops in southeastern South Dakota are most prevalent in river valleys such as those of the Big Sioux at Dell Rapids and South Falls, the Vermillion at Parker, the James south of Mitchell, Wolf Creek at Salem, and Pierre Creek at Alexandria. The color of Sioux Quartzite ranges from pink to orange, purple, and blue; its silica content varies from 96% to nearly 99%; its compressive strength ranges from 1.52×10^5 to 4.96×10^5 kPa; and crushed pieces vary from equidimensional to slabby. The stone's softening point commonly exceeds 1,800°C, and its density is about 1,682 kg/m^3 .

One of the most productive portions of the Sioux Quartzite outcrop belt extends from Jasper in the southwest corner of Minnesota westward to Sioux Falls, Spencer, and Mitchell in South Dakota. Within this district, several companies quarry and crush quartzite for construction applications; one also ships metallurgical-grade material to a ferrosilicon producer in Iowa. The Jasper Stone Co. in Jasper, Minnesota, produces dimension stone for several markets. It also produces some quartzite memorials or monuments, but its chief products are split and sawed blocks for lining tube-type grinding mills, acid tanks, and chutes. As a by-product of its dimension stone operations, Jasper Stone produces quartzite cubes that measure 1.0, 1.2, or 1.6 cm on a side. These are pretumbled for use as grinding media in pebble or ball mills.

Artificially rounded grinding pebbles have also been produced from the Sioux Quartzite near Sioux Falls, South Dakota. Other producing sites in Minnesota are Pipestone, Luveme, and New Ulm, but stone from those locations is sold mostly for use in construction. Some blocks for lining tube mills and chunks as grinding media have been produced by New Ulm Quartzite Quarries, Inc., in Nicollet County, Minnesota. This company also has sold crushed Sioux Quartzite as ganister for steel furnace refractories, for filtration rock, and for fluxstone used in copper smelters. The rock is excellent for the manufacture of refractory silica brick.

Other important resources of specialty silica stone in the central United States are the Baraboo Quartzite in Sauk and Columbia counties, Wisconsin, and the Nesnard Quartzite in Michigan, both

of which are Precambrian (Huronian) in age. The Baraboo Quartzite District is 45 km long, 3 to 19 km wide, and encompasses nearly 583 km². The formation is about 1,220 m thick and consists of massive beds of hard, very tough quartzite comprised of round quartz grains cemented by secondary quartz. Where free of thin slate or schist partings along bedding planes, the stone has a compressive strength of nearly 5.0×10^5 kPa. Until it ceased operations in 1988, Baraboo Quartzite Co. quarried stone from the Netzebaum Quarry near Devil's Lake, Wisconsin, marketing crushed, sized, and pre-tumbled deburring and burnishing media to foundries and metal stamping plants worldwide. Grinding media and liner blocks for pebble mills and ganister for refractory applications also have been produced from the Baraboo Quartzite. In north-central Wisconsin, the Rib Hill and Powers Bluff formations are medium-grained quartzites that contain 99.07% SiO₂ and are suitable for specialty applications.

High-purity quartzite is widespread in the western United States, especially in eastern Washington. The Addy Quartzite of Cambrian age crops out over 648 km² in Stevens County, Washington (Murphy and Brown 1985), and most exposures are within 20 km of a railroad. Until 1991, Northwest Alloys, Inc., a subsidiary of Aluminum Company of America (Alcoa), produced 22,000 tpy of Addy Quartzite from the Blue Creek mine in Stevens County and used the output in the production of silicon metal and ferrosilicon at its plant in Addy, Washington, where ferrosilicon capacity was 27,500 tpy. Elsewhere in Stevens County at Valley Lane Mountain Silica Co. mines part of the Addy Quartzite that is complexly faulted and consists of alternating hard and soft, friable zones. Products contain <0.005% Fe₂O₃. Addy Quartzite also has been quarried at Kettle Falls in Stevens County. Ferry, Pend Oreille, Spokane, and Whitman counties in Washington have either produced or have the potential to produce quartzite for specialty markets.

The Eureka Quartzite of Middle Ordovician age crops out over more than 260,000 km² from Idaho into Southern California (Murphy and Brown 1985). It ranges up to 99.9% SiO₂ and has been mined in Clark County, Nevada, for refractory, metallurgical, and other uses. Quartzite was produced at the Canyon Creek Quarry near Maiden Rock in Beaverhead County, Montana, for use as fluxstone at an elemental phosphorus and ferrophosphorus plant in Silver Bow County, west of Butte, Montana (Rice, Lawson, and Berg 1989).

Quartzite for silicon metal production has been quarried at Rogue River near Gold Hill in Jackson County, Oregon. It also has been produced from the Precambrian Dripping Spring Formation at Oracle, Arizona. Quartzite from the Tintic Formation has been mined in Tooele County, Utah, primarily for the manufacture of refractory coke oven shapes. Quartzite for furnace-lining refractories also has been produced west of Douglas, Arizona. The Sawatch Quartzite of Late Cambrian age is a gray-white, hard, massive formation that lies on an eroded Precambrian surface. It is as much as 40 m thick in the Mosquito Range of Colorado and may be suitable for specialty markets.

Metallurgical-grade quartzite from other sources in the U.S. Northwest has been used in the production of elemental phosphorus and ferrophosphorus at electric furnace facilities. Examples in Idaho include stone quarried in Caribou County for a plant at Soda Springs and the Kit Creek mines in Bannock County, which supply plants at Pocatello.

Novaculite

United States

The Arkansas Novaculite Formation outcrops occur in several narrow belts that extend along the borders of the Benton–Broken Bow

Uplift portion of the Ouachita Mountains between Little Rock, Arkansas, and Atoka in southeastern Oklahoma. This portion of the Ouachita Fold Belt ranges from 25 to 65 km in width and extends east–west for 320 to 360 km. Mining operations that produce novaculite for commercial uses such as oilstones, hones, files, and whetstones, and for other specialties, are concentrated in Garland County just northeast of Hot Springs, Arkansas. A few deposits also are mined in nearby Pike and Montgomery counties, Arkansas. In 2005, the Arkansas Geologic Commission listed 10 companies as novaculite producers in this area. Nearly all commercial whetstone mines are confined to the massive lower member of the formation.

In Oklahoma, the outcrop belts of novaculite continue from the Potato Hills east of Tahlequah through Latimer, Pushmataha, and McCurtain counties and westward to near Atoka in Atoka County. Silica rock that has been called novaculite is part of the Caballos Formation in Brewster County, southwestern Texas. It is intensely folded and fractured but crops out prominently and extensively in the Marathon Uplift Area (Jaster 1957). In the counties of Alexander and Union in southern Illinois, widespread deposits of primary novaculite and alluvial novaculite gravel are present in the same area where major deposits of tripoli are mined. A novaculite locality near Marquette, Michigan, also had been reported (Jaster 1957); deposits outside the United States however, have not been well documented.

Vein Quartz

Angola

Production of lascaras from the Pocarica vein deposits near Conda in Cuanza Sul Province was nationalized in 1979 with the establishment of Miniquartzo to manage operations. In 1975, Angolan exports of lascaras had reached a level of 3,900 t; in 1980, exports ceased. One cultured quartz producer at Libramont, Belgium, used to purchase nutrient quartz from Angola but switched to Namibian lascaras in 1989.

Brazil

Brazil has the largest known reserves of natural, piezoelectric-grade quartz crystal and lascaras in the world, with the total estimated at 26.8 Mt (Smith 1984b). On the Brazilian altiplano, an extensive plateau underlain by Precambrian and Lower Paleozoic rocks, there are hundreds of small, deeply weathered vein and alluvial deposits scattered over thousands of square kilometers, and are a twice the size of Texas (Bates 1960). This area is located along the southeastern margin of the Brazilian Shield. Production comes mostly from the states of Minas Gerais, Santa Catarina, São Paulo, and Bahia, although significant reserves also are known in Espírito Santo, Paraíba, Paraná, Rio de Janeiro, and Rio Grande do Sul. The richest deposits are in Minas Gerais.

Some piezoelectric-grade crystal is produced in Brazil, but shipments from the official export cities of Rio de Janeiro, Bahia, and San Salvador consist predominantly of lascaras for growing cultured quartz crystals and for the manufacture of fused quartz preforms after extensive chemical refinement in Europe. Of the total quantity of quartz produced in Brazil, approximately 97% is lump for industrial applications such as silicon metal and silicon alloys manufacture, and the remaining 3% consists of piezoelectric crystal, lascaras, and decorative specimens. Quartz for silicon metal smelting is produced at Gouveia in Minas Gerais.

Canada

The Mount Rose deposit of high-purity, lascar-grade vein quartz is located near Armstrong, British Columbia. The Fs quartz vein,

situated 40 km northeast of Kamloops, British Columbia, has supplied milky quartz for silicon carbide manufacture in Oregon. The vein deposit is at least 400 m long and 3.5 to 15 m wide. Near Oliver in southern British Columbia, quartz veins that are 0.3 to 4 m wide cut the Oliver Plutonic Complex of Late Jurassic age. They are widest in the porphyritic quartz monzonite phase of the complex and have been quarried for fluxstone and ferrosilicon manufacture. The Gypo deposit near Oliver reportedly produces less than 10 ktpy of lump quartz (Simandl, Jakobsen, and Fischl 1992). The White Rock quartz, kaolin, and mica deposit 45 km northwest of Shelburne, Nova Scotia, contains residual quartz from leucocratic granite, which underwent hydrothermal alteration. Current plans are to produce ground silica as a replacement for white marble chip and sand (*Industrial Minerals* 2001).

Chile

Lump quartz is produced from vein deposits for use as fluxstone at copper smelters. The largest producer has capacity for 200,000 tpy, but the +0.635-cm stone is not of exceptional chemical purity. A pegmatite deposit containing electronic- and possibly optical-grade quartz also has been found in Chile.

Egypt

Quartz vein deposits occur in Egypt at 38 locations in the Eastern Desert. The ycut across basic and ultrabasic metavolcanics. The deposits of Abu-Marwa (20 Mt) and Gebel Delhami I and II (60 and 10 Mt, respectively) contain very-high-grade quartz that averages 99.02% to 99.98% SiO₂, 0.40% to 0.26% Al₂O₃, and 0.15% to 0.18% Fe₂O₃. There is potential for production of high-quality silica products such as fused silica. Egypt currently exports quartz in 1- to 25-cm lumps or sub-100 mesh powder (Ibrihim 2002).

Greece

In eastern Macedonia, metallurgical-grade lump quartz has been mined from vertical pegmatite veins 1 to 8 m wide in schist host rock at Paranesti, Thessaloniki. The quartz contains 99.5% SiO₂, 0.04% Al₂O₃, 0.03% Fe₂O₃, and 0.01% each of CaO, K₂O, and Na₂O. Most has been exported to silicon metal manufacturers (Griffiths 1985a; Clarke 1987; Georgiades 1988).

Guyana

Quartz crystal of possible optical and electronic quality is associated with diamonds in alluvial deposits in Guyana.

India

India produces lump quartz containing 99.8% SiO₂ for domestic metallurgical uses and for export, which is used predominantly in the manufacture of fused quartzware for the electronics industry. There are more than 100 vein quartz mines in India, 40 of which produced >1,000 tpy. One producer exported 21,800 t of high-purity quartz in 1990 (Russell 1991). Andhra Pradesh led in production, followed by Karnataka, Rajasthan, Gujarat, Tamil Nadu, Haryana, and Madhya Pradesh (Smith 1984a). The Indian Bureau of Mines reported 128 quartz mines producing 279,385 t in 2003–2004 (Indian Bureau of Mines 2004).

A large pegmatite deposit was discovered in the 1990s at the village of Uchapalli in the state of Andhra Pradesh. Current quartz crystal (3,000 tpm) and silica sand (10,000 tpm) serve markets for ceramics and other applications (*Industrial Minerals* 2004).

Italy

Lump quartz has been produced at Montioni, Sanfront, Martiniana Po, and Sondalo, Italy, for the following markets: ferrosilicon, sili-

con metal, refractories, filtration, abrasives, chemicals, and blast furnace steelmaking (Robbins 1986). One company has produced lump quartz at Sondalo in Lombardy for silicon metal manufacture, and the majority is ground into potter's flint for the ceramics industry (Clarke 1987).

Malagasy

The chief source of lumps in Malagasy is vein and associated alluvial placer deposits in the northeastern coastal and central plateau regions.

Namibia

In Namibia quartz for the electronics industry has been recovered as a by-product of lithium ore production at the Rubicon mine near Karibib. Another large quartz deposit is located at Marbad near Windhoek (Murray 1989).

Portugal

Quartz crystal and lump quartz have been mined at three sites in Guardia, Portugal, for sale to silicon metal and ferrosilicon manufacturers (Clarke 1987).

Republic of South Africa

A dike of massive, high-purity quartz in Precambrian host rocks near Pietersburg in the northern Transvaal region of South Africa is known as the Witkop deposit and is quarried by Samancor Ltd. The open-pit mine, located 380 km north of Johannesburg, supplies –38 +25 mm lump to a silicon metal smelter nearby (Griffiths 1989).

Spain

About 20 industrial silica producers in Spain have a capacity of 3.3 Mtpy, and about 70% of this capacity is controlled by two companies: Belian-owned SCR-Sibelo SA and Arenas Siliceas SA (ASSA). Nine other companies are each responsible for about 7% of silica production. The majority of the smaller companies produce silica as a by-product of feldspar and kaolin production. The glass and foundry industries consume most of the silica production. Additional markets include abrasives, hydraulic fracturing, chemicals industry, filtration, and others (Sims 1998).

Cuarzos Industriales SA mines a vein of quartz or quartzite at Vivero and exports most of its annual output to silicon metal and ferrosilicon producers in France, Germany, Norway, and Sweden (Griffiths 1985b).

Sri Lanka

Veins of massive high-purity quartz (>99.8% SiO₂) have been found at more than 50 locations in the areas of Openaika, Pelmadulla, Pusella, Rattota, and Ratnapura in Sri Lanka (Harben 1991). The deposit at Galaha (Ambalamana) contains inferred reserves of 6 Mt (Herath 1990).

Venezuela

Quartz crystal for growing cultured quartz and for the manufacture of silicon metal and silicon alloys is produced at Santa Elena, Bolivar.

United States

Hydrothermal quartz veins in sandstone and shale are the most common sources of electronic-grade quartz crystals and lumps around the world. In the United States, minor quartz crystal deposits have been found in California, Idaho, Oklahoma, and Virginia, but major deposits are near Hot Springs, Arkansas, in the foothills of the Ouachita Mountains. Arkansas deposits are mined mostly for

quartz crystal specimens, not for electronic-grade crystal. World-renowned crystals with the exceptionally smooth, clean faces are extracted from veins and cavities in sandstone at two small open pits in Garland County. The best-quality, water-clear specimens having highly polished faces are found in cavities filled with reddish brown, sticky, rouge-like clay.

The only producer of lascas in the United States is Coleman Quartz, Inc. This company mines one of two massive bull quartz veins that lie mostly conformably between units of thinly bedded and deeply weathered shale at an open pit near Paron, Arkansas, 48 km northeast of Hot Springs in Saline County. Veins range from 2.4 to 3.7 m in width and extend for 0.4 km in strike length. Annual production varies from 450 to 570 t. The entire deposit has not been drilled yet, but resources are estimated at 200,000 t. Mine-run material is hauled by trucks to the company processing plant 48 km away. The quality of finished lascas produced in Arkansas is equal to or slightly superior to that of lascas produced in Brazil, and it is usually less variable. Total impurity levels range from 25 ppm for grades #1 (90% clear) and #2 (50% to 60% clear) to 44 ppm for grade #3 (translucent) and 54 ppm for grade #4 (opaque). Impurities include 15 to 20 ppm Al; 2 to 25 ppm Na; 2 to 10 ppm K; 2 to 5 ppm Fe; and 1 ppm each of Ca, Mg, Li, and Ti (Griffiths 1987b). The relatively high sodium level is associated with bubble fluid inclusions.

In Connecticut, between the towns of Ledyard and North Stonington, the massive Lantern Hill vein quartz deposit was mined for its quartz crystal. The vein measures 2,000 m long and 300 m wide and yields products that grade 99.0% to 99.4% SiO₂. A similar deposit is located just north of Glasgow about 16 km north of Lantern Hill. Vein quartz and high-purity quartzite deposits were once mined in Adams County, Pennsylvania, and at Port Henry and Fort Ann, New York. Bull quartz dikes have been found west of Wirtz in Franklin County, Virginia, and numerous vein quartz deposits are known in the North Carolina counties of Anson, Moore, Montgomery, Harnett, Buncombe, and Transylvania. In Texas, massive quartz veins occur in Precambrian rocks of the Llano Uplift and in the Carrizo Mountains of Culberson and Hudspeth counties.

High-purity, metallurgical-grade silica resources are abundant in the western United States, particularly the Pacific Northwest. Silicon metal and ferrosilicon plants at Rock Island, Washington, and Springfield, Oregon, now use mostly quartzite, but in the past they were supplied with lump quartz from massive vein deposits at the following locations: (1) north of Weiser, Idaho; (2) at Basin and west of Galen, Montana; and (3) near Hawthorne, Nevada. The deposit near Weiser is a quartz plug within granodiorite and yielded material averaging 99.78% SiO₂. The Basin deposit is a quartz plug within quartz monzonite and yielded metallurgical lumps grading with more than 99.5% SiO₂. Near Galen, a massive quartz body averaging 99.82% SiO₂ is present within Precambrian limestone and quartzite on the southwestern slope of the Flint Creek Range. The vein near Hawthorne, Nevada, measures nearly 850 m long and 95 m wide, is associated with Jurassic granite, and yielded stone that averaged 99.89% SiO₂ (Peterson 1976). Similar deposits in western Montana are located at Deer Lodge, Haines Point, and Quartz Creek.

The Quartz Mountain deposit in Spokane County, Washington, is a large vein of massive quartz within granitic host rock. It has been quarried as a source of lump quartz for silicon metal and ferrosilicon producers. Other deposits in eastern Washington include (1) the Latshaw deposit, a 200-m² plug of quartz 20 km north of Spokane with 98% SiO₂, which has been mined mostly for ganister; and (2) massive quartz veins at Mount Spokane and near

Mica Peak. In central Washington, a dike of white quartz, 15 m wide and averaging 96.6% SiO₂, is found near Wenatchee and another large vein is located near Merritt in Chelan County. In western Washington, three large quartz veins are located near Marblemount in Skagit County, and another has been mined at Rockport, 13 km to the southwest. Other deposits of massive quartz have been quarried for ganister in King and Pierce counties. Altogether, there are 36 known massive quartz deposits in 13 counties in Washington, most of which are found as veins and pods in metamorphic rocks or as the cores of pegmatites.

Elsewhere in the western United States, a pure quartz dike 300 m long and 60 m wide has been mined in Jackson County, Oregon. Lenses of massive quartz or quartzite more than 60 m thick are found in metamorphic rocks of Paleozoic age 30 km northeast of Oro Grande and 15 km east of Victorville in San Bernardino County, California. They have been quarried mostly for ganister. The Veta Grande mine near Carson City, Nevada, is another massive vein deposit that has yielded metallurgical-grade lump quartz.

Other Countries

Chamber-type pegmatites that contain quartz crystals are of Precambrian age in Brazil, Malagasy, and Ukraine, but they are of Late Paleozoic age in central Kazakhstan, China, Mongolia, the northern Ural Mountains, and the Plateau Central in France. Hydrothermal quartz veins that yield piezoelectric crystals in the Urals are found in Proterozoic mica schists and lower Ordovician quartzites. Inclusion-free quartz from hydrothermal veins at Detkovice in the Czech Republic contains 99.43% SiO₂ and 0.07% Fe₂O₃ after hand sorting. Similar deposits at Graupa, Czech Republic, contain 99.86% SiO₂ and 0.062% Fe₂O₃ after hand sorting and only 0.003% Fe₂O₃ after further washing, calcination, magnetic separation, and chemical refining (Kuzvart 1984). Elluvial placer deposits of quartz crystals in the Ural Mountains of Ukraine may contain gold in economically recoverable amounts.

Other producers of high-purity lump quartz for silicon metal and silicon alloys manufacture as well as specialty glass and refractory products are Finland, France, and former Yugoslavia. Silicon and ferrosilicon producers in Japan use quartz imported from China, Korea, and India. Elluvial placer deposits of quartz crystals containing no gold or diamond coproducts have been found in China. Other vein deposits of quartz crystal or lascas are known in Uganda, South Africa, and Australia. High-purity quartz in pegmatites was discovered recently in Cordoba Province in Argentina.

Silica Pebble

Canada

A large deposit of well-rounded quartzite pebbles is found near Cypress Hills, Alberta. As grinding media, pebbles from this deposit compare favorably with flint pebbles produced in Denmark (actually Greenland). Lump quartz has been produced from a deposit on the southwestern shore of Lake Baskatong at Charlevoix near St. Ludger, Quebec. The material quarried was used mostly in silicon metal manufacturing and, to a much lesser extent, as grinding pebbles.

Europe

Silex is a term used commercially for flint, chert, or chalcedonic silica that is produced in several European countries, including France, Belgium, England, and former Yugoslavia. Silex is used in the form of round pebbles as grinding mill media and as cut blocks, known as Belgian block, for iron-free grinding-mill linings. Silex from Belgium is an extremely fine-grained, tough, chalcedonic

form of silica containing secondary calcite and radial chalcocite (Griffiths 1987b). Silex from former Yugoslavia is somewhat coarser grained and contains tightly packed quartz crystals. Flint pebbles produced in France, Belgium, England, and Denmark (Greenland) are available in two grades and in 7 to 12 sizes ranging from 1.3×1.6 cm to 13.3×15.2 cm. Some pebbles from Denmark are as much as 20.3 cm in diameter. Pebbles of "Select" quality from Dieppe, France, contain 98.43% SiO_2 , 0.02% Fe_2O_3 , and 0.10% Al_2O_3 .

Blocks of silex, or buhrstone, have been produced in Belgium from deposits just east, north, and west of the town of Mons. Blocks range in thickness from 60 to 160 mm, are rectangular or conical, and are used for lining cylindrical, tube-type pebble and ball mills. The blocks, cut and fabricated by hand, have been recovered from flint nodules in a marl quarry at Eben-Emael. The lowest stratigraphic intervals, at a depth of more than 30 m, have produced the best-quality flint. The average chemical composition is 94.0% SiO_2 , 4.9% $\text{CaO} + \text{CaCO}_3$, 0.9% MgO , and 0.1% Fe_2O_3 . One company in Belgium produced approximately 1,000 tpy of finished blocks (Benbow 1989) and another in Jaen, Spain, produced about 500 tpy (Clarke 1987). Silex blocks and crushed silex also have been produced from flint pebbles mined at Dieppe, France.

Flint nodules as grinding-mill media are produced from Cretaceous chalk formations in western and northern Europe. Perhaps the largest resource is in the Paris Basin, where a 400-m-thick section of chalk contains flint nodules (Kuzvart 1984). Flint pebbles also are produced from chalk deposits as a by-product at cement operations in southeastern England. At Northfleet and Shoreham, Clarke (1984) reported pebble capacity at approximately 1,000 tpy, although output in 1984 was only 500 to 600 tpy. Pebbles are washed to remove chalk and iron oxides for use mostly in ceramics. Three sizes are produced: $-10.16+5.08$, $-5.08+2.54$, and -2.54 cm (Clarke 1984).

United States

One of the most important sources of metallurgical-grade silica gravel for silicon metal and high-purity ferrosilicon production in the eastern United States is the high-level terrace deposits of the Citronelle (Lafayette) Formation of Pliocene or Holocene age. These are fluvial channel and bar deposits found in raised terraces that roughly parallel the present course of the Pee Dee River in North Carolina and of other major rivers in the coastal plain of South Carolina, Georgia, Florida, and Alabama. They consist of unconsolidated sand and gravel that lie unconformably on Late Cretaceous sediments. The most productive area encompasses 65 km² and is centered at Lilesville in Anson County, North Carolina. The Pee Dee terraces near Lilesville contain a well-developed basal gravel zone 1.5 to 6 m thick overlain by sand and a few lenses of gravel and clay. They consist of 46% sand and nearly 54% gravel; the gravel is 75% to 83% quartzite and 17% to 25% vein quartz (Callahan and Craig 1990).

Sand and gravel from Pee Dee River terraces have been mined near Lilesville, North Carolina, for construction sand, metallurgical-grade pebble, and clear or white pebbles exceeding 5 cm for packing acid to be used in the chemicals industry (Callahan and Craig 1990). The pebbles also have been used as grinding-mill media. Dredging on Beech Island in the Savannah River has produced sand and gravel from floodplain deposits near Augusta, Georgia. Metallurgical-grade gravel has been produced from similar deposits in Harnett County, North Carolina.

Lower-purity ferrosilicon (e.g., 50% Si) has been manufactured in the southeastern United States from silica gravels dredged from the Coosa River north of Montgomery, Alabama,

and from the Alabama River between Montgomery and Selma, Alabama. In Florida, subrounded quartz and quartzite pebbles have been dredged from the Escambia, Apalachicola, Flint, and Chattahoochee rivers. Additional river-bed gravel deposits have been produced at Lecanto and Crystal River, Florida. Blocks for lining grinding mills and artificially rounded grinding pebbles were formerly fabricated from silica pebbles recovered from beds of Ocala Limestone in Florida. Quartz and quartzite pebbles in the Bryn Mawr Formation of Pliocene age have been mined for metallurgical and refractory applications in Harford County, Maryland, and to a lesser extent in nearby Baltimore, Carroll, and Howard counties. Grinding pebbles and blocks for lining grinding mills have been produced from residual deposits of chert derived from the Fort Payne Formation near Iron City in Wayne County, Tennessee.

Numerous alluvial deposits containing laterally extensive but thin beds and lenses of flint pebbles occur in interstream divides, river terraces, and major stream valleys in the Gulf of Mexico Coastal Plain of Texas. These deposits extend west from the Guadalupe River to the Rio Grande. Grinding pebbles that can be milled to a quality equal to that of similar pebbles produced in Europe have been mined in Texas from deposits in Frio, Bastrop, Llano, and Travis counties; pebbles in deposits associated with the Colorado and Brazos rivers, however, generally are unsuitable for use as grinding media. Some flint, as stock from which blocks for lining grinding mills are cut, has been produced from the Edwards Formation in western Travis County, Texas. Flint nodules from mining operations in the Austin Chalk Formation in south-central Texas have been recovered for captive use as an abrasive medium in the production of ground silica flour.

Silica pebbles, apparently derived from the Sioux Quartzite, are abundant along the shores of Lake Superior between Grand Portage and Pigeon Point, Minnesota. As grinding-mill media, they compare favorably in performance with flint pebbles produced in Europe. Many years ago, silica pebbles recovered from the beach between Oceanside and Encinitas, California, were used as grinding-mill media. Because they were harder, coarser-grained, and rougher in texture than flint pebbles from Denmark, the silica pebbles were faster cutting when used for grinding hard materials. Round silica gravel used in water filtration has been produced at several locations in the United States, including Muscatine, Iowa; Eau Claire and Fairwater, Wisconsin; and Thompson, Ohio.

TECHNOLOGY Exploration

Exploration for deposits of specialty silica materials is guided by knowing which geologic formations are likely to contain rock of suitable quality. Geologic reconnaissance and mapping are then conducted in areas where these formations are present. At hard-rock prospects of sandstone, quartzite, novaculite, and vein quartz, evaluation normally requires drilling and drill sample testing to establish the extent and amount of reserves. Percussion drilling is seldom adequate because physical properties of the stone are as important as, or even more important than, its chemical purity. Chip samples from percussion drilling provide some indication of chemical purity but are unsuitable for many physical property measurements. Diamond-bit core drilling, therefore, is usually necessary at some stage in the evaluation process. Problems of poor core recovery are common when holes are drilled at angles between horizontal and vertical and especially where the silica rock is highly fractured, jointed, or friable. Where conglomeratic sandstones are sought for their silica gravel content, core drilling must be close spaced to delineate pebble-rich zones.

At prospects where silica gravel is present in unconsolidated sediments, or where host rocks enclosing quartz veins are deeply weathered, drilling can be impractical. In such cases bulldozers or backhoes dig trenches to locate and sample the resource; then samples are washed and screened to determine the yield of product per cubic meter excavated. Exploration of river gravel deposits is done by dredging.

Mining

Deposits of vein quartz in Brazil are small and irregular in shape, and are mined mostly by hand in open pits that are seldom more than 20 m deep. Bulldozers remove overburden, and pumps dewater the pit. Clear, piezoelectric-grade crystals of small size are common, but those that weigh 250 g or more are rare, accounting for only 1/10,000 (0.01%) of the total mass of a vein filling (Kuzvart 1984). The ratio of clear crystal to total material mined ranges from 1:1,000 to 1:1,000,000, so enormous quantities of milky quartz are extracted to recover only a few kilograms of piezoelectric crystal (Lamey 1966). In exceptionally rich pockets, the yield of such crystal can be as much as 0.4% or even 1.6%.

During World War II, 40,000 m³ of vein quartz mined in Arkansas yielded 200 t of rock crystal, but only about 2 t of the crystal were suitable for piezoelectric applications (Kuzvart 1984). In the 1990s, three deposits of vein quartz had been mined for quartz crystal specimens and lascas in Arkansas. At the Paron mine in Saline County, there is little or no overburden, and thus very little drilling and blasting. Massive bull quartz for lascas production has been mined with a backhoe during the summer months, and stockpiles containing about 2,000 t have sustained processing operations for a year. Two crystal specimen operations in Garland County, Arkansas, used similar mining methods as those at Paron; however, the pits at the former are much deeper, no drilling and blasting has been used, and pockets of crystals have been mined by hand. Bull quartz extracted from these pockets has been used as feed for lascas.

Sandstone and quartzite for nonconstruction dimension stone are quarried in a manner that uses joints and bedding planes to advantage. Primary vertical cuts along quarry walls or for separating key blocks can be made with channeling machines, although drilling and broaching is more standard practice. In drilling and broaching, rows of vertical holes 51 mm in diameter are drilled; then the channel cut is made with pneumatic or hydraulic wedging hammers or by detonating very light charges of black powder. Quarry blocks are freed from a bench or ledge by drilling rows of horizontal holes and then either detonating low-velocity explosive charges or using the plug-and-feather method of manual wedging. Blocks are moved from quarries to finishing plants with fixed or mobile derricks, front-end loaders, or trucks. Similar methods are used for quarrying whetstone-grade novaculite in Arkansas, where the yield of usable stone from the total amount quarried, or within a deposit, ranges from a maximum of 10% for hard, translucent grades to a maximum of 25% for softer grades.

Metallurgical-grade quartzite deposits in Oregon and Washington are quarried by conventional drilling and blasting in open pits with benches 12 m high and 6 m wide (Peterson 1976). Similar methods are used in extracting quartzite on Badgeley Island, Ontario (Guillet and Kriens 1984). In Stevens County, Washington, the friable portion of Addy Quartzite has been mined in two open pits with benches as high as 45 m. About 50% of the rock can be ripped by bulldozer, but the rest requires drilling and blasting. Conventional drilling and blasting also is used in open-pit mining of conglomeratic sandstone that contains metallurgical-grade pebbles, such as from the Sharon Formation in Ohio.

Metallurgical-grade quartz gravel from the Alabama River between Selma and Montgomery, Alabama, and at Beech Island, South Carolina, near the Savannah River has been recovered by dredging. Suction dredges are suitable for deposits consisting of loose sand and gravel, whereas bucket-ladder or suction cutterhead dredges are used for deposits that contain beds or lenses of clay. Raised fluvial terrace deposits of metallurgical gravel or pebble, such as those along the Pee Dee River in the Carolinas, have been mined with front-end loaders, draglines, and hydraulic excavators.

Processing

Brazilian lascas is quartz that is defective for piezoelectric (e.g., radio component) or optical applications because it is cloudy or milky instead of clear or contains optical or electrical twinning, cracks, or bubble fluid inclusions. It is produced by hand sorting and trimming such material from higher-quality, electronic-grade quartz crystals.

In Arkansas, mine-run vein quartz is crushed and wet screened to $-3.175 + 1.27$ cm, washed, leached in vats of hot oxalic acid, and then rinsed several times with water. It is then hand sorted, dried, and finally examined on a light table for defects before being packaged in 45.36-kg bags. Defective rejects, -5.08 cm mine-run rock, and the -1.27 cm screenings represent waste that averages about 50% of the rock mined, so 2 t of vein quartz are mined for 1 t of finished lascas sold.

Processing metallurgical-grade quartzite and novaculite consists only of crushing, washing, and screening to sizes ranging from $-10.16 + 3.81$ to $-3.81 + 0.32$ cm. Metallurgical-grade quartz and quartzite gravels from river channel and raised terrace deposits are processed similarly, except that no crushing is required.

Quartzite, sandstone, and jasper slabs for nonconstruction dimension stone historically were split by hand. Because they were rough on all six sides, more mortar was required for their installation. Quarry blocks today are cut with wire saws and are split hydraulically. Acid blocks have either two or four sides sawed smooth with the other sides hydraulically split and rough. They consist of beams and slabs of sandstone that are sawed to a thickness of 10.16 to 20.32 cm. Grinding mill and chute liner blocks usually are sawed on all six sides. Red and gray jasper (quartzite) in Minnesota is still cut, trimmed, and shaped by hand into rectangular adamant silica blocks measuring 5.08 to 12.7 cm thick, 10.16 to 15.24 cm wide, and 20.32 to 25.4 cm long for lining pebble mills. The unevenness or irregularity of the surfaces of these blocks is an advantage because it reduces the need to install lifters in a mill.

To increase the yield of salable product from each quarry block, one producer in Minnesota cuts and shapes cubes of adamant silica by hand for use as grinding media in competition with flint pebbles produced in Europe. Cubes are pretumbled in a mill to round off the edges and reduce high initial wear that results in about 20% weight loss. The smallest cube that can be hand cut economically measures about 5.08 to 6.35 cm on a side, so larger cubes cannot be used as deburring media. Crushed quartzite has been pretumbled near Baraboo, Wisconsin, and sold as a deburring medium in eight sizes ranging from $-19.05 + 14.29$ to $-3.175 + 2.38$ mm.

Grindstones made mostly of sandstone are produced in Europe as blocks that are cut and shaped, measuring 0.6 to 1.5 m across. Pulpstones from the same sandstone beds are cut and shaped into blocks 1.5 m in diameter and 0.9 to 3.0 m wide. The stone is used for grinding logs into paper pulp and often is seasoned for 1 to 2 years after it has been quarried, but before it is cut (Bate-man 1959).

Novaculite oilstone s, files, and whet stones are produced in Arkansas by sawing quarry blocks with diamond-tipped saws and then shaping and lapping the cut stones by hand. The yield from carefully selected quarry blocks ranges from about 10% for hard, translucent grades to 25% for softer grades, and a maximum yield of 30% to 40% for perfect stone, which is rarely found. This means that the overall yield from all novaculite quarried, or within a deposit, ranges from only 1% for translucent grades to 6% or 7% for softer grades. At least one company in the district crushes, screens, and pretumbles waste or scrap novaculite generated at whetstone operations, and markets 11 different sizes from 5.08 to 0.635 cm and finer as deburring media for barrel tumbling and vibratory finishing.

Specifications

Metallurgical Applications

Crushed quartzite and novaculite lumps and round quartz and quartzite pebbles from fluvial deposits and conglomeratic sandstones are used in electric furnace production of silicon metal, ferrosilicon (FeSi), and other silicon alloys. Because vein quartz is more brittle and usually generates excessive fines during handling, most FeSi producers prefer quartzite, even though its Al_2O_3 and Fe_2O_3 content tends to be higher. Also, vein quartz often contains fluid inclusions, which cause it to decrepitate into additional fines when exposed to furnace temperatures. For metallurgical applications, silica rock should be tough (i.e., not friable), should have a high thermal shock resistance, should be free of fines when delivered, and should not crumble or decrepitate into fines when heated.

Fines cannot be tolerated in submerged arc electric furnaces because they reduce the porosity of the charge, which blocks the flow of gases, causes premature fusion and crusting, and results in a gas buildup that produces furnace blowouts. Blowouts are sudden releases of high-temperature gas consisting of CO and SiO, resulting in a loss of silicon and, therefore, reduced efficiency. High-purity novaculite has been used in silicon metal and FeSi production, but it generates fines when heated, creating foam that accumulates in the furnace. Costly downtime is spent periodically cleaning this accumulation of foam.

Silicon metal producers prefer to use quartz or quartzite lumps that exceed 2.54 cm in diameter, have a minimum softening point of 1,700°C, and do not decrepitate below 950°C. Lumps can range from 1.27 to 10.16 or 1.27 cm in average diameter, but -10.16 + 3.81 and -7.62 + 2.54 cm sizes commonly are used most. The rock should contain at least 98.5% or 99% SiO_2 (typically 99.3% to 99.8% SiO_2) and less than 0.1% Fe_2O_3 ; 0.15% Al_2O_3 ; 0.2% CaO; 0.2% MgO; and 0.2% loss on ignition (LOI). LOI is directly proportional to the tendency of a rock to decrepitate on heating. Fe_2O_3 and CaO are especially critical impurities for metallurgical-grade silicon.

Silica feed for chemical-grade silicon production should have high reactivity and very low alumina content. Some grades of silicon metal require feed containing less than 0.05% Fe_2O_3 ; 0.10% Al_2O_3 ; 0.005% CaO; and 0.002% TiO_2 . In all cases the rock should contain essentially no phosphorus, sulfur, or arsenic impurities, which are particularly objectionable because they form poisonous gases in the furnace. Metallurgical-grade quartz from Brazil is typically high in titanium, so silicon metal produced from it is suitable for secondary aluminum refining but not for manufacturing chemicals such as silanes and silanes.

Ferrosilicon producers can accommodate smaller lumps of silica rock ranging in diameter from 0.32 to 10.16 cm, the size varying in direct proportion to the silicon content of the alloy produced.

Table 2. Typical composition of quartz gravel for ferrosilicon manufacture

Gravel Type	Composition, wt %					
	SiO_2	Al_2O_3	Fe_2O_3	CaO	P	Ti
North Carolina terrace gravel	99.2	0.068	0.41	0.031	0.007	0.006
Alabama river gravel	98.7	0.27	0.53	0.039	0.009	0.018

Source: Alsobrook 1994.

The rock should contain more than 96% SiO_2 and preferably more than 98% SiO_2 . It also should contain less than 0.4% Al_2O_3 (usually less than 0.25%) and 0.2% Fe_2O_3 . During smelting, Al_2O_3 influences the consumption of electric energy, which can amount to as much as 40% or 45% of the manufacturing costs. Sulfur content should be very low, although phosphorus can range up to 0.1%. Iron and carbon content usually is not as critical as the amount of alumina, alkali, and alkaline earth metals. One U.S. producer's maximum specifications are 0.03% Fe_2O_3 ; 0.20% Al_2O_3 ; 0.01% CaO; and 0.02% TiO_2 . Silica rock for silicomanganese (75% Si, 25% Mn) does not have to be of such high purity. Typical analyses of quartz gravels used in FeSi production in the southeastern United States are shown in Table 2.

The Alabama river gravel in Table 2 is produced in various sizes, including -15.24 + 2.54 and -7.62 + 2.54 cm. Quartz gravel from North Carolina is produced in sizes ranging from +5.08 to -0.635 + 0.3175 cm.

In furnaces used to produce silicon carbide, a bed of -10.16 + 2.54 cm silica rock, through which gas is drawn, filtered, and cleaned, is placed on the floor. Although angular rock has more surface area, round river rock is preferred because it compacts into a looser, more permeable bed.

In smelting iron, nickel, zinc, lead, and copper ores, the price of a acid flux is more important than its chemical purity, so local sources of -4.445 + 1.905 cm stone are normally used. The charges to blast furnaces and basic open-hearth furnaces used in steelmaking are trimmed with washed -1.59 + 0.635 or -2.54 + 0.79 cm river gravel that contains >99% SiO_2 and is usually locally available and inexpensive.

The electric furnace production of elemental phosphorus uses -2.54 + 0.3125 cm lump quartz or -3.175 + 0.635 cm quartz pebble from river channel deposits. In general, quartz or quartzite used as fluxstone in metal and phosphorus smelting should contain >90% SiO_2 and <1.5% Al_2O_3 , 1.5% Fe_2O_3 , and 0.2% combined CaO and MgO.

Abrasive Applications

Quartzite, flint, jasper, and novaculite for use as abrasive media in grinding mills and deburring equipment must have high crushing strength, high specific gravity, toughness or durability, high purity, homogeneity, high hardness, and resistance to staining, fracturing, chipping, and high temperatures. The rock should have low porosity and must contain no toxic substances or dark-colored metallic impurities such as iron and manganese. It must be tightly cemented and chemically inert in the presence of strong alkalis and acids. The media should be round and closely sized. It also should produce a white powder when abraded. The size and shape of constituent grains and their cleavage and fracture characteristics are also important.

High-density grinding media are preferred because their greater impact and grinding force mean that less mill volume is

needed for a given load of media, or that a faster grind can be obtained without reducing the media load. In either case, production capacity is greater than with less-dense media. Novaculite is not usually suitable as a grinding medium because of its comparatively low specific gravity, friability, and low resistance to breaking on impact during milling. Crushed quartzite usually does not qualify for high-impact applications because crushing can produce microfractures in the rock that cause it to break apart during use. Properties that determine the suitability of silica rock for use as a grinding medium also determine its suitability as grinding mill lining.

Silica rock that qualifies as a grinding-mill medium and lining material is also normally suitable as a deburring abrasive, where closely controlled sizing is required to minimize lodging. Certification tests are carried out in a 0.28-m³ tub-type vibrator that is loaded with 90.7 kg of media and 4.5 kg of angle iron and is operated at 1,800 vibrations per minute for 24 hours. A steady, uniform rate of cutting and wear is desired for the development of a fine, high-luster finish on the deburred part. Performance of the abrasive medium is evaluated in terms of its cutting rate, wear rate, cutting efficiency, and the quality of finish produced on the metal part, which should be free of scratches. The cutting rate is the weight percent of metal removed, the wear rate or chipping factor is the weight percent of media lost as nonrecyclable fines, and the cutting efficiency factor is the ratio of cutting rate to wear rate, with high values preferred.

Very few types of sandstone qualify for use as grindstones, which require uniform hardness and sharp, even grains. The rock must be cemented tightly enough to be sound and tough, but not so tightly cemented that it glazes during use. Coarser grains grind faster but produce a rougher surface. Pulpstone also requires that the cement be weak enough to wear and permit the harder quartz grains to protrude. Coarse-grained sandstone produces wood fiber that can be too coarse (Bateman 1959).

Electronics

Quartz crystals for use in electronics and optics should weigh no less than 50 to 100 g (Kuzvart 1984). Piezoelectric-grade crystals should contain at least 16.4 cm³ of flawless material (Lamey 1966). Even clear crystal is unfit if it is optically or electrically twinned or if it contains phantoms, cracks, liquid bubble inclusions, rutile fibers, or intergrowths with other minerals. Phantoms are growth outlines within a crystal that are commonly marked by very fine clay particles (Bates 1960).

Pieces of quartz crystal that weigh 10 to 30 g and defective material trimmed from piezoelectric-grade crystals can be used as the nutrient in growing cultured (synthetic) quartz crystals if their iron and aluminum content is low enough. Crystal growers prefer to use a nutrient (i.e., lascalas) that contains <50 ppm total impurities, although material containing 50 to 100 ppm impurities can be used where requirements are less critical. Iron and aluminum are the most important contaminants because they govern the amount of undesirable sodium and lithium that enters the crystal during the growth process.

Nonpiezoelectric-grade pieces of ultrapure quartz that weigh 10 to 30 g also can be fused and fabricated into optical fiber preforms (e.g., rods and tubing); precision optical and electro-optical blanks, billets, and prisms; specialty lamp tubing; and quartzware apparatus (e.g., crucibles) for semiconductor electronics and laboratory applications (Kuzvart 1984). Manufacturing transparent fused quartz (vitreous silica or quartz glass) products requires a feed that contains less than 30 ppm (0.003%) total impurities; this means a silica content of at least 99.997%. The minimum silica purity required in manufacturing opaque fused quartz glass is 99.8% (Griffiths 1987b).

Acid Tanks and Towers

Blocks of sandstone and quartzite for lining acid tanks, towers, and trays are resistant to hydrochloric and sulfuric acids, but not to hydrofluoric or high-temperature phosphoric acids. Blocks should have good abrasion resistance, a crushing strength of 55×10^3 to 70×10^3 kPa, and a transverse strength of 8.3×10^3 to 9.0×10^3 kPa. Quartz and quartzite gravel used as a packing medium in acid towers must have low porosity (e.g., less than 3%), high crushing strength, high degree of size uniformity, and high surface area per cubic meter. Gravel should be resistant to dissolution by sulfuric acid and should have a neutral or slightly acid pH; a pH of 7.5 or higher can cause problems. Low porosity is required for low acid absorption, and a high crushing strength minimizes the generation of fines that can plug gas orifices and other equipment at the base of a tower. The packed bed of gravel should contain a large percentage of void space per cubic meter.

Air Preheaters

High-purity quartz river gravel is used in three of the four layers that serve as a heat-transfer medium in the chambers of air preheaters. Gravel that is 12 to 15 mm in diameter is used for the bottom (first) layer, accounting for 5% of the weight of the bed. Gravel that is 3 to 5 mm in diameter is used for the second and topmost (fourth) layers, accounting for about 70% of the weight of the bed. Gravel must contain at least 99% SiO₂; it should be round so that the bed has sufficient void volume to allow adequate heat transfer and pressure drop. Angular fragments restrict air flow. Gravel also should have high thermal conductivity, high heat storage capacity, and high thermal efficiency (e.g., 98%) and be closely sized.

Filtration

Rapid gravity filters at municipal water treatment plants contain quartz gravel 2.54 cm in diameter at the base, grading upward to 3.2 mm at the top, for a total bed thickness of 30.5 to 45.7 cm. According to American Water Works Association Standard B100-01 (AWWA 2001) specifications, only uncrushed media can be approved for municipal filtration installations. The media should contain <25% flat or elongate fragments having length:width ratios of 5:1 or more. Crushed rock is angular, so it tends to interlock, as do elongate fragments, in a filter bed. When the bed is backwashed periodically to flush out entrained sediment, media fragments that are locked together will erupt. Round quartz gravel does not interlock and provides the 35% to 40% void space required in a filtration bed. Although gravel need not be of high chemical purity, it should have high specific gravity, tolerance of acid and alkaline source waters, chemical inertness, good mechanical strength to maintain particle shape during loading and compaction, high coefficient of uniformity of size, and an effective size that meets filter specifications.

Trickle filter installations use silica rock that is $-11.43 + 3.81$ cm as the support medium on which bacteria are grown for digesting raw sewage sludge. The rock should be of high chemical purity (e.g., >98% SiO₂), but not necessarily high density. It should be angular so that it has high surface area. Filter beds used in drying sewage sludge for compost applications require silica gravel with a high coefficient of size uniformity and a particle size of between 3.2 and 12.7 mm. Gravel that is $+15.9$ mm in diameter is used in septic leach fields.

Refractories and Other Uses

Quartzite (ganister), quartz gravel, and vein quartz used in manufacturing refractory products usually are crushed to between -3.81 cm

and -2.38 mm and must be low in iron, alkali, and phosphorus impurities. The stone must have low porosity after being fired at $1,500^{\circ}\text{C}$. Fine-grained quartzites usually have lower porosity than coarse-grained quartzites after firing. Even more stringent chemical specifications apply to novaculite used in producing special vitreous silica refractory materials. The best quality novaculite for this purpose, from Arkansas, contains 99.19% SiO_2 ; 0.02% to 0.03% Fe_2O_3 ; 0.10% to 0.25% Al_2O_3 ; and 0.043% $\text{Na}_2\text{O} + \text{K}_2\text{O}$ and is crushed to $-3.81 + 1.27$ cm.

For use as aggregate in furan polymer concrete, where it is loaded at 90 wt %, silica rock must be angular but can range from $44\text{ }\mu\text{m}$ to 6.35 mm.

USES

Electrometallurgy

Specialty silica gravel and lump metallurgical-quality quartz are used in the production of silicon metal and silicon alloys and as a flux in the smelting of elemental phosphorus, iron, nickel, zinc, copper, and lead.

Depending largely on the purity of the silica feed, silicon metal is produced in electronic grades for semiconductor markets, in chemical grades for manufacturing silicones and silanes, and in metallurgical grades for secondary aluminum refining. Consumption of quartz raw material ranges from 2.6 to 3.5 t per finished ton of 96.0% to 99.7% Si metal.

Although FeSi is produced in at least six different grades ranging from 20% to 95% Si, standard grades are 50% Si (typically 48%) and 75% Si (typically 76%). In addition to silica rock, the charge to an electric furnace consists of coal, coke, or charcoal as the reductant, wood chips to provide porosity, and steel scrap or iron ore as the source of iron. Consumption of quartz raw material per finished ton of alloy ranges from 1.05 to 1.1 t for 45% to 50% FeSi, from 1.7 to 2.0 t for 75% FeSi, and from 2.3 to 2.5 t for 90% FeSi.

Steelmaking consists of electric furnaces that remelt scrap, blast furnaces that reduce iron ore pellets to pig iron, and basic oxygen furnaces (BOFs) that convert iron into steel. The principal use of silica rock in steelmaking is as an acid flux and slag conditioner at blast furnace operations. Its functions are (1) to correct, balance, or otherwise adjust the basicity ratio ($\text{CaO}:\text{SiO}_2$) of the burden when too much lime has been charged; (2) to raise the volume of slag sufficiently to ensure complete removal of sulfur and alkalis; and (3) occasionally to clean the furnace. Electric arc furnace mini-mills are operated with a basic, not acid, furnace environment, so they use lime or dolomitic lime and fluorspar instead of silica as fluxes. In remelting scrap, they do use alloys such as 75% FeSi and silicomanganese (SiMn). For more complete discussions on fluxes in steelmaking, the reader is referred to the chapters on metallurgical fluxes in this volume.

Elemental phosphorus is still produced in the United States in Idaho. It is manufactured by first nodularizing beneficiated phosphate sand in rotary kilns, then smelting the nodules to elemental phosphorus in electric furnaces charged with fine coke and quartz pebbles.

Abrasives

Novaculite from Arkansas and silex from Belgium are cut into whetstones, oilstones, hones, files, and other special shapes for residential, industrial, leisure, and craft uses. Residential uses include sharpening kitchen knives and other cutlery such as scissors, shears, and lawn and garden tools. Industrial uses include sharpening and honing cutting surfaces; and polishing metal surfaces in watch and clock manufacture and repair, in gun and reciprocating jet engine manufacture and repair, and in tool and die work. Leisure

applications include sharpening sports knives, arrowheads, fishhooks, and spear points. Craft applications include gun engraving, jewelry making, sharpening woodcarving tools, and other engraving (Austin 1991). Hard Arkansas whetstones are used for fine finishing and edging work, whereas Ouachita Stone whetstones are used in coarse sharpening of large tools such as scythes.

Price lists from Arkansas novaculite producers usually contain four grades, about a dozen shapes, and hundreds of different sizes of cut stone products. Grades are Soft Arkansas for medium work, Hard Select Arkansas for fine work, and True Hard Arkansas and Translucent for extra-fine work. The most popular grade is Soft Arkansas, which is used by woodcarvers, sportsmen, butchers, commercial knife sharpeners, and homemakers. The Translucent grade is used mostly for obtaining an extremely fine polish on industrial and surgical instruments. Shapes include bench stones; triangular and square files; special round, flat, bevel, diamond, and oval files; slip stones; carving tools; pocket stones; penknife pieces; and hones.

Oilstones for fine sharpening have been made from fine-grained sandstone quarried in Ohio. Waste from whetstone operations in Arkansas is used as an abrasive medium in wet (vapor) pressure blasting; as a grinding and deburring medium; as a $74\text{-}\mu\text{m}$ loose-grain abrasive for cleaning printing press plates; and in the manufacture of cuticle stone. A large U.S. producer of cuticle and coaster stones in Bedford, Indiana, has used a patented process that uses epoxy resins to bond scrap novaculite, which have been ground to 149 and $74\text{ }\mu\text{m}$.

Pretumbled novaculite of non-whetstone-grade and hand-cut quartzite cubes are used in barrel tumbling and vibratory machines for light burr, rust, and scale removal, radius formation, cleaning, and degreasing. Applications include the refining, burnishing, and high-luster finishing of cast and punched parts made of mild steel, hardened steel, yellow brass, aluminum, and stainless steel. Additional applications include deflashing, degating, and deburring of cast and extruded polytetrafluoroethylene (PTFE) rings and other plastic parts. Rough, untumbled, and unrounded media are seldom used.

The deburring market is highly diverse and fragmented, ranging from numerous small tool and die shops to huge metal casting foundries and stamping operations in the automotive and aerospace industries. The U.S. abrasive media market consists predominantly (+99%) of wet (versus dry) deburring operations. A typical 0.57-m^3 vibratory machine uses a 907-kg load of abrasive media and requires nearly 23 kg per day of new media, so the daily makeup represents an average 2.5% of the media load. Novaculite is not suitable for use with complicated, intricate castings where abraded particles can lodge in blind holes and tight spots, but it can be used with lighter-weight, simpler castings.

Quartzite (jasper) quarried in Minnesota and silex (chalcedonic silica) produced in France are cut and shaped mechanically by hand into rectangular blocks that are used in lining tube or cylindrical, tile-type ball and pebble mills. Grouted into place with high-alumina cement or epoxy resin loaded with alumina or silica, jasper linings seem to last indefinitely in mills used for grinding pyrophyllite, feldspar, high-purity quartz, industrial silica flour, talc, gypsum, clays, and wollastonite, for example. They are used primarily where iron contamination from metal alloy liners or alumina contamination from ceramic liners cannot be tolerated. The same quartzite is cut into cubes that are prerounded and used as the grinding medium in cylindrical or conical ball and pebble mills. Flint pebbles and silex (buhstone) cubes from Texas, France, Belgium, England, and the former Yugoslavia also are employed for this purpose.

Natural silica grinding media have been replaced to a large extent by high-density, high-alumina manufactured ceramic media.

They are still used for some nonmetallic minerals and ores, as mentioned earlier, as well as for some metallic ores. They are preferred for fine grinding materials that are sensitive to contamination by discoloration, such as specialty coatings (paints), certain chemicals, ceramic glazes and enamels, or organic pigments, white Portland cement clinker, and technical ceramic raw materials (e.g., zircon). A major use for silica media is in grinding porcelain glazes and lacquers, because their use does not cause the product to become cloudy during grinding.

Although largely replaced now by synthetic abrasives, grindstones made from fine-grained sandstone are still used for sharpening edge tools such as saws, machine knives, scythes, shears, and other harvesting and die-making equipment. Hard sandstone, quartzite, and quartz pebble conglomerate have been used as millstones, which are large circular stones that include buhrstone and chaser stone. True buhrstone is chalcedonic silica, and is used in grinding grain, paints, fertilizers, and graphite. Chaser stone has been used for grinding feldspar, quartz, barite, and other nonmetallic minerals (Bateman 1959). Sandstone also is cut into pulpstones for grinding logs into pulp for paper manufacture.

Acid Tanks and Towers

At South Amherst, Ohio, sandstone (firestone) is quarried and cut into blocks or bricks used at steel mills for lining soaking pits, acid tanks, acid wash trays, and steel pickling tanks. The blocks also are used at chemical plants and foundries, by oil-field service companies, and to line acid towers. Acid blocks cut from quartzite at Jasper, Minnesota, are used mostly in the chemical industry.

Acid towers usually are packed with ceramic media of various sizes and shapes, but can be packed with quartz or quartzite gravel. There are hundreds of applications for such towers, including the drying (dehydration) and purification of gases such as chlorine at chemical processing plants. Sulfuric acid or another acid is introduced at the top of a tower containing a packed bed of gravel, and it coats the surfaces of the packing as it trickles downward. Wet chlorine gas is then introduced at the bottom of the tower, and as it migrates upward through the packing, its water content is stripped by the gravel's acid coating.

Refractories

Sandstone, quartzite, quartz pebbles, conglomerate, and non-whetstone-grade novaculite are crushed and used as gneiss in manufacturing refractory bricks, tiles, kiln furniture, and other shapes as well as ramming mixes, mortars, patching compounds, and other monolithic specialties. Such products are used in lining cupolas, ladles, Bessemer converters, metal-pouring shrouds and nozzles, crucibles, mixer cars, by-product coke oven doors, and blast furnace hot stoves and checkers at steel mills. They are used also in lining kilns for firing ceramic products and in the glass industry for lining glass tank crowns and regenerator checkers. High-purity, non-whetstone-grade novaculite also can be fused in high-temperature rotary kilns to manufacture refractories. These water-quenched chunks of vitreous silica are crushed, closely sized, and sold as shell and core sand to investment casting foundries. Vitreous silica has an extremely low coefficient of thermal expansion and good dimensional stability at high temperatures.

Electronics and Optics

Natural electronic-grade quartz crystal was the principal form of quartz used in electronics and optics until 1971, when cultured (synthetic) quartz crystal first predominated. Cultured crystal has now displaced natural crystal in nearly all applications.

Lascas mining and processing in Arkansas ceased in 1997. No firms reported the production of cultured quartz crystal in the United States in 2004. Capacity for cultured quartz crystal production in the United States still exists, and it relies entirely on imported and stockpiled lascas for feed material. It requires between 1.3 and 1.4 kg of lascas to produce 1 kg of as-grown cultured quartz. Cultured quartz crystal production has increased steadily over the past several years, especially in Asia (Dolley 2005).

The worldwide consumption of further purified, lascas-grade quartz in the manufacture of specialty lamp tubing, fiber-optic preforms, precision optical and electro-optical devices, and fused quartzware for electronics (e.g., semiconductor) and laboratory markets is easily 10 times the consumption of lascas in the cultured quartz industry. In the manufacture of vitreous silica or fused quartz products, the ratio of quartz feed to finished product ranges from 1:1 to 3:1. Most of the production of fused quartz is consumed in-house by manufacturers for applications such as laboratory ware in the manufacture of semiconductors and quartz tubes and rods as the raw material for fiber optics (O'Driscoll 1997).

Other Uses

Air preheaters operate continuously at 1,165°C to 1,294°C and are used in the thermal destruction of volatile organic compounds (VOCs) present in offgases from industrial facilities such as painting booths. Their heat-transfer chambers are equipped with perforated plates at the bottom, above which are placed four layers of heat-transfer media. The bottom (first) layer consists of coarse quartz gravel, the second and top (fourth) layers consist of finer quartz, and the third layer, where the heating elements are installed, consists of synthetic mullite aggregate. Altogether, the four layers constitute a bed averaging approximately 30 t of media in each preheater.

Applications for specialty silica stone in water filtration range from rapid sand or rapid gravity filters to trickle filters and drying beds. The former is used to purify municipal water supplies, and the latter is used to filter municipal sewage sludge used as compost at mushroom farms and for other agricultural purposes. Water filtration applications also include commercial and industrial water treatment installations and septic leach fields. The second and fourth quarters usually are the annual peaks for filter media sales. Another filtration application of quartz gravel is for cleaning gases during silicon carbide manufacture, where it is placed as a lining on the floor of electric furnaces.

Other commercial applications for specialty silica rock, often produced as a by-product, include the following construction products: roofing granules and chips; decorative, exposed, semi-light-weight aggregate in precast concrete panels and other white architectural concrete products; aggregate in polymer concrete used to protect concrete flooring from acids; aggregate bonded with epoxy resins to manufacture curtain walls; aggregate for sub-base road construction; nonpolishing, skid-resistant aggregate for asphalt highways; riprap and railroad ballast; and nonskid aggregate in the top coating of concrete flooring subjected to heavy wear such as from forklift traffic.

Non-whetstone-grade novaculite is ground and used as an industrial filler or extender in latex paints, silicone rubber, and plastic casting, molding, and potting compounds (frits and glazes), such as for large electrical insulators.

Miscellaneous uses include poultry, pigeon, and parakeet grit (mixed with crushed oyster shells); sandblasting sand; decorative landscaping and garden stone; sodium silicate manufacture; the polishing of electronic microcircuit dice pedestals; aquarium

chips; aggregate for swimming pool plaster; and fine aggregate in abrasion-resistant linings.

ECONOMIC FACTORS

Production

According to the USGS (Dolley 2003), no vaculite from Arkansas accounted for most of the value and quantity of specialty silica stone sold or used by U.S. producers in 2003. The Arkansas Geological Commission (1999) listed 10 companies that produce whetstone and oilstone in Arkansas. The USGS reported seven producers of specialty silica stone in Arkansas (Dolley 2003). The whetstone and oilstone industry in Arkansas includes integrated companies that quarry crude no vaculite and cut finished products, companies that cut finished shapes from purchased crude stone, and companies that quarry and sell crude no vaculite or that produce pretumbled deburring media from purchased scrap. The USGS last reported the production of crude silica stone (in Ohio) for grindstones in 1998 (Bolen 1998). Finished specialty silica stone products sold or used by U.S. producers in 2003 amounted to 513,000 t valued at \$3.63 million, including grindstones, oilstones, and whetstones (Dolley 2003). U.S. production of industrial silica gravel for electrometallurgical, filtration, and other specialty applications in 2003 amounted to 1.14 Mt valued at \$15.3 million (Dolley 2003). Table 3 summarizes U.S. production statistics for several forms of specialty silica materials for 1999 to 2003. Similar statistics for other countries are seldom published.

In 1997 mining and processing of quartz lascas ceased in the United States (in Arkansas), and no U.S. firms reported the production of cultured quartz crystals in 2004. Cultured quartz crystal production capacity still exists in the United States using imported and stockpiled lascas as feed material. In the past several years, cultured quartz crystal was increasingly produced primarily in Asia. Electronic applications accounted for most industrial uses of quartz crystal; other uses included special optical applications (Dolley 2005).

In the United States, production statistics for cultured quartz crystals were withheld to avoid disclosing company proprietary data. Trade data for cultured quartz crystal and devices with mounted quartz crystal are available, but lascas import data are not available. Exports of cultured quartz crystals (excluding mounted quartz crystals) totaled about 92 t, and imports (excluding mounted quartz crystals) totaled about 3 t in 2004. The United States is 100% import reliant. Brazil, Germany, and Madagascar are reportedly the major sources for lascas, and Canada is becoming an increasingly important supplier. Other possible sources of lascas are China, South Africa, and Venezuela (Dolley 2005).

U.S. production of industrial silica gravel for silicon metal and ferrosilicon manufacture in 2003 amounted to 594,000 t valued at \$8.49 million (Dolley 2003). Data for silica gravel used in filtration and nonmetallurgical flux applications were withheld in 2003 to avoid disclosing company proprietary information. The USGS reported that silica gravel production under the category "Other uses, specified" amounted to 541,000 t valued at \$6.8 million (Dolley 2003). Similar statistics for other countries are seldom published.

Silica stone for which U.S. production statistics are unavailable are (1) Arkansas novaculite used in manufacturing silicon metal and alloys, vitreous silica refractories, oil-field proppants, deburring media, and fillers; (2) quartzite quarried in Minnesota and South Dakota for ferrosilicon production, grinding mill pebbles and liners, and fluxstone; (3) high-purity quartz mined from pegmatite and vein deposits in South Dakota and New Mexico for the manufacture of specialty glass products; (4) sandstone quarried in

Table 3. Specialty silica stone production in the United States

Specialty Silica Stone	1999	2000	2001	2002	2003
Special silica stone, crude*					
Mine production, t	697	553	705	748	1,070
Value, thousand \$	183	158	234	240	313
Special silica stone, finished†					
Sold or used, t	475	312	393	386	513
Value, thousand \$	3,060	4,610	4,040	\$3,740	3,630
Lascas					
Mine production, t	0	0	0	0	0
Consumption, ‡ t	128	146	W§	W	W
Silica gravel**					
Sold or used, kt	1,940	1,660	1,060	1,420	1,140
Value, thousand \$	28,900	24,400	17,600	19,400	15,300

Adapted from Bolen 1999; Dolley 2001, 2002, 2003; Dolley and Bolen 2000.

* Includes grindstones, oilstones, whetstones, and deburring media but excludes grinding pebbles and tube-mill liners.

† Includes grindstones, oilstones, and whetstones but excludes grinding pebbles, tube-mill liners, and deburring media.

‡ Excludes quartz consumed in the manufacture of fused quartzware.

§ W = Withheld to avoid disclosing company proprietary data.

** For silicon metal and ferrosilicon manufacture, filtration, flux, and other uses.

Table 4. Average unit values of specialty silica materials produced in the United States

Specialty Silica Material	Unit Value				
	1999	2000	2001	2002	2003
Special silica stone					
Crude, \$/t	249	286	332	321	292
Finished products, \$/kg	6.44	14.76	10.29	9.69	7.08
Silica gravel†					
Silicon, ferrosilicon, \$/t	18.33	17.81	17.23	14.69	14.30
Filtration, \$/t	17.71	23.36	22.03	31.31	40.08
Nonmetallurgical flux, \$/t	12.22	8.97	11.50	10.05	10.08
Other uses, \$/t	12.11	na†	12.99	na	9.07
Overall average (silica gravel), \$/t	14.67	14.69	16.57	13.66	13.47

Adapted from Bolen 1999; Dolley 2001, 2002, 2003; Dolley and Bolen 2000.

* Calculated by using unrounded data

† na = Not applicable

Ohio for grindstones and lining acid tanks and towers; and (5) highly refined quartz grain produced from alaskite deposits in North Carolina for the manufacture of fused quartz products.

Pricing

Table 4 shows the average unit values of specialty silica materials produced in the United States from 1999 to 2003. The values shown are heavily skewed toward whetstone-grade novaculite and do not represent all specialty silica materials as defined in this chapter.

Lascas production in Arkansas ceased in 1997. At that time, the USGS reported that the average value for lascas was \$1.20/kg (Bolen 1998). The USGS estimated the average value of as-grown cultured quartz to be about \$81/kg in 2003. Similarly, the USGS

estimated the average value of lumbered quartz, which is as-grown quartz that has been processed by sawing and grinding, to be about \$176/kg in 2003. The U.S. Department of Commerce (DOC), which is the major government source of U.S. trade data, does not provide specific import or export statistics on lascas. Some lascas was imported from Brazil in 2003, according to some consumers (Dolley 2003). In previous years, the U.S. Census Bureau provided data on quartz crystal export and import quantities and values; that data included zirconia, however, which inadvertently was reported to be quartz crystal not including mounted piezoelectric crystals.

Table 4 summarizes prices for silica gravel produced in the United States. Prices reported for silica gravel produced in silicon metal and ferrosilicon manufacture ranged from \$4.53/t in the Midwest to \$14.82/t in the South. Silica gravel used in the filtration market ranged from \$33.14/t in the West to \$51.43/t in the Northeast. The average price range for silica gravel in nonmetallurgical applications had a range of \$9.99/t in the West to \$16.53/t in the Midwest. The largest discrepancy in average price per ton of silica gravel was reported for the "Other uses, specified" category from \$10.41 in the Midwest to \$51.43 in the Northeast (Dolley 2003). The cost of transportation generally doubles the free on board (f.o.b.) prices quoted by silica producers. Prices are slightly higher for larger sizes (e.g., $-10.16 + 3.81$ and $-7.62 + 2.54$ cm) than for smaller sizes (e.g., $-3.81 + 1.27$ and $-3.81 + 0.95$ cm). Silicon metal and 75% FeSi manufacture require higher purity and larger sizes, whereas less pure and smaller stone (e.g., inexpensive river gravel) can be used in producing 50% FeSi, silicomanganese (SiMn), ferrochromium silicon, and magnesium ferrosilicon. Blast furnace operations in the steel industry do not require high-purity silica rock as an acid flux, so they normally trim with river gravel that is dredged or mined locally and delivered at competitive prices. Nonferrous metal smelters (e.g., elemental phosphorus smelters) likewise are extremely sensitive to raw material pricing and do not require high-purity fluxstone.

The value of crude Arkansas novaculite depends on its suitability for cutting it into finished whetstones and related products. Generally, Washita grade is less expensive than Black Hard Arkansas grade. Industrial files and special shapes are priced higher than sporting goods products.

In 2003, silica stone product exports from the United States had a value of about \$7.8 million. Exports were categorized as "hand sharpening or polishing stones" by DOC and accounted for most of the silica stone products exported in 2003. The value of imported silica stone products was \$6.3 million in 2003. These imports were hand sharpening or polishing stones, which accounted for most of or all the imported silica stone products in 2003. A portion of the finished products that were imported may have been made from crude novaculite produced in the United States and exported for processing (Dolley 2003).

Rounded flint pebbles from France, Belgium, England, and Denmark are available in as many as 12 sizes for use as grinding media in pebble mills. In the United States, they are priced according to the size the customer orders; small orders generally are more costly than bulk quantities. Also, the smallest pebbles command the highest prices because they are scarce; but they provide the fastest grind. Pricing also depends on whether the pebbles are of Standard or Select quality; the most popular pebble is Standard #1, which is $-6.35 + 3.81$ cm in size.

Cut and pretumbled cubes of jasper (quartzite) from Minnesota are now rarely used as grinding media in pebble mills. Cut blocks of Minnesota jasper for ball and pebble mill linings are priced higher if purchased through distributors rather than directly from the producer. Before the operation closed in 1988, pretumbled

chunks of quartzite from a producer in Wisconsin were sold as deburring media. Prices varied not by the size of stone but also by the size of the order, namely, less than 1,815 kg, between 1,815 and 9,075 kg, and more than 9,075 kg.

Round river gravel for use in water filtration is packed in 22.68-kg, 45.36-kg, and 1-t bags and shipped in lots ranging from 36 to 36,000 t. Prices of filter gravel vary with the stone size and whether it is sold direct to municipal waterworks, to contractors who install water treatment plants, or to manufacturers of filter plants. In the United States, round, high-purity quartz gravel for use in air preheaters also is priced similarly and packaged in 1,360-kg bags.

Transportation

The place value of specialty silica materials varies inversely with their market value. High-priced products such as whetstone-grade novaculite, lascas, fusing-grade lump quartz, flint grinding pebbles, silex and quartzite grinding-mill linings, electronic-grade quartz crystal, and some metallurgical-grade lump quartz and quartzite are items of international trade. Some quartz gravel for water filtration also is exported. Lower-priced materials such as are used in refractories, as fluxstone at ferrous and nonferrous metal smelters, and in the manufacture of some silicon alloys are shipped only to local or regional markets.

Silica raw materials of metallurgical-grade for silicon metal and alloys production used to be obtained within 500 km of the smelter. Rising power costs have forced many electric furnace operations to relocate closer to supplies of low-cost energy, and rising transportation costs have forced others to relocate closer to steel mills. In both cases, silica rock now is hauled from more distant sources (Murphy and Brown 1985). Centers of ferroalloy production in Canada are located where hydroelectric power is available and comparatively inexpensive, for example, in British Columbia; near Welland, Thorold, and Niagara Falls, Ontario; and near Beauharnois, Quebec. Major centers of ferroalloy production in the United States are also where hydroelectric power is available, such as in the Tennessee Valley Authority service territory (i.e., Alabama, Kentucky, Ohio, Tennessee, and West Virginia), the Niagara Falls, New York, area, and the Pacific Northwest (Washington and Oregon).

Some U.S. manufacturers of silicon metal and alloys purchase (1) quartz gravel from North Carolina delivered in open-top, gondola-type railcars holding payloads averaging 68 t (Peterson 1976); (2) crushed Sioux quartzite delivered by rail or river barge from South Dakota; or (3) high-purity novaculite delivered by low-cost river barge in 1,360-t payloads from Arkansas. Other manufacturers, particularly those with operations located close to their silica source, prefer to receive just-in-time shipments by truck to minimize inventory costs. In any case, electric power costs generally represent at least 33% of the total direct operating cost for silicon metal production, whereas silica raw materials account for about 11% and 8% of the direct operating costs for ferrosilicon and silicon metal manufacturing, respectively. Lump quartz from Spain is used in producing 75% FeSi and silicon metal in Norway, where half its delivered price includes transportation.

Alternative Materials

Grinding-Mill Linings

Pink granite from Salisbury and Faith, North Carolina, was once used in lining pebble mills, but it has been replaced by Minnesota jasper (quartzite), which is harder and tougher and can be shaped more accurately. Blocks of Minnesota jasper still are used for lining tile mills at feldspar grinding operations. Hardinge mills for

grinding table and wheelstonite are lined occasionally with the lightest, BB grade of silex (buhrstone) blocks measuring 25.4 to 27.94 cm long, 10.16 cm wide, and 10.16 to 12.7 cm thick. Silex blocks from France and Belgium are not readily available and are very expensive, so they are seldom used today.

Most ball and pebble mills are lined with ceramic materials, chromium-molybdenum steel alloys, aluminum alloys, fused alumina, or special rubber. Where an iron-free lining is required, natural stone has been replaced largely by 5.08-cm-thick, single-piece porcelain ceramic liners that contain 27% to 74% Al_2O_3 . Ceramic liners also are constructed with precast porcelain blocks set with special cements or epoxy resins. They are used in grinding paint, ceramic, and chemical materials.

Grinding-Mill Media

Manufactured abrasive media, including carbon steel and chrome alloy steel balls, glass beads, high-alumina porcelain balls, and zirconia beads, have widely replaced flint pebbles, silex, and jasper chunks and cubes in ball and pebble mills. High density, high-alumina, porcelain grinding media are manufactured as balls, discs, cylinders, and rods ranging from 1.59 mm to 7.62 cm in diameter with alumina content from 87% to 99%. They are made in various grades of hardness, which averages about 8 on the Mohs scale, and they have a specific gravity of 3.4, which is 40% to 50% of forged steel. Their bulk density averages about 2,210 kg/m^3 , compared to 1,680 kg/m^3 for Minnesota jasper.

The prices of high-alumina ceramic grinding media depend on their size, shape, and Al_2O_3 content; small diameter sizes are more expensive than large diameter sizes. Smaller sizes are used for really fine grinding, for example, for inks, paints, and chemicals.

Factors in choosing grinding abrasives include the price of the media, grinding speed, media wear or loss, product contamination, and mill lining wear. In most applications, high-alumina ceramic materials are the most cost-effective, explaining why they have captured most of the grinding media market. Their high specific gravity ensures high grinding speed, and their toughness minimizes fracturing, wear, and loss. Although their high density can cause strain on mill bearings, they are longer lasting than Belgian silex pebbles, and their use usually extends the life of grinding-mill linings. Feldspar producers typically experience a media loss of only 0.55 kg per ton of ground feldspar. Some ground silica flour producers use pretumbled jasper (quartzite) cubes or flint pebbles in combination with high-density porcelain ceramic balls as a blended medium to reduce costs and the load on mill bearings.

Forged steel and stainless-steel balls from 1.27 to 15.24 cm in diameter often are used where iron contamination of the product is of no concern. Zirconia grinding media have a high specific gravity and possess wear resistance similar to ceramic materials. Glass beads range in specific gravity from 2.5 for lead-free glass to 2.94 for leaded glass. They vary in diameter from <1 to 1.5 mm. Chunks of recycled high-silica refractory brick have been used as a grinding medium, but they cause excessive wear to the mill lining at the discharge end. In some instances the grinding medium (e.g., nepheline syenite) has been fabricated from the same rock as that being ground.

Deburring Media

As in the case of grinding mill media, natural stone abrasives once used as deburring media have been displaced largely by manufactured products, including glass beads, fused aluminum oxide, high-alumina ceramic materials, stainless steel, and even plastics. Such media are used in vibratory and tumbling machines for the deburring and surface finishing of stamped metal parts and foundry castings, and for deflashing cast plastic parts.

High-alumina ceramic and fused or sintered aluminum oxide tumbling media are manufactured in a variety of shapes, called preforms, including cones, tubes, pyramids, and stars. They are harder, tougher, and more abrasive than natural stone media and do not present a silica hazard. They also are produced in crushed and rounded form, called random shapes or nuggets. Their bulk density ranges from a low of 1,360 kg/m^3 for ceramic media to a high of 2,080 to 2,400 kg/m^3 for fused aluminum oxide. Pricing depends on the size of medium, its Al_2O_3 content, and the quantity ordered. Small sizes are priced 7.5% to 8.5% higher than large sizes. The higher the Al_2O_3 content, the faster the cutting ability and, therefore, the higher its price; so the highest priced media are small, complex preforms having very high alumina content. Preforms having the highest Al_2O_3 content cut fastest, but they have the lowest efficiency because of a high rate of wear. They are used in applications where an extra-fast cutting rate is more important than media loss and composition.

Ceramic media may be too aggressive in some applications and not aggressive enough in others. Polyester plastic preforms, which are less aggressive, average 1,040 kg/m^3 in bulk density. Prices for stainless-steel deburring media tend to be higher than those for ceramic media. Emery and corundum also have been used as random-shaped, natural abrasive deburring media.

Acid Tanks and Towers

Extruded bricks can be used instead of silica pebble as a lining for acid towers. Bricks are composed of coarse, -0.84-mm silica sand plus ball clay or an organic binder. Special ceramic, plastic, or metal materials can be used instead of quartz gravel as the packing medium for such towers. Plastic media are least expensive, but they are not wetted easily by acids and can be used only with low operating temperatures. Where operating temperatures are high, ceramic and special metal packing media are used. Ceramic materials are wetted more easily by acids and are less expensive than metallic media.

Air Preheaters

Instead of high-purity quartz gravel, most manufacturers of air preheaters use high-alumina ceramic particles to fill the metal chambers. Ceramic media are heated to high temperatures and serve as heat exchangers in stripping VOCs from industrial exhaust gases that are blown through the chambers.

Silicon Metal

At East Selkirk, Manitoba, silicon metal is smelted from silica sand instead of conventional metallurgical-grade quartzite. Silica sand is imported from the United States and is smelted in a plasma furnace to produce silicon metal for the manufacture of silicone fluids, resins, and elastomers.

Cultured Quartz

As the seed for growing synthetic quartz crystals, plates cut from specially grown cultured seed crystals have nearly replaced those cut from natural crystal. A slow deterioration of crystal grown from synthetic seeds requires that producers periodically start the process over with high-purity natural seed plates. High-purity silica sand represents the major potential competitor to lascas as the nutrient in growing cultured quartz crystals.

Whetstones, Hones, and Grindstones

Natural abrasives have been displaced by manufactured abrasive products made of materials such as fused aluminum oxide and silicon carbide. In most applications synthetic materials last longer,

making them more cost-effective, although whetstones, hones, and oilstones made from Arkansas novaculite continue to fill a niche in the abrasives markets. Some pulpstones still are fabricated from granite and other types of stone.

GOVERNMENTAL CONSIDERATIONS

Policies adopted by national governments can affect the availability, pricing, and consumption of some specialty silica materials. The Brazilian government, for example, established minimum prices for first-, second-, and third-quality Brazilian lascas in the export market, and in 1974 it embargoed shipments of lascas from Brazil. As a result, prices increased nearly sixfold that year and nearly tenfold subsequently. This action led to lascas production in the United States, Angola, and Namibia. Nationalization of lascas operations in Angola in 1979 and the civil war there have interrupted supplies of Angolan lascas since 1980.

In the past, the government of India followed policies that restricted exporting certain minerals. Then, in the early 1990s, India began to promote its minerals for export to generate foreign exchange earnings (Russell 1991).

Import Tariffs

Lascas for growing cultured quartz crystals and manufacturing fused quartzware products are imported into the United States free of tariffs for countries with normal trade relations. This applies to lascas designated as crude Brazilian pebble from Brazil and as quartzite from Namibia. No tariffs are levied on U.S. imports of other types of special silica stone such as flint or silex pebbles from Europe and metallurgical-grade quartzite from Canada. Although the United States is self-sufficient in industrial sand and gravel, Canada and Mexico are the largest U.S. trading partners in this regard, mainly because of their proximity to U.S. markets. No import tariffs are imposed on industrial sands of 95% or greater silica and not more than 0.6% iron oxide, or on industrial sand less than 95% silica. An ad valorem tax of 3% is levied on imports of piezoelectric quartz.

Depletion

For industrial sand or pebbles, the depletion allowance for federal income tax purposes in the United States is 14% for both foreign and domestic production. The rate allowed for natural electronic-grade (radio-grade) quartz crystal is 22% for domestic production and 14% for foreign production.

U.S. Stockpile

The United States designated natural electronic-grade quartz crystal as a strategic and critical material after World War II and purchased crystal from Brazil for the National Defense Stockpile (NDS). Since that time, the technology for growing synthetic quartz crystals has been developed and cultured quartz has now displaced natural crystals in essentially all applications. As a consequence, the NDS inventory has been reduced periodically by selling excess material on the open market, primarily for specimen and gemstone uses. The federal government reported that sales from the NDS during 2003 amounted to about 97,240 kg of natural quartz crystal valued at \$365,166. At the end of 2003, the NDS contained about 6,804 kg of natural quartz crystal (Dolley 2003).

Environmental Regulations

Most of the types of specialty silica materials discussed here are essentially entirely crystalline silica, which in its respirable form has been known to cause silicosis, a disabling pulmonary disorder. Ultrafine silica particles of about 0.5 μm are believed to constitute

the greatest health hazard because their surfaces exercise a strong oxidizing effect comparable to that of ozone. This effect is especially pronounced for quartz particles that have been recently ground, because freshly fractured and exposed surfaces are more chemically reactive than aged or weathered surfaces.

The silicosis risk associated with crystalline silica has caused consumers in some markets to abandon them in favor of alternative materials, in large part because of a monograph issued in 1987 by the International Agency for Research on Cancer (IARC). In that monograph, IARC classified crystalline silica as a Group 2A (i.e., probable) carcinogen in humans. The subsequent IARC data sheet listing suggested that all material safety data sheets for products containing 0.1% or more crystalline silica should contain a cancer warning. A number of federal and state agencies in the United States adopted that suggestion and require appropriate product labeling.

The facts and issues involved in the current crystalline silica debate are too many and too complex to be analyzed meaningfully here. They are addressed in more detail in other chapters of this volume, and they have had an adverse impact on demand for silica stone products. Because of the ongoing controversy, for example, one major U.S. manufacturer of abrasive media refused to introduce and market a new line of novaculite-based deburring media, despite the fact that more than 99% of all deburring operations are carried out in an aqueous environment where essentially no dust is generated.

PROBLEMS AND FUTURE TRENDS

The outlook for specialty silica materials, with the exception of ultrapure quartz grain and lascas, is not particularly attractive. Manufactured materials have already displaced natural silica in most abrasive and other industrial applications and can be expected to slowly penetrate the niches that remain, especially at the high end of the price range. This applies to novaculite for whetstones, hones, oilstones, and deburring media; sandstone as grinders and blocks for acid tank linings; quartz pebbles for acid tower linings and packing media and as the heat-transfer medium in air preheaters; quartzite and silex as blocks for grinding-mill linings and as pretumbled cubes for grinding and deburring; and pebbles of flint and silex as grinding-mill media.

At the low end of the price range, quartz gravel should continue to experience modest growth in demand for use in water filtration, partly because it faces little competition from cost-effective substitutes. There are likewise few substitutes for quartz gravel, quartzite, and perhaps high-quality novaculite for use as fluxes in ferrous and nonferrous metal smelting and as raw materials in the manufacture of silicon metal and various silicon alloys, although these end-use industries are typically highly cyclical.

Until means are devised for using high-purity silica sand instead, lascas should continue to be the untested feedstock in producing cultured quartz crystals for optics and electronics, particularly for products such as personal computers, electronic games, and cellular telephones. The markets for cultured quartz, and therefore lascas, are somewhat cyclical but should experience a higher rate of growth than most other markets for naturally occurring, specialty silica materials.

Overall annual growth in filtration markets is about 1% to 2%. Much of the growth is from demand in Eastern Europe, Asia, South America, and Central America. Mature markets in the United States and Western Europe also will continue to grow. Silica sand in rapid gravity filtration grew about 5% between 2001 and 2002. Pressure vessel and slow filter bed markets remained static (Taylor 2004).

The strongest rate of growth in demand should be experienced by ultrapure, fusing-grade quartz grain for specialty glass

and fiber-optic, precision optical, semiconductor, high-intensity lighting, electro-optical, and laboratory applications. Competition from synthetic silicas will intensify in these high-tech markets as the need for raw materials of higher and higher chemical purity intensifies. This need is driven largely by the trend to higher-capacity memory devices in the semiconductor industry, but also by developments in fiber-optic communications. Ultra-pure synthetic silica is produced by Sol-Gel technology, and commercial production of synthetic fused silica containing less than 2 ppm total impurities (including hydroxyl and chlorine ions) also is produced in the United States.

Although few commercial applications for specialty silica materials generate significant amounts of crystalline silica dust, silicosis and carcinogenicity issues will continue to adversely affect future market demand for these products. Producers willing to accept this situation should focus on developing resources of leucosil, ultrapure quartz grain, filtration-grade quartz gravel, and metallurgical-grade quartzite that are located close to geographic concentrations of major consumers.

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Soda Ash

Ken Santini, Ted Fastert, and Ray Harris

INTRODUCTION

Soda ash is the common name for sodium carbonate (Na_2CO_3), an alkali compound that is one of the largest inorganic chemicals in terms of production of all domestic inorganic and organic chemicals, excluding petrochemical feedstock. Although most people have never heard of soda ash, it is an important industrial compound used to manufacture glass, chemicals, soaps and detergents, pulp and paper, and many other familiar consumer products. People have used natural alkalis for thousands of years; their industrial manufacture began in the last half of the 18th century.

Natural deposits of sodium carbonate were exploited as early as 3500 BC, when the ancient Egyptians used natural soda ash in making glass. They also mixed lime and soda ash to make sodium hydroxide (caustic soda), which was combined with silicate minerals from the Sinai Desert. This made soluble silica that, when added to a aluminum-rich silt from the Nile River, produced silica-aluminate cement mortar with excellent bonding properties for construction. Romans in the 1st century AD also used natural soda ash in glass manufacture but expanded its use to treat colic pains and skin eruptions and to make bread.

Elsewhere, people obtained alkali from wood ash. They learned over time that different types of wood yielded various ashes with different properties; therefore, various plants were burned specifically for their ashes. Ash from plants grown in salt-bearing soils (such as saltwort) and from kelp and other seaweeds, especially Spanish *barilla*, were so different from ashes obtained from other vegetation that it became known as soda ash (because of its sodium content) versus pot ash, a potassium-based alkali ash. About 13 t of *barilla* ashes produced 1 t of sodium carbonate and 14 kg of iodine as a by-product. The difference between the two ashes was relatively obscure until Duhamel Dumonceau made the distinction clear in 1736. The term *soda ash* developed from common usage and is perhaps better known today than its synonym, sodium carbonate. A primary source of soda ash is *trona*, a sodium-carbonate-bearing mineral whose name is traced back to Arabic origin. Trona also is known by other names such as *urao* (Venezuela), *kaum* (Nigeria), *natron* (from Greek *nitron* and Latin *natrium*), and *szeško* (Hungary).

The beginning of the Industrial Revolution in Western Europe in the mid-18th century soon put a strain on the availability of raw materials to meet consumer demands. One of these scarce materials was soda ash. Because of the Seven Years' War with England and the Napoleonic Wars with other parts of Europe, France could not obtain sufficient quantities of Spanish *barilla* or

other supplies of vegetable alkali to meet the growing demand. Efforts were needed to synthesize soda ash. In 1775, the French Academy of Sciences offered a large prize of 2,400 livres to anyone who could find an inexpensive method to make soda ash. In September 1791 at St. Denis, Nicolas Leblanc (1742–1806), a French chemist, developed such a technique using salt, sulfuric acid, coal, and limestone. The French Revolution interfered with its development and his patent and factory were confiscated, with Leblanc receiving only token compensation. Although Napoleon later returned the factory, Leblanc was not able to raise enough capital to reopen it, and he committed suicide in 1806. A small but not particularly successful Leblanc process plant was established in England in 1814. It was not until 1823 in Liverpool, England, that the process first became commercially successful. The process was introduced in Germany in 1843 and in Austria in 1851 (Harness and Coons 1942). Soda ash production by the Leblanc process reached its peak of about 599.5 kt in 1880, after which it began to decline as the Solvay process became more popular. The Leblanc process was used to a limited extent in Europe during World War I and had disappeared by World War II.

The Solvay process, also known as the ammonia-soda process, was developed by brothers Alfred and Ernest Solvay in 1861 based on a concept by Fresnel that had been known since 1811. For the next 50 years, implementing the concept evaded industrial chemists because no large-scale and economic means could be found to commercialize it. Although Ernest Solvay was unaware of the existence of an ammonia-soda concept, he solved the problem by using carbonating towers. The Solvay process produced soda ash from salt, limestone, and coke, with ammonia as a catalyst. With a capital investment of 136,000 francs, the Solvay brothers built the first plant at Couillet, Belgium, in 1863, and production began in 1865. Synthetic soda ash production was 1.5 tpd in 1866, and reached 10 tpd by 1872. Carbonating towers, patented in 1872, made ammonia-soda manufacturing a successful continuous process. Their second plant was built in 1872 at Dombasle, France. In 1874, the first Solvay plant in England was built at Northwich by Ludwig Mond, the namesake of Brunner Mond and Co. (formerly Imperial Chemical Industries), the company that currently operates the two English Solvay plants.

In the United States, William B. Cogswell in February 1879 heard a presentation on the Solvay process and sailed to Europe to meet with the Solvay brothers to seek their support for using their process in New York. At first, the brothers were not interested; Cogswell was as persistent, however, and ultimately gained their

support. The Solvay Process Co. was formed on September 21, 1881, and construction began immediately on the first Solvay plant at Geddes, near Syracuse, New York. The plant went onstream on January 10, 1884, and produced 11.18 kt in its first year of operation. In 1910, rotary calciners increased capacity to 1 ktpd. By 1930, plant capacity was up to 2.4 ktpd. The facility remained in continuous operation for more than 100 years. By 1939, 10 Solvay soda ash plants were in operation in 6 states. The Syracuse plant ceased production on January 6, 1986, and officially closed by February 1986. Ironically, this facility was the first Solvay plant as well as the last. Other than production from the first Solvay plant, most U.S. soda ash supplies during the 19th century came from imports. The remainder of the U.S. supply was obtained from small natural soda ash deposits in Nevada and California that served western consumers.

The first commercial natural soda ash operation in the United States began in Nevada in 1868 at the Ragtown Soda Lakes, better known as Big Soda Lake and Little Soda Lake, which are the remnants of extinct volcanoes about 7 km west of the present town of Fallon. Asa L. Kenyon, a pioneer who settled in the area in 1855 to sell provisions to settlers passing through, acquired the lake properties and in 1868 sold the smaller lake to Higgins and Duffy, who sold it to a San Francisco group known as Doe and Dowd. Little Soda Lake was primarily dry most of the year and reportedly had a mass of crystallized sodium carbonate on its surface that was more than 10 m thick, whereas Big Soda Lake was filled with water that was saturated with many salts, including sodium carbonate and borax.

Two types of solar processes produced the soda ash—a summer process in which trona precipitated in evaporation ponds on the perimeter of the lakes with soda ash being the final product, and a winter process in which natron precipitated with thermonatrite being the final product. Soda ash production from Little Soda Lake averaged about 300 tpy, whereas output from Big Soda Lake, which began operation in 1875, averaged about 450 tpy. Most of the soda ash was sold to miners in Virginia City, Nevada, to treat silver ore and to soap manufacturers in Reno, Nevada. Soda ash also was bagged and transported to Hazen, Nevada, where it was shipped by rail for \$19/st to San Francisco for further refining, after which it sold for between \$55 and \$65/st.

With the beginning of the Nevada Reclamation Project in 1902, the lake brines were increasingly diluted by infiltrating groundwaters from the Truckee–Carson irrigation project that conveyed water to California. By the end of 1907, the brines were so dilute that soda ash production became impractical and rising lake levels began covering the evaporation ponds and buildings. The soda ash producers brought claims against the U.S. government on June 17, 1917, citing that they believed there was a direct correlation between the flooding of their operations and the irrigation project, and that the government should be responsible for damages of \$205,000. On April 7, 1919, the U.S. Court of Claims decided in favor of the government. After years of appeals and investigations, which ultimately proved that the canals were responsible for the rising lake levels, the case was resolved on November 21, 1921, with the U.S. Supreme Court ruling in favor of the government. The case was a landmark decision because it set a new legal precedent that "... the government is not liable for all actual damages resulting from public improvements, but only for such damages as inevitable to result and which with due diligence and expert study could have been anticipated" (*San Francisco [CA] Bulletin* 1921). The fact that the soda ash producers gave a right-of-way to the government before 1907 was the main reason why they lost their case (Taylor 1987–1988). The right-of-way stated "that in consideration of the premises, the first party hereby releases the second party from all

claims and damages for entry, survey, or reconstruction of said works" (U.S. Supreme Court Case Nos. 26 and 32: *John Horstmann Co. v. U.S.* and *Natron Soda Co. v. U.S.*, October Term, 1921).

More than 85 years have passed since Big and Little Soda Lakes were flooded. Today, the two lakes lie quietly in the virtually barren landscape of western Nevada. No traces remain of the first natural soda ash operation in the United States except at the bottom of Big Soda Lake, which sometimes is explored by local divers to see the remains of the wooden buildings, rusting steam tractors, and beehive ovens that once produced soda ash. The site has been nominated for the National Register of Historic Places, a fitting tribute to this historic operation.

Natural sodium carbonate was also observed in other areas besides Nevada. In 1835, the Reverend Samuel Parker crossed the Rocky Mountains and noticed Epsom salts on the land surface near Independence Rock, Wyoming. As early as 1849, Mormon pioneers are believed to have used the natural sodium bicarbonate occurring along the Sweetwater River in Wyoming for laundry and medicinal purposes. The Western Alkali Corp. began commercial development of sodium carbonate brines there, producing *sal soda*, or washing soda, in solar evaporation ponds from 13 wells about 100 m deep. The operation ceased in 1920 because of high operating costs (Milani 1983).

The largest natural deposit of trona known in the world is at Green River, Wyoming. The deposit was discovered accidentally in January 1938 when the Mountain Fuel Supply Co. was drilling for oil and gas (Lindeman 1954). The company abandoned the well as a dry hole, but the company's geologist, William T. Nightingale, observed sodium carbonate in the drill cores at the well site. Core samples were sent to Roger C. Wells and Joseph J. Fahey of the U.S. Geological Survey (USGS), who verified the presence of trona. In 1940 Robert D. Pike, a consulting chemical engineer, recognized the economic potential of refining soda ash from the trona but not until he convinced the Westvaco Chemical Corp. (which merged with FMC Corp. in the fall of 1948) of this did commercial interest begin. In 1947, the first mine shaft was sunk about 460 m deep, and active mining began on a developmental basis later that year. Calcined trona was sold from 1950 (38,814 t mined and sold the first year) to 1953, when the first refined soda ash plant came onstream with an annual capacity of about 272 kt. Today there are four natural soda ash producers in Wyoming with a combined annual nameplate capacity of approximately 13.5 Mt (Kostick 2004).

Beginning with the first world energy crisis in 1973 and the growing international concern for the environment, worldwide synthetic soda ash output steadily decreased until 2001. During 2001, China added new Solvay process capacity and surpassed U.S. production of natural soda ash in 2003. Most of the world continues to use the Solvay process, which is energy, capital, and labor intensive and generates by-product calcium chloride and sodium chloride that cause environmental problems when discharged. In 2004, synthetic soda ash represented approximately 70% of total world production, with natural soda ash constituting the balance of about 30%. Of the estimated 40.3 Mt of total soda ash produced during 2004, 11 Mt of natural soda ash (approximately 27%) originated from the United States, with Botswana, Kenya, and China accounting for the remaining 3% (Kostick 2004, 2005).

GEOLOGY

Mineralogy and Physical and Chemical Properties

Several sodium-carbonate-bearing minerals are found in deposits throughout the world. The most important economic mineral is

trona (sodium sesquicarbonate), which has the following physical and chemical properties:

- Chemical formula: $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
- Crystal system: monoclinic
- Cleavage: perfect on (100)
- Appearance: massive trona from Green River, Wyoming, deposits is clear to dark amber depending on impurities. Searles Lake, California, deposits are fine-grained masses to acicular and bladed crystals; clear to white to gray; and porous.
- Hardness: soft to semihard; 2.5 to 3.0 Mohs hardness
- Molecular weight: 226
- Specific gravity: 2.17 g/cm³
- Melting point: >70°C
- Solubility: 20 % maximum by weight in water; soluble in hydrochloric acid; when heated, loses water, the sodium carbonate dioxide.
- pH: 10.1 (1% solution)

The physical and chemical properties of soda ash (sodium carbonate–anhydrous) are as follows:

- Chemical formula: Na_2CO_3
- Appearance: white, granular solid
- Molecular weight: 105.99
- Specific gravity: 2.533 g/cm³
- Bulk density: 0.59 to 1.04 g/mL
- Melting point: 851°C
- Heat of formation (ΔH_f): 1,131 kJ/mol
- Solubility: 33% maximum by weight in water
- pH: 11.6 (1% solution)

Origin

Various theories have been proposed to explain the origin of sodium carbonate found in natural deposits. Different deposits may have been formed from a combination of one or more physical and chemical processes. These include (1) the evaporation of sodium carbonate–rich thermal spring water; (2) carbonation of sodium sulfide (from bacterial decomposition of sodium sulfate) to sodium carbonate; (3) ion exchange in sodium-bearing soils; (4) concentration–temperature–dependent equilibrium relationships among carbon dioxide, sodium bicarbonate, and carbonate that converts carbonate solutions to sodium bicarbonate, or carbon dioxide removed from sodium bicarbonate solutions to form carbonates; and (5) leaching of alkaline carbonates or basic–ultrabasic rocks. The sodium may have been derived from the leaching of sodic feldspars or volcanic ash deposits, and the carbon dioxide from the atmosphere and biogenic processes.

Most groundwaters in metamorphic or igneous terrains produce alkaline solutions on evaporation (Hardie and Eugster 1970). The relative absence of chloride and sulfate in these types of rocks permits solutions to become predominantly sodium- and carbon-dioxide-bearing. The chemical fractionation of inflowing waters and brines within closed depositional basins can produce different minerals accumulating in separate areas. The mechanisms can be mineral precipitation, selective dissolution of efflorescent crusts, degassing of brines, or redox reactions (Eugster and Jones 1979). Groundwater percolating through siliceous soils such as those developed on granite or windblown sands can become highly alkaline and enriched in sodium carbonate (Garrels and Mackenzie 1967). Very high carbon dioxide concentrations (up to 10% of soil gas) are known to occur in soils as a result of biological activity.

Table 1. Sodium-carbonate-bearing minerals

Mineral Name	Chemical Composition	Na_2CO_3 , %*
Thermonatrite (monohydrate)	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	85.5
Wegscheiderite	$\text{Na}_2\text{CO}_3 \cdot 3\text{NaHCO}_3$	74.0
Trona (sesquicarbonate)	$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$	70.4
Nahcolite (sodium bicarbonate)	NaHCO_3	63.1
Bradleyite	$\text{Na}_2\text{PO}_4 \cdot \text{MgCO}_3$	47.1
Pirssonite	$\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 2\text{H}_2\text{O}$	43.8
Tychite	$2\text{MgCO}_3 \cdot 2\text{Na}_2\text{CO}_3 \cdot \text{Na}_2\text{SO}_4$	42.6
Northupite	$\text{Na}_2\text{CO}_3 \cdot \text{NaCl} \cdot \text{MgCO}_3$	40.6
Natron (sal soda or washing soda)	$\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$	37.1
Dawsonite	$\text{NaAl}(\text{CO}_3)(\text{OH})_2$	35.8
Gaylussite	$\text{Na}_2\text{CO}_3 \cdot \text{CaCO}_3 \cdot 5\text{H}_2\text{O}$	35.8
Shortite	$\text{Na}_2\text{CO}_3 \cdot 2\text{CaCO}_3$	34.6
Burkeite	$\text{Na}_2\text{CO}_3 \cdot 2\text{Na}_2\text{SO}_4$	27.2
Hanksite	$2\text{Na}_2\text{CO}_3 \cdot 9\text{Na}_2\text{SO}_4 \cdot \text{KCl}$	13.6

* Includes bicarbonate converted to carbonate.

This can produce more than 200 mg/L of carbon dioxide in the soil water (Jakucs 1977). The Pretoria Plain in the Republic of South Africa, the sandhill regions of Nebraska, and the Sind of Pakistan are examples of sodium carbonate in soil waters (Barbour 1916; Cotter 1923; Dutoit 1948). In lakes, the continual generation of CO_2 by algae and bacteria can aid deposition of monomineralic beds of trona (Eugster 1971). Semiarid rather than arid climates are most favorable for producing alkaline waters because the evaporation rate is too rapid to stabilize the soda solutions in very arid regions (Perelman 1967).

In sedimentary rock terrains, the drainage usually contains too much chloride, sulfate, and calcium to produce either brine or solid sodium carbonate salts. Although sodium carbonate solutions originate from the weathering of igneous rocks, these same waters can interact with other waters or with other rock and soil types in the area of accumulation so that mixed chloride and sulfate salts are the final products (Risacher, Echeñique, and Ballivian, unpublished data).

Mode of Occurrence

Sodium carbonate resources commonly occur as precipitates in shallow, nonmarine alkaline lakes and marshes and usually coexist with various chloride and sulfate salts. For this reason, it is not uncommon to find different sodium-carbonate-bearing minerals within the same deposit. Table 1 lists some minerals that contain sodium carbonate in varying concentrations.

Because sodium carbonate generally was deposited in shallow bodies of water, many of the deposits were subjected to vast seasonal changes in area and mineral concentration, and were susceptible to destruction by mechanical and chemical erosion caused by the relative softness and solubility of the minerals. Therefore large economic sodium carbonate deposits are relatively rare and are considered geologically young, ranging from the Eocene to Pleistocene epochs. Pre-Tertiary deposits are virtually absent from the geologic record.

Mannion (1975, 1983) presented a list of the more common forms of sodium carbonate occurrences:

1. Natron crystals in cool, wet environments on the bottoms of ponds or at shallow depths in salt marshes, as at Lake

- Goodenough, British Columbia (Cummings 1940), and Owens Lake, California (Smith and Friedman 1975)
2. Powdery surface efflorescences of the monohydrate around alkaline lakes or marshes, as in the alkaline soils of the lower Danube River Valley, Hungary, and at Lake Nyasa, Tanzania (Orr and Grantham 1931)
 3. Relatively hard but porous deposits of trona, either around the shores or at the bottoms of shallow alkaline lakes or playas, as at Lake Magadi, Kenya (Baker 1958; Eugster 1970), Owens Lake, California (Dub 1947), and Lake Chad Basin, Africa (Eugster and Maglione 1979)
 4. Older beds of buried trona, nahcolite, or other sodium-carbonate-bearing minerals, as the Green River Formation in Wyoming (Bradley and Eugster 1969; Culbertson 1971; Deardorff and Mannion 1971; Wiig, Grundy, and Dyni 1995; Leigh 1998), in Colorado (Smith and Milton 1966; USBM 1972), and at Railroad Valley, Nevada (Free 1913)
 5. In solution as a constituent of brine, either surface or subsurface, as at Searles Lake, California (Smith 1979), and Makgadikgadi, Botswana (Massey 1973; Lefond 1981)

Although certain deposits are made up of combinations of the five forms of occurrences, sodium carbonate deposits can be classified by their economic importance (Kostick 1983). The five forms, ranked by decreasing potential economic significance, are buried, surface or subsurface brines, crystalline shoreline or bottom crusts, shallow lake bottom crusts, and surface efflorescences.

Occurrences of Sodium Carbonate

Large and small natural deposits containing sodium-carbonate-bearing minerals exist in several countries throughout the world. Most of the deposits contain solid salts, solutions, or both.

Most of the deposits listed are geologic occurrences and are neither large enough nor of sufficient sodium carbonate content to be of economic potential. Many small-scale deposits such as those in Chad and the Sudan have been mined strictly for local consumption.

Africa

Africa has numerous sodium carbonate occurrences scattered throughout the continent. The arid to semiarid climates in parts of Africa prevent the dissolution and transport of the soluble carbonate minerals. Some of the occurrences are small, isolated lake deposits whereas others are major deposits found in a chain in the East African Rift Valley. Garrett (1992) contains an excellent description of all the major and minor soda occurrences in the Rift Valley.

A \$504 million natural soda ash facility commenced production in April 1991 on the Sua Pan in the Makgadikgadi Basin in northeastern Botswana. The project is operated by Soda Ash Botswana (SAB), a joint venture between the government (48%) and the African Explosives and Chemical Industries (AECI) consortium (52%) with its partners AECI (25.5%); the Anglo American Corp. (12.75%); and De Beers Holdings (12.75%). The facility produces about 300 ktpy of refined soda ash from underground brines and 600 ktpy of sodium chloride. Most of the soda ash is marketed in South Africa, which had relied heavily on soda ash imports from the United States. SAB also exports soda ash to Zambia and Zimbabwe, both using about 15 kt annually. The sodium carbonate reserves at Sua Pan exceed 360 Mt.

Impure sodium carbonate in the form of natron mixed with halite has been obtained from crystallizing pans among sand dunes in the northeastern section of Lake Chad (Eugster and Maglione 1979). Most of the crude material has been for local consumption;

it had been reported, however, that a few thousand tons of crude trona had been previously exported to Nigeria. Some of the reported uses are as follows:

- People use it as a remedy for stomach aches and constipation.
- People mix the natron with ashes of burned wheat stalks to make a crude soap.
- Chadian herders give it to cattle as a salt lick.
- People mix it with raw tobacco to flavor it for chewing.
- Tanners use it as an additive with certain tree gums to tan hides and skins.

Wadi Natron in Egypt, about 80 km northwest of Cairo and 35 km west of the Nile River, consists of up to 20 individual lakes, some of which dry completely during the summer (Lucas 1912; Atia, Hilmy, and Bolous 1970). Trona obtained from these lakes has been used for more than 5,500 years. Soda ash was used to make ornamental glassware and in the mummification process. Samples of trona have been found in one of the pharaohs' tombs at Thebes, suggesting the importance of its unique value. Other occurrences have been reported at El Barnugi in Lower Egypt, at Mahamid, and at Wadi Tumilat in Upper Egypt. Trona has been identified in cores taken from the outer Egyptian shelf of the Nile Cone in the Mediterranean Sea. The trona probably was eroded from the continental margin 18,000 to 23,000 years ago and buried very quickly in the deep marine environment (Stanley and Sheng 1979). Ethiopia has several sodium-carbonate-bearing lakes. The lakes in the southern part of the Rift Valley are richer in sodium carbonate than those in the north.

The second major natural soda ash facility in Africa operates at Lake Magadi in Kenya. The 65-km² deposit is probably the largest of all those in the Rift Valley. Trona has been mined since 1914 by the Magadi Soda Co., Ltd., owned by Brunner Mond Holdings, Ltd. (formerly Imperial Chemical Industries; the parent company of Brunner Mond and Co.). The trona is excavated by bucket dredgers mounted on a floating pontoon. The ore is crushed and made into slurry so that it can be pumped through a floating pipeline to a refinery on the shore. The slurry is screened, washed, rescreened, and dewatered to remove salt and mud. The trona is calcined to remove the CO₂ and converted into soda ash. The operation has an annual production capacity of about 350 kt.

The lake bed is underlain by about 45 m of relatively pure trona with some interbedded trona and trona-bearing muds. The sodium carbonate content of the trona is approximately 45.2% and the sodium bicarbonate content is about 35.7%; this equates to ~68% sodium carbonate equivalent. Brine is found within 1 m of the surface. The alkaline spring water that delivers the sodium carbonate to Lake Magadi is considered to be the result of weathering and leaching of igneous silicate minerals (Baker 1958). Dilute groundwater from the igneous highland regions recharges a deep reservoir, which in turn supplies the warm springs with concentrated carbonate waters (Eugster 1970). The same process appears to be responsible for the alkaline waters at Lake Natron, Lake Nakaru, Lake Elmenteita, and Lake Bogoria (Orr and Grantham 1931). Based on the flow rates of the rivers and springs and the rate of evaporation, it is estimated that about 200 kt of new trona crystallizes annually in Lake Magadi (Garrett 1992).

An alkali lake is located in Malawi in a downfaulted rift basin. Alkaline hot springs and alkaline igneous intrusives in the area were the presumed source of the sodium carbonate in Lake Chilwa. Trona, or *kaum*, is found in many small lakes and in alkaline soil in Nigeria. It also accumulates as effervescent crusts on the surface of a sandy area in Dallol Bosso in western Nigeria (Garrett 1992).

Several pans in Namibia contain sodium carbonate that the local population has used for centuries. In the Owambo Basin, the two Otjiwalunda pans (No. 1 and No. 2) have been known since 1915 and contain trona (78.65%); salt (0.31%); thenardite (0.94%); and burkeite on the surface (Dutoit 1948; Schneider and Genis 1991). The deposit grades from almost pure trona to trona mixed with other salts. A rare sodium carbonate mineral, pirssonite, was reported to occur with the thenardite from the No. 2 Otjiwalunda Pan. Also in the Owambo Basin are the Ngandjela Pan and the Ngandjela East Pan, which also contain halite and trona intermixed with thenardite. The Naruunda and Onanzi pans that are also located within the region contain brines enriched with various sodium-bearing minerals. Production has ranged from 70 to 4,189 t.

The Pretoria Salt Pan in the Republic of South Africa is an extinct volcanic crater containing sodium carbonate. The first commercial development began in 1912 when the government leased to P.A. Ogilvie the rights to mine crude trona from the deposit. The lease was ceded later to South African Alkali Ltd., which mined about 400 t in 1914. Calcined trona was produced from 1915 to 1918 and refined soda ash from 1919 to 1922. Most of the calcined trona was used to neutralize the acidity of the mine water at the Witwatersrand mines (Wagner 1922). About 19 kt of trona were produced from the Pretoria Salt Pan during its brief operation.

At Bir El Natron in Sudan, a large deposit of trona is found mixed with halite and burkeite. Trona comprises about 35% of the ore body. Some production has been reported, but quantitative information is not available. Chataud (1890) reported the occurrence of trona near Fezzan in the Sahara. In Tanzania, Lake Natron is a large sodium carbonate deposit containing an estimated 150 Mt of soda ash resource covering 1,039 km². It is about 30 km south of Lake Magadi in Kenya. Total resources may be about 1 Gt when including the additional sodium carbonate brines and crystals intermixed with mud layers. Lake Natron lies in the eastern Rift Valley, which contains additional sodium carbonate deposits in other countries. The brine concentration and composition of Lake Natron is nearly identical to that of Lake Magadi in Kenya. The source of the sodium carbonate in Lake Natron originates from three carbonatite volcanoes, including the active Oldoinyo Lengai volcano, which erupts with sodium carbonate lava and ash. Several studies have been made to develop the deposit, the most recent in 1990. Lake Eyasi in Tanzania is also an alkaline lake that has produced some crude soda ash on a limited scale.

Lake Katwe in Uganda contains trona, burkeite, and hanksite that formed when about 50 small springs reacted with carbonatite and other volcanic rocks in the area. Approximately 5 kt of crude trona are recovered from the lake annually.

Antarctica

Although there are no reported deposits of trona on this continent, occurrences of efflorescences of various sodium salts have been documented in the Vestfold Hills, Bunger's Oasis, and McMurdo Sound regions (Dort and Dort 1970). Some evaporite minerals found are halite, mirabilite, thenardite, and bloedite, which are commonly associated with sodium carbonate deposits elsewhere in the world.

Asia

China, Mongolia, India, Pakistan, Tibet, and the former U.S.S.R. are known to have several sodium carbonate occurrences. Some of the geologic and mining information regarding sodium carbonate deposits in Asia is old, nonexistent, or unavailable for many of the occurrences. Some new information was published within the past decade and is included here.

More than 50 sodium carbonate deposits have been reported in China. China has several alkali lakes and at least two major buried trona deposits, in the 265-km² Wucheng Basin and at Anpeng in the 13-km² Biyang Basin, both in Henan Province.

The Eocene Wucheng deposit was discovered in 1971 during petroleum exploration. The deposit contains 36 trona horizons that are interbedded with oil shale and argillaceous dolomite (Lu 1998; Zhang 1998). They cover 4.66 km² and are buried 643–974 m below the surface. The lower 15 trona beds typically are 0.5–1.5 m thick, with a maximum of 2.38 m. These beds contain 40%–60% sodium carbonate and 0.3% sodium chloride. The upper 21 beds contain halite and are generally 1–3 m thick, with a maximum of 4.56 m. These beds contain 20%–40% sodium carbonate and 20%–60% sodium chloride. Resources are reported to be 37 Mt of sodium carbonate equivalent. The deposit is solution-mined and feeds a soda ash plant.

The Eocene Anpeng nahcolite deposit was discovered in 1976 during petroleum exploration. It is 60 km southwest of the Wucheng trona deposit. The nahcolite beds occupy 8 km² at depths of 1.3–2,520 m (Lu 1998; Zhang 1998). Seventeen nahcolite beds ranging from 0.6 to 3.6 m in thickness have been identified. They are associated with oil shale, dolomite, and sandstone. This deposit is also solution-mined to produce soda ash. Northwest of the area of the nahcolite beds, sodium bicarbonate and sodium carbonate brines occur in porous dolomite in beds 1–5 m thick. The nahcolite beds range from 48% to 95% sodium bicarbonate and up to 40% sodium carbonate.

Several soda lakes or *nor*s are found in Inner Mongolia, such as in the Ju League and Xilin Gol League, and in other areas of China, such as in Hami in Xinjiang Province. The Quaternary Qagan Nur deposit, also known as the Chaganor deposit in Inner Mongolia, contains 11 Mt of sodium carbonate and is the largest. It occurs in a basin with an area of 21 km². Nine trona beds ranging in thickness from 0.6 to 3.47 m are present. Sodium carbonate content ranges from 26% to about 29%. The main minerals are trona and natron associated with mirabilite and halite. This deposit also supplies feedstock to a soda ash plant. Zhang (1998) describes other small deposits—the Ordos alkali lakes in Inner Mongolia.

Sodium carbonate is found with mixed salts in India in alkaline soils, lakes, and brines. Sambhar Lake and Lonar Lake, which is the world's only known basalt impact crater, contain about 22 Mt of soda ash reserves (Fredriksson et al. 1973). Lonar Lake contained about 85 m³ of brine in 1910 and produced about 600 t of soda ash in 1903. Up to 20 kt of crude trona was mined annually from various sources at different times in the 20th century.

In Pakistan, several hundred small shallow lakes contain sodium carbonate, chloride, and sulfate. Some of the lakes have trona crusts and natron, which crystallizes during the winter.

Several sodium-carbonate-bearing lakes such as Zabuye Caka, Bangkog Cuo, and Guogaling Cuo are reported in the Qinghai-Xizang Plateau of Tibet. Trona, natron, the monohydrate, halite, northupite, mirabilite, and hydromagnesite are commonly associated with the brine. Potassium, lithium, rubidium, and cesium alkali metals are associated with sodium chloride, sulfate, and carbonate ions—similar to the chemical composition of Searles Lake, California, and certain lakes in South America.

The Kazakhstan and the Kulundinsk depression of Altay near Slovgorod and Barnaul in Siberia have produced some natural soda ash from alkali lakes containing natron and brine. Alkali lakes have also been reported near Chita in eastern Siberia; in the Araxes Plain of Armenia; in Kazakhstan; in Krasnaya Polyana, the Kazakh-Tauz region of Azerbaijan; and in the Carpathians. Most of these lakes are too small and remote for large-scale commercial development.

Plants to produce soda ash from natural soda sources have been built at Lake Tanatar and the Petukhov Lakes, both near Mikhaylovskiy (Batalin, Stankevich, and Kasimov 1974). Natural soda ash production in the former U.S.S.R. reached its peak in the 1950s with only about 60 kt of output (Shabad and Sagers 1987). Soda ash has also been produced as a by-product of alumina refining from nepheline syenite (a sodium–potassium–aluminum silicate) at several locations, including the Pikalevo plant in Leninograd Oblast. The Kola Peninsula is the primary location where the nepheline syenite is a coproduct with apatite. The nepheline is sintered with limestone in rotary kilns to produce alumina, soda ash, potash, and cement. The alumina content in the nephelinite was only about half that of bauxite; the process was considered to be economical because it produced coproducts.

Australia

Although salt pans containing sodium chloride and sodium sulfate are common in Australia, there are no significant surface occurrences of sodium carbonate. Alkaline springs occur near Herbertson, Queensland. In the Bowen and Sydney basins of Queensland, dawsonite has been found, some of which reportedly occurs as alterations of other minerals from sodium carbonate mineralization formed by the leaching of alkaline or ultrabasic rocks.

A sodium bicarbonate bearing brine (1.6%–2.5% NaHCO_3) was discovered at a depth of 600–1,100 m while exploring for petroleum. Resources have been estimated to be between 500 Mt and 1 Gt of sodium carbonate equivalent. Additional exploration and drilling may locate a trona or nahcolite source of the brine.

Europe

Saline and alkaline lakes are not common in Europe because the present climate is not conducive for development. Sodium carbonate efflorescences have been reported near Szeged in the Danube Valley in Hungary. Chatard (1890) reported processing of the crude soda (known as *szekso*) into refined soda ash. Alkaline brines have been found in Fulophasa, Hungary, at depths of 30 m. Trona and searlesite have been reported in Miocene lacustrine marls and clays in northern Bosnia.

Turkey is the third country in the world that has known buried trona deposits. The Beypazari deposit is approximately 100 km northwest of Ankara. The deposit was discovered in 1982 during drilling for lignite. Based on drilling, the deposit covers about 8 km² in the Beypazari Basin. The trona is associated with shale in the lower part of the Miocene Hirka Formation. Trona beds were deposited as two lens-shaped bodies within a zone 70–100 m thick in the lower part of the shale unit. A total of 33 trona beds have been identified: 16 in the lower trona lens and 17 in the upper lens. The total thickness of the lower trona sequence is from 40 to 60 m, and the total thickness of the upper trona sequence is about 40 m. The interval between the lower and upper lenses ranges from 30 to 35 m. The total thickness of trona beds in both lenses varies between 21 and 34 m in the central part of the deposit and between 2.5 and 12 m along the margins. The thickness of individual trona beds in both horizons ranges from 0.4 to 2 m. The principal sodium carbonate minerals are trona and nahcolite. Sodium oxide content of the trona ranges from 37% to about 42%, and the nahcolite content ranges from 30% to approximately 36%. Proven reserves are estimated at 210 Mt (Helvacı 1998). Feasibility studies and joint venture proposals to develop the Beypazari resource have been conducted since the mid-1980s. In 1983 the state-owned mining group Etibank (later named Eti Holding) held the trona deposit. Eti Holding sought a private-sector partner in 1998. The Park Group was awarded 76% interest, with Eti Holding a 22% share, and the state-

owned Vakıfbank was awarded a 2% share in Eti Soda. In 2004, the Export–Import Bank of the United States received an application to finance \$50 million in U.S. equipment and services to construct an operation that would have an annual production capacity of 1 Mt of soda ash. There was no decision regarding the status of the project by the end of 2004 (*Industrial Minerals* 1999, 2002; Kostick 1999, 2002, 2004).

Rio Tinto Madencilik (a subsidiary of Rio Tinto Minerals Development Company) discovered a second deposit in 1998 at Kazan, about 35 km northwest of Ankara. The deposit contains 12 trona beds that range in depth from 420 to 850 m, with estimated resources of 607 Mt at an average grade of 31% trona. The deposit is low grade in comparison to the Green River, Wyoming, trona deposit. The trona will be solution-mined using directional horizontal drilling technology. This technology is currently being used in the Piceance Creek Basin, Colorado, to mine nahcolite. Beginning in 2004, Rio Tinto initiated a 3-year pilot project to determine the viability of solution mining. Small-scale production is planned to begin in 2007, with projected startup of a 900-kt py soda ash plant scheduled for 2011 (*Industrial Minerals* 2002, 2003a; Kostick 2002, 2003).

North America

Soda ash occurs in natural deposits found in Canada, Mexico, and the United States. The largest trona resource discovered to date is near Green River, Wyoming.

Canada. There are several small soda ash deposits in British Columbia, in western Canada. They tend to be located in the same zone that extends into the saline lakes of Washington. Commercial production of soda ash was reported from some of the deposits between 1928 and 1945. Most of deposits are located in shallow basins in glacial drifts overlying basaltic lava flows. The sodium carbonate is primarily found in brines with some surface crystal layers and crusts. Cummings (1940) estimated that the soda lakes in British Columbia contained about 103 kt of sodium carbonate reserves.

Mexico. Several alkaline thermal springs, subsurface brines, thin crusts, and surface efflorescences contain sodium carbonate in various locations in Mexico. Until it was closed in 1994, the only other natural soda ash operation in the Western Hemisphere outside the United States was at Lake Texcoco, 20 km northeast of Mexico City at San Cristóbal Ecatepec. In about 1900, three lakes comprised a large part of the region: Texcoco, Xochimilco, and Chalco. The last two contained potable water, whereas Texcoco consisted of brackish water. Fearing that Mexico City might be flooded, Texcoco was allowed to dry by diverting feeder streams to canals. The hot climate accelerated the evaporation rate and concentrated the brines that percolated down through the lake-floor clay sediments. The brine tends to concentrate on top of two impermeable zones about 53 m deep. The upper zone is richer in sodium carbonate and contains about 120 Mt of sodium carbonate resource, whereas the lower zone contains about 40 Mt. Additional sodium carbonate probably was introduced by local volcanic activity from two volcanoes—Popocatepetl and Ixtaccihuatl—120 km to the south of the deposit. Andesitic volcanics also occur east and west of Mexico City. The resource covers about 52 km².

A small pilot plant was constructed in 1940, and production of soda ash began in 1948 with a capacity of about 100 tpd. More than 512 wells in the deposit collect the subsurface brines, which are sent to a spiral solar evaporator that is 841 ha in area and 50–60 cm deep. The incoming brine was concentrated from 4% (sodium carbonate content) to 6%–7% in the rainy season and 9%–10% in the dry season. Weaker brine would stay in the outside perimeter of the

concentrator for about 1 year and in the inside perimeter, where the maximum concentration occurred, for about 6 months. The concentrated brine was pumped from the center of the spiral concentrator to the nearby soda ash refinery where it was carbonated into sodium bicarbonate and then calcined into soda ash. Until September 1988, a subsidiary of a government-controlled holding company operated the facility. In 1994, a private group owned the 200-ktpy operation.

Another sodium carbonate resource in Mexico is located at Bahia de Adair on the northern coast of the Gulf of California; it was first described in 1898. The area consists of four small playa lakes. The highest concentration of sodium carbonate occurs at depths from 6 to 19 m. Crusts on the surface average about 31% sodium carbonate. Exploration of the area did not detect any significant buried trona deposit. In 2002, Minera MGM de CV (a wholly owned subsidiary of Morgan Minerals, Inc., of Toronto, Canada, and Productos Químicos Roda SA de CV of Torreón, Coahuila, Mexico) formed the joint venture company, Tronamex SA de CV. The company planned to develop the Adair trona deposit in Sonora, approximately 20 km north of Puerto Penasco on the east coast of the Sea of Cortez. Resources are estimated at 100 Mt, of which about 80% is in subsurface brines. The initial plan is to mine a shallow trona bed (0.3–2 m thick) and to solar-evaporate brines to produce an animal-feed additive. The company produced a small amount of product in 2003 and 2004 (*Industrial Minerals* 2001, 2003b; Kostick 2001, 2003).

Other occurrences in Mexico are deposits in Chihuahua; the Durango, Sayula, and Zatecas basins; Lake Cuitzeo; Valle de Santiago; and Laguna de Xaltocan and Laguna de Zumpango, both in the Valley of Mexico (Garrett 1992).

United States. Sodium carbonate occurrences are found in Alaska, California, Colorado, Nebraska, Nevada, Oregon, Utah, Washington, and Wyoming.

Near Owens Lake, California, human activities since the early 1860s have resulted in several episodes of high evaporation. In conjunction with the lack of outflow from Owens Lake, these episodes caused the deposition of saline minerals such as trona and associated sediments. Between 1861 and 1917, increased withdrawals from the Owens River for agricultural purposes greatly reduced water inflow to the lake. In 1913, the Los Angeles Aqueduct was completed, which diverted virtually all the remaining Owens River flow from Owens Lake. By 1926, Owens Lake had reached its current condition, which is essentially dry with small areas of highly concentrated brine occurring at certain times on the surface of the lakebed. Owens Lake is 4.9 km long by 3 km wide with an area of 87 km².

From 1960 to 1993 various companies drilled more than 1,000 auger, drive-pipe, and core holes. Based on the drilling data, the evaporite deposit has a maximum thickness of 3 m. The evaporite deposit is exposed at the surface and consists of various horizons of crystalline material overlying lake-bed sediments. In cross section, the deposit is lenticular, with the thickest section near the western side of Owens Lake (Santini and McCormick, unpublished data; Brown, Lamos, and Scarr 2004).

Approximately 70% by weight (or 65% by volume) of the porous evaporite deposit comprises various minerals, and about 30% by weight (or 35% by volume) is interstitial brine. Trona is the predominant mineral present in the evaporite section. Other minerals are burkeite, thermonatrite, and halite. The chemical composition of the evaporite deposit is 41.5% sodium carbonate and 25.0% sodium bicarbonate; this equates to ~57% sodium carbonate equivalent. In addition, various amounts of sodium chloride and sodium sulfate are present. The most recent reserve estimate

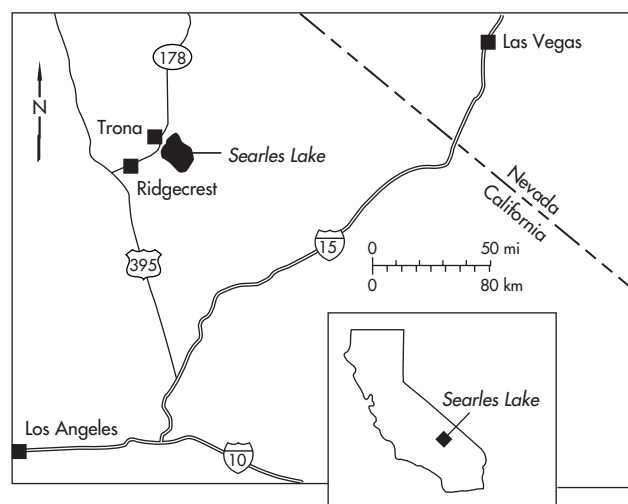


Figure 1. Location of Searles Lake, California

(1996) is 100 Mt of evaporite minerals in situ, of which approximately 52 Mt of sodium carbonate equivalent is present.

The first natural soda ash operation in California began in 1887 at Keeler, on the northeast shore of Owens Lake (Ver Planck 1959). The Inyo Development Co. constructed solar evaporation ponds that were filled with lake water at the beginning of warm weather. The brine was allowed to evaporate until it reached a density of 30°Be, after which trona began to crystallize. If unwanted salts began to form, the operator drew off some of the mother liquor and replaced it with fresh lake water. At the beginning of October, the ponds were drained and the harvesting of trona, which was about 1.9 cm thick, began. The trona was converted to a 95% pure soda ash product by heating it in beehive furnaces to remove the water of crystallization and excess carbon dioxide contained in the sodium bicarbonate. By 1900, Inyo had an annual capacity of 10 kt. Other natural soda ash companies set up operations on the perimeter of Owens Lake in the early 20th century and prospered for several decades until the late 1960s, when competition from Wyoming natural soda ash increased. Lake Minerals Corp. controlled the deposit in 1981, when Cominco American, Inc., acquired the company. In 1989, Cominco and Vulcan Chemicals formed the joint venture company, Owens Lake Soda Ash Co. The objective was to begin soda ash production by 1997, but, eventually, the decision was made not to proceed, and subsequently Lake Minerals was acquired by U.S. Borax Inc. In 2005, Lake Minerals Corp. mined crude trona from the surface for use at its Boron, California, operation as a reagent in the production of borate products.

Searles Lake, California, is a large playa lake deposit occupying the lowest part of Searles Valley, a closed structural basin filled with alluvium and nonmarine evaporates (Moulton and Santini 1995). The playa lake deposit is 16 km long by 10 km wide with an area of about 104 km² (Figure 1).

In Searles Lake, brine-bearing evaporite horizons alternate with mud beds. Three major subsurface evaporite horizons have been identified and are termed, from bottom to top, the Mixed Layer, Lower Salt, and Upper Salt. The evaporite beds were formed by desiccation of runoff from the eastern Sierra Nevada during Quaternary time. The resulting beds are generally thicker in the lake center, then thin and pinch out at the edges of the lake.

The saline beds are generally brine saturated, white to pink, hard, and very porous. The important ions are sodium, potassium,

carbonate, bicarbonate, sulfate, chloride, and borate. These ions are present in the brines in various concentrations, and combine to form the major evaporite minerals trona, nahcolite, halite, hanksite, burkeite, borax, theardite, sulfahalite, and glaserite. The mud beds, in general, are dark green to brown, soft, porous, and may have a distinct mercaptan (rotten egg) odor. The stratigraphic section from bottom to top is as follows:

1. The Mixed Layer is a sequence of mud and evaporite beds about 67–95 m below the surface. The lower Mixed Layer is divided into several units based on mineral composition. These deeper beds contain trona, but also halite and theardite. The upper Mixed Layer is divided into several units based on differences in electrical conductivity and mineral composition. These horizons are predominantly trona, which are solution-mined for soda ash production.
2. The Bottom Mud is 30 m or greater in thickness and forms a bowl-shaped body composed of mud beds containing saline minerals.
3. The Lower Salt ranges in thickness from approximately 12 m in the playa lake center to zero at the edges. The unit is composed of seven evaporite beds separated by six mud beds. These evaporite horizons are predominantly trona and halite, although borax, burkeite, nahcolite, and northupite are also found.
4. The Parting Mud is 3 m thick in the playa lake center and thickens to 8 m or more toward the edges, and contains some saline minerals.
5. The Upper Salt ranges from 23 m at the playa center to zero along the edges. The horizon can be divided into two units. The lower unit is generally thinner in the playa center and thickens toward the edges, before it pinches out. It is composed mostly of trona and halite, with minor amounts of burkeite and theardite. The upper unit is thickest at the playa center and thins toward the edges. It is composed of halite and hanksite, with some trona beds, and minor amounts of borax and sulfahalite.
6. The Overburden Mud consists of a central halite facies, approximately 7 m thick, which grades toward the edges to a mud facies that is up to 10 m thick.

The Searles Lake sodium carbonate resources have been reported to be 1.06 Gt. In addition, there are substantial resources of sodium borate, sodium sulfate, potash, and sodium chloride (Fairchild, Lovejoy, and Moulton 1998). The sodium carbonate content of the brines are Mixed Layer, ~6.5%; Lower Salt, ~5.5%; and Upper Salt, ~4.4%.

John Wemple Searles, who discovered borax crystals on the surface in 1862, first recognized the economic potential of Searles Lake. Although he and his brother Dennis formed the San Bernardino Borax Mining Co. in 1873, it was not until 1908 that the California Trona Co. was formed to produce soda ash using the equipment from the Searles' old borax plant. The operation never succeeded, and the plant went into receivership in 1909. The American Trona Corp. was organized on June 12, 1913, and acquired the properties of the California Trona Co. An embargo on German potash because of World War I prompted the company to produce potash rather than soda ash. On June 4, 1926, the American Potash and Chemical Co. (which acquired American Trona Corp.) was formed, but it was not until 1931 that the first soda ash was produced at the Trona plant. The company merged with Kerr-McGee Chemical Corp. on December 29, 1967. Soda ash production at the Trona plant ended in July 1979 because of equipment obsolescence and rising operating costs, and because the company brought onstream

its Argus soda ash facility, adjacent to the Trona plant, which continued to produce boric acid, potash, and sodium sulfate coproducts.

The Argus plant was designed to produce only natural soda ash. It was commissioned in July 1978 and currently has a nameplate capacity of 1.45 Mt.

Kerr-McGee also operated a second soda ash plant known as the Westend plant that it acquired from Stauffer Chemical Co. in October 1974. The plant originally was built in 1918 to produce borax but experienced operating problems. Borax was successfully produced in 1926 and soda ash in 1927 by the Westend Chemical Co., which ultimately merged with the Stauffer Chemical Co. in 1956. The operation continued to produce soda ash until January 1988. Kerr-McGee sold all the Searles Lake facilities to North American Chemical Co. on December 1, 1990. IMC Global acquired the chemicals and salts businesses in 1998 and in 2004 sold these interests to Searles Valley Minerals.

The Piceance Creek Basin is located in northwestern Colorado. It has an areal extent of approximately 18,700 km². The basin contains the second-largest known sodium carbonate resource in the world. Potential sources of sodium carbonate are nahcolite and dawsonite (sodium–aluminum carbonate). The Parachute Creek Member of the Eocene Green River Formation contains nahcolite, dawsonite, and halite (saline minerals) associated with oil shale. These saline minerals are found primarily in the north-central area of the Piceance Creek Basin. The saline minerals are generally limited to the lower part of the Parachute Creek Member. The main concentration of nahcolite occurs in the Saline Zone that has a maximum thickness of about 335 m. This zone contains oil shale, oil shale with disseminated nahcolite (crystals and crystal aggregates), bedded nahcolite, and bedded halite. There are 26 nahcolite horizons present in the Saline Zone. Only the Boies, Love, Greeno, and TI beds, however, are greater than 60% nahcolite and greater than 2 m in thickness. The Boies bed is the highest quality and has the greatest thickness of all the nahcolite horizons. It contains about 80%–85% nahcolite and is up to 9 m thick. It is currently solution-mined for sodium bicarbonate. Past solution mining for sodium carbonate production targeted the Saline Zone with 23% nahcolite and less than 1% halite. The nahcolite-rich Boies bed is not present in this area. As a result, the minable horizons are oil shale with disseminated nahcolite and the thinner nahcolite beds (i.e., the Love bed, etc.) previously mentioned (Santini, unpublished data; Day and Santini 1997; Day 1998; Hardy et al. 2003).

Resources of 29 Gt of nahcolite and 17 Gt of dawsonite, equivalent to 18 and 6 Gt, respectively, of soda ash resources, are available as single-mineral extraction or as a by-product of oil shale processing (Dyner 1980). Commercial development to mine nahcolite in conjunction with oil shale was proposed in the early 1980s; leasing obstacles and economic problems, however, prevented successful commercialization. Single-mineral extraction using solution mining on sodium leases began as a pilot program in the mid-1980s; large-scale development did not begin until the late 1980s, however, but was subsequently stalled because of declining market conditions for nahcolite used for flue gas desulfurization. In 1989, NaTec Ltd., a partnership between Industrial Resources Inc., and CRS Serrine, was formed to solution-mine nahcolite for sulfur dioxide scrubbing applications. The company experienced difficulties because of depressed markets. In 1992, North American Chemical Co. acquired 50% of NaTec's interest in the project, creating White River Nahcolite Minerals, Ltd. In 2003 Amerasia, Inc. partnered with The Sentient Group, an experienced international resource investment company, to acquire the company from IMC Global, the acquisition taking place through Amerasia's subsidiary, Natural Soda, Inc. This operation was later

sold and is currently being operated by Natural Soda, which produces sodium bicarbonate.

During the late 1990s American Soda LLC was founded to produce both sodium carbonate and sodium bicarbonate from this nahcolite resource. The operation continued under the ownership of American Soda until September 2003, when Solvay Chemicals purchased the assets. Solvay Chemicals continued to produce both soda ash (0.9 Mtp y capacity) and 90 ktp y of sodium bicarbonate until the summer of 2004, at which time the soda ash production facility was closed and the nahcolite feed shut down. Today the unit continues to produce sodium bicarbonate from soda ash from Green River.

The buried deposit in Green River Basin, Wyoming, is the largest trona resource in the world, covering more than 3,100 km² in southwest Wyoming. It is the result of the repeated evaporation of Lake Gosiute, a freshwater lake that formed in the Eocene epoch, and named by Clarence King in 1878 after a group of Native Americans who inhabited this area. The sodium and the carbonate constituents of trona owe their respective origins to the leaching of the extensive pyroxene-andesite volcanic ash horizons and the seasonal influxes of carbonate-rich sediments into the local depositional basin. Subsurface thermal springs also contributed a significant quantity of dissolved alkaline carbonates as well as sodium, calcium, silica, and bicarbonate ions. Trona can precipitate only in the presence of abundant carbon dioxide, which most likely was supplied from the atmosphere or the biogenic decay of Eocene plant and aquatic remains (Bradley and Eugster 1969). Leigh (1998) and Garrett (1998) contain additional information about the formation of trona in the Green River basin.

The Wilkins Peak Member (~ 410 m thick) of the Eocene Green River Formation contains 42 trona beds, 25 of which exceed 1.22 m in thickness and 175 km² of area. Eleven of these beds exceed 1.83 m in thickness. The beds dip slightly to the southwest, and are numbered from bottom to top. The center of trona deposition in the basin moved northward with time. Bed 1 was deposited the farthest to the south and Bed 25 about 40 km to the north. Halite, thin interbeds of sediments, and organic matter are the principal impurities within the trona horizons. The halite appears to occur most frequently in beds 5–18 and generally south and west of most of the producers. It has not been reported in beds 1, 4, 8, or any bed above 19. In the production areas, the chloride content is nearly always less than 0.5%. This is generally attributed to the mineral northupite, which occurs in thin shale stringers within the trona beds. The beds that have been mined (17, 19, 20, 24, and 25) contain 85%–95% trona, less than 15% insolubles, and less than 0.5% Cl, at depths ranging from approximately 240 to 520 m (Bed 25 to Bed 17). Beds 12 and 14 appear to contain minable trona directly beneath some of the current workings (Brown 1995; Wiig, Grundy, and Dyni 1995; Dyni 1997; Santini, unpublished data).

Many investigators have studied, described, and mapped the Green River trona deposit, and Wiig, Grundy, and Dyni (1995) did the most recent resource evaluation. Their resource estimates were derived using drill logs and geophysical information. The total resource is estimated to contain 127 Gt of trona in 22 beds greater than 1.22 m thick. Assuming that 1.8 t of trona yields about 1.0 t of soda ash, about 71 Gt of soda ash resources could be potentially obtained from the 76 Gt of bedded trona and the 51 Gt of interbedded or intermixed trona and halite that are in beds greater than 1.22 m thick. The resource occurs between 220 and 1,000 m below the surface in beds that range in area from 130 to 2,200 km² (Wiig, Grundy, and Dyni 1995).

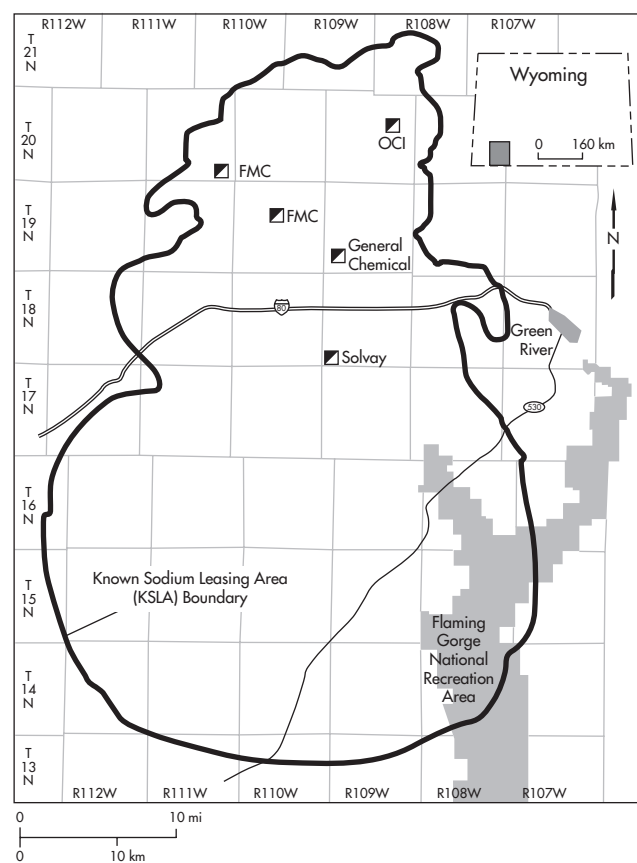


Figure 2. Trona and soda ash operations in Green River Basin, Wyoming

Because this deposit is the most important geologic sequence of trona deposition currently known in the world, it will continue to supply soda ash for world consumption for centuries to come. Figure 2 shows a map of the Green River Basin with the approximate boundary of the known sodium leasing area and the location of the four soda ash producers (Solvay Chemicals, FMC Wyoming, OCI Chemical, and General Chemical).

The Yukon Flats basin of Alaska contains a series of shallow saline and freshwater lakes. Potash salts in the area have been known since 1929. In 1978, trona samples were identified in efflorescent crusts about 1 cm thick in certain lake margins and dry lake beds. The lakes trend in a northeasterly direction and occupy an area of about 240 by 48 km.

Although the sand hills area in northwestern Nebraska has numerous small lakes that contain primarily potassium carbonate, sodium carbonate occurs in some of the alkaline lakes. In Jess Lake, the sodium carbonate content is about 36% (Barbour 1916). Water draining through the sandy soils collects at the bowl of impervious mud bottoms.

Sodium carbonate also occurs in several lakes in south-central Oregon. Abert, Alkali, and Summer Lakes contain the most sodium carbonate of all the late-Pleistocene lakes in the region. Alkali Lake apparently was mined for a period beginning in 1955 by A.M. Matlock (*The Ore-Bin* 1955). Deposits of mixed salts formed in pot-holes, which were small brine pools where the brine was evaporated and the salts precipitated from the concentrated solution. The potholes resembled those formed in some Canadian lakes,

such as those in La St Chance Lake. Natron, sodium chloride, sodium sulfate, and some potassium salts were obtained from the deposit. Approximately 100 t had been mined by September 1955.

Trona, nahcolite, and other authigenic sodium minerals have been found while core drilling in the southwestern part of the Uinta Basin near Duchesne, Utah. The bedded deposit, with a maximum thickness of about 34 m, has an area of about 223 km² and lies about 73 to 128 m below the surface. Because the deposits are deep, solution mining would probably have to be used if this deposit were developed. Although current data indicates that this location contains less trona than in the Green River Basin in Wyoming and less nahcolite than in the Piceance Creek Basin in Colorado, the presence of sodium carbonate-bearing springs indicates the possibility of larger commercial deposits in the region (Dyni, Milton, and Cashion 1985).

Washington has several sodium carbonate deposits in lakes in the north-central portion of the state. The lakes with the highest sodium carbonate content are Mitchell Lake (5-ha area), Omak Lake (1,550-ha area), Soap Lake (350-ha area), and Salt Lake. These lakes contain varying concentrations of sodium salts, including natron, gaylussite, sodium chloride, and Glauber's salt. Carbonate Lake and Mitchell Lake produced commercial soda ash before World War II. Carbonate Lake was permanently flooded in 1950 when a dam was constructed as part of the Columbia irrigation project. The deposit no longer exists as a sodium carbonate resource (Bennett 1962).

Other sodium carbonate occurrences have been reported in Arizona, Montana, and North Dakota; detailed information regarding their geology, however, is scarce.

South America

Although South America has some of the world's largest salars (salt pans), it apparently lacks significant resources of natural sodium carbonate. Salars occur at high and low elevations, but most of the known surface salts are sulfate or sulfate-chloride varieties. Occurrences have been reported in the Los Andes Province of northwestern Argentina; in Bolivia; western Minas Gerais in Brazil; Chile; southern Peru; and Venezuela. The sodium carbonate deposits that occur in the area where Argentina, Brazil, and Chile meet are small and are considered economically insignificant (Catalano 1926; Cordini 1967).

Approximately eight sodium carbonate occurrences are found in the Santa Cruz Province of Argentina. Perhaps one of the best described deposits in the area is the Salina Juan Domingo play a lake, which averages 56.3% sodium carbonate and 8.3% sodium bicarbonate (Bernasconi and Cangioli 1982). Natron occurs on the surface, with trona and other carbonates found in the bottom muds. The dry lake bed may contain about 1.5 Mt of sodium carbonate equivalent. La Ernestina Lake in the Ultracan area and other nearby lakes such as Laguna el Carancho in La Pampa are reported to contain sodium carbonate (Cordini 1967).

Two alkaline lakes in Bolivia contain sodium carbonate: Cochi Laguna, 50 km south of Chiquana, which contains a trona and thermonatrite crust 6–10 cm thick, and Collpe Laguna, east of Salar de Chaivira. Collpe Laguna is a lake with an alkaline crust and contains subsurface sodium-carbonate-bearing brine in the bottom muds.

Several sal lakes occur in the Upper São Francisco area northeast of Brasília, Brazil. Some of the lakes contain soda ash crusts and shallow brine, with the average content ranging between 23% and 41% sodium carbonate. Sodium carbonate occurrences also are found in Urucuia, Carinhanha, Rio Correntes, and Rio Grande.

Trona and gaylussite occur in the surface crusts of the Lago de Laguinillus Valley of Venezuela. The salts average about 47% sodium carbonate. Between 50 and 80 t/y of crude trona (*urao*) have been produced by local residents. Another deposit is located at Urao Lagoon.

TECHNOLOGY

Exploration and Evaluation of Deposits

In formulating an exploration program for trona, it is essential to review the geologic characteristics of the deposits of the Green River Basin, Wyoming; Searles Lake, California; and Owens Lake, California. Vine and Santini (unpublished data) developed a list of factors favorable for the occurrence of buried and playa lake trona deposits:

- Green River Basin model (buried deposit)
 - Sedimentary basin containing nonmarine sediments
 - Lacustrine facies, including fine-grained, laminated sediments
 - Oil shale or similar organic-rich sediment of algal origin
 - Evaporite minerals, including shortite, pirssonite, gaylussite
 - Travertine algal mounds, bioherms, stromatolites, spring pots
 - Gypsum is absent or rare; other sulfates are minor
 - Alkaline spring or well waters; efflorescences in soil
 - Authigenic minerals, including magadiite, lacustrine clays, fluorite, potassium feldspar, zeolites
 - Altered volcanic ash, especially zeolitized
 - Evidence of solution, including collapse, brecciation
- Dyni (1998) discusses exploring for Green River type deposits.
- Searles Lake and Owens Lake model (playa lake deposit)
 - Closed basin with more than 2 km² of playa surface
 - Arid climate (high shorelines above present playa)
 - Organic-rich muds, odor of H₂S
 - Evaporite minerals or salts present
 - Authigenic minerals such as zeolites, fluorite, stevensite, hectorite, magadiite, opal
 - Travertine algal mounds, bioherms, stromatolites, spring pots
 - Gypsum absent or rare; other sulfates minor
 - Alkaline pH
 - Volcanic + crystalline terrain > sedimentary terrain in drainage basin
 - High geothermal gradient or thermal springs present

If a target justifies further exploration and evaluation, the next phase is a drilling program. Core drilling is the recommended method for both buried and playa lake-type deposits. Downhole geophysical logging methods, chemical analysis, x-ray diffraction, and so forth are also employed to evaluate both types of deposits.

In the Green River Basin, core drilling has been supplemented by downhole geophysics, including gamma ray, sonic, caliper, neutron, and rock density. The gamma-ray logs are used to determine trona thickness in conjunction with the lithologic logs.

X-ray diffraction is used to determine the mineralogy of the core samples. Typical chemical analyses include CO₃, HCO₃, Na, Ca, Mg, K, Cl, SO₄, and water insolubles. The trona content can be determined by titrating the water-leachable portion of core samples. Specifically, percent trona can be calculated from soluble Na₂CO₃, NaHCO₃, or Na₂O.

In the lake deposits of the Sevier Lake (brine-saturated evaporite), both core and brine samples are collected. After coring through an evaporite horizon, investigators collect brine samples by setting a packer and swabbing the hole. Drill core is subjected to x-ray diffraction and the same suite of chemical analyses described for Green River (i.e., CO_3 , HCO_3). In addition, acid insolubles and boron are determined at Sevier Lake (produces borate products also). The brine samples are subjected to the same suite of chemical analyses (minus insolubles) as the core samples. Specific gravity is also determined. Additional test work for selected core samples includes effective porosity and horizontal permeability determinations (Santini 1987). Downhole geophysical logging methods described for Green River are also used at Sevier Lake.

Mining

The Intermountain Chemical Co., a subsidiary of the Food Machinery Corp. (now FMC Corp.) began commercial mining of Wyoming trona in 1948. Because trona is similar to coal, except that trona is somewhat harder, early trona mining used some of the conventional coal-mining equipment. As mining technology improved over the next few decades, newer equipment—such as continuous miners—was adapted for trona mining in the early 1960s. Longwall mining, shortwall mining, and solution mining were introduced in the early 1980s. Dredging of sodium carbonate minerals from tailing ponds, another type of mining, began about 1985.

All Wyoming trona mines use room-and-pillar mining with multiple entry systems. Most have used one or more types of mining (conventional, continuous, longwall, shortwall, or solution). Two of the mines, FMC and Solvay, currently (2005) use the longwall method in addition to continuous mining. In addition, each company normally has several crews operating at different places in the mine during a production shift. Normally, room-and-pillar mining has an ore extraction efficiency rate of about 45% (the remaining 55% of ore remains as pillars for structural integrity). The pillars are part of the reserve base used for economic evaluation of ore reserves.

Extraction rates vary as does the depth of mining. Rooms are mined to form panels of varying dimensions, depending on the type of mining technology used. The heights and widths of the rooms and pillars depends on several factors, including the trona bed thickness, local conditions, and the depth of the particular mine. The deeper the mine, the greater the overburden pressure on the pillars, which may need to be larger to support the overlying strata. Usually pillar dimensions are greater in areas of long-term support, such as near main production and ventilation shafts and main entries. Removing the trona creates about 2 m of subsidence on the surface, although it is virtually unnoticeable. An average pillar measures about 21×24 m. The maze of interconnecting underground workings in each of the five Wyoming mines is extensive. FMC, for example, has more than 3,200 km of underground streets in its 39-km² area—more than the total length of the aboveground streets in San Francisco.

Conventional mining had been the primary method of mining trona ore but continuous mining is gradually replacing it. No conventional production is operating in the Green River basin today; currently, all production is by continuous miners, longwall, or solution.

In 1960, two European mining methods were introduced to Wyoming: the French, or pseudo-longwall, method and the English, or pseudo-shortwall, method. Both used a combination of borer miners and conventional equipment. Mining problems were reduced once extraction was limited to about 50%. Basically, two types of continuous miners are used: the drum-type and the borer-

type. The drum-type miner is used for short- to medium-life mine developments (10–18 years). Each mine operates on the advance and retreat methods; therefore, it is imperative that parts of the development remain in good condition for worker safety, ore haulage, and air ventilation requirements. Today either shuttle cars or continuous haulage units transport the ore cut by a continuous miner to the conveyor belt for haulage from the mine.

Boring machines mine long-term mainline entries (>30 year life) in some of the mines. The oval opening cut by these miners is more stable and has a longer life than the rectangular opening cut by a drum-type miner. The maximum single-pass boring machine opening is approximately 2.7 m high \times 4.9 m wide. Productivity has continued to increase as cutting-head designs have improved and haulage systems have been upgraded. Boring machines are now used for the short- and medium-life mine developments in conjunction with the drum-type miners.

Both FMC Wyoming Corp. and Solvay Chemicals, Inc., are the only natural soda ash producers that use longwall mining to augment their mining technology. Allied Chemical Co. (now known as General Chemical Corp.) was the first company to use longwall mining beginning in 1973 but abandoned the method after several years. FMC first installed longwall equipment in March 1981 but was hindered by the slow cutting rate of the equipment as well as slabbing and spalling problems with the trona. From July 1987 until May 1989, longwall mining temporarily ended with improvements in the machinery. These enhancements included slab retaining plates on the canopies of the shield supports that hold the trona face in place and a automatically retract as the shearer advances. Compared with continuous miners, longwall equipment is more expensive initially; the higher production and extraction rates, elimination of roof-bolting requirements, and greater safety for the miners, however, more than offset the expense. The longwall unit consists of an electric shearer with a lead and trail drum, an armored face conveyor, and face shields. The maximum panel width cut has increased to approximately 230 m with a maximum panel length of 2,900 m. The pillars left between panels are used for roof support. The roof of the mined-out areas ultimately collapses to relieve the stresses, creating massive piles of rubble called *gob*. The method also has an ore recovery rate of about 75% compared with the 45% for normal room-and-pillar mining with continuous mining equipment.

Roof bolting is the primary method of roof support used in the Green River mines. The majority of bolts used are rebar bolts that are fully grouted with an epoxy resin. A roof plate under the head of each bolt supports the immediate roof. Some bolts with mechanical expansion anchors are used where conditions are suitable. Normal roof bolt spacing is on 1.2-m intervals. It is common practice to leave some trona in the roof of the opening because the trona is more competent than the overlying shale and marlstone. The holes are drilled and the bolts are installed using a separate roof-bolting machine or bolters mounted on continuous miners.

After the ore has been cut, it must be transported to the production shaft where it is hoisted to the surface. Normal practice is to use 10- to 20-t-capacity shuttle cars (either diesel or electric) to move the mined rock to a feeder-breaker, which meters the ore onto a conveyor belt. A series of conveyor belts then delivers the ore to the production shaft. The trona may be crushed further before it leaves the mine. An alternative to shuttle cars is a continuous haulage unit that can use either conveyor belts or flexible steel conveyors. These units are more productive than shuttle cars because they eliminate the lost time that occurs as shuttle cars change places and haul to the belt conveyor.

The practice of solution mining reportedly was used more than 2,000 years ago in China to recover salt from deep subsurface

formations. FMC conducted a single-well solution-mining test in Wyoming in 1945 but encountered poor results and decided to pursue underground mining instead. Carl A. Bays endorsed the use of hydraulic fracturing used by the oil and gas industry to interconnect well pairs in the mid-1950s. Between 1955 and 1958 solution mining was conducted using this technique with moderate success. After years of further work and testing, FMC announced on January 14, 1981, its intention to construct a demonstration plant by mid-1981 using solution mining to recover trona from the deeper beds on state lease Section 36, T17N, R110W, which was about 26 km south of its existing refinery.

A well pair consists of an injection well and a production well located a few hundred meters apart. After the wells were drilled to about 655 m (bottom of Bed 1), steel casing was set into place and cemented to the well wall from the surface to below the bottom of the bed. The casing and cement were breached at the desired location of the fracture by using one of several techniques—cutting tools, jet notching, or explosive perforations. Several monitor wells were also drilled along the perimeter of the section to check if there were any excursions of the injection fluid. Water was slowly introduced through the casing to initiate hydraulic fracturing. Each injection well was pressurized to exceed the overburden lifting pressure plus the tensile strength of the trona horizon. Once this occurred, the horizon ruptured and the solution entered the bed and followed the path of least resistance. Ideally, the fracture should move horizontally toward the production well. Once communication was made with the production well, a solvent (caustic soda) was added to the water to completely dissolve the trona. If only water were used, the sodium bicarbonate contained in the trona would precipitate, deposit at the bottom of the solution-mined cavity, and cover the surface of the soluble trona, thereby reducing the quantity of sodium carbonate in solution and minimizing the utilization of the resource.

An extraction rate of 30% for trona solution mining was derived years ago based on information obtained from engineers engaged in solution mining of salt, potash, and nahcolite. Although there are no published reports to confirm or refute this estimate, it is conceivable that the extraction rate could be higher as more well pairs are established within an area and horizontal drilling is used to establish better communication and contact with the solvent within the trona beds.

FMC has been discharging tailings and spent solutions to its tailing ponds since about 1953. For about 50 years, sodium carbonate decahydrate crystals have been collecting on the bottom of these ponds. This represents a large, alternative resource available for recovery. Beginning about 1985, FMC used a dredge to extract about 160 kt of crystals annually from the 485-ha pond. The crystals are slurried, dewatered, melted, and processed into soda ash in the refinery. Other producers have similar ponds where sodium carbonate decahydrate has collected since the plants were built. At some time in the future they may collect and process these crystals as well. Because of environmental considerations and the cost of constructing and maintaining tailing ponds, three producers are injecting waste tailings underground. This minimizes future buildup of insoluble materials in the tailing ponds. In addition, two of the Wyoming soda ash producers are selling their spent purge liquors that contain several percent of dissolved sodium carbonate in solution. Local power utility companies purchase the liquors to scrub SO₂ from stack off-gas.

Feed for the Searles Lake operations comes from brine-bearing evaporate horizons in the lake. A system of wells (injection and production) and pipelines for each plant produces brine from the

horizons. Each system is designed to produce the best brine available for the plant it supplies. For some, solar ponds concentrate brine to increase plant production. For others, effluent is injected into an evaporite horizon (i.e., the Mixed Layer horizon) to manufacture brine by solution mining. Brackish water for plant use is obtained from a system of wells and pipelines on the north, west, and south sides of Searles Valley. The wells are completed in the alluvial sands and gravel beds that surround the saline body (Moulton and Santini 1995).

U.S. Borax Inc. operates a small mine at Owens Lake. The evaporite deposit is exposed at the surface. Trona is selectively mined with an excavator, stockpiled adjacent to areas of excavation (to debrine), and later spread out on the surface to air dry (Santini, unpublished data).

Nahcolite in the Piceance Creek Basin was solution mined for soda ash production beginning in 2000. The solution mining concept was based on work completed by Shell Oil Co. in the early 1970s (Hardy et al. 2003). The company conducted field testing for in situ recovery of oil from shale and discovered that nahcolite could be leached using high-temperature steam. The Shell method allows for the recovery of bedded nahcolite, in addition to nahcolite disseminated throughout the oil shale. American Soda later improved on this method, injecting pressurized water at high temperatures into wells drilled to approximately 670 m. Dissolution of the nahcolite produced vertical cavities.

Processing

Processing natural soda ash is significantly different than the chemical processes used to make synthetic soda ash. Processing trona ore and sodium-carbonate-bearing brines involves different mineral separation technologies, whereas manufacturing synthetic soda ash can be accomplished using one of several techniques.

Natural Soda Ash

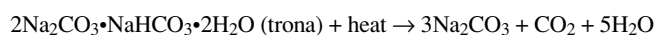
Although trona ore averages approximately 90% pure sodium sesquicarbonate (with 10% accessory minerals), the ore must be further refined to produce a 99+% soda ash product. Sodium-carbonate-bearing brines contain a variety of other soluble minerals, including sodium sulfate, sodium chloride, potassium chloride, and borax, that must be physically and chemically removed from the brine to process the sodium carbonate content into refined soda ash.

Searles Lake Brine Process. A vast array of production wells covers the surface of Searles Lake to supply the Argus soda ash refinery with sodium-carbonate-bearing brine feedstock obtained from the Mixed Layer brine and the Lower Salt brine. The brines are pumped to the plant and are carbonated in carbonation towers with CO₂ gas obtained from calciner gas (from the conversion of soda ash from sodium bicarbonate) and from the monoethanolamine (MEA) towers that process the power plant's flue gases into purified CO₂ gas. The sodium carbonate in the brine is converted to sodium bicarbonate, which precipitates and then is collected, filtered, and calcined to light soda ash. This intermediate product is transferred to surge bins, which feed into one of three rotary bleaching units that operate at 427°C to remove residual organics. The material is concentrated and sent to sodium monohydrate crystallizers operating at 88°C that produce a larger-sized crystal. The product is screened, dewatered, washed in centrifuges, and dried and dehydrated in steam tube dryers at 260°C. The crystals are finally screened at 16 mesh and sent to storage. The final product is 99.7% sodium carbonate. The barren, or spent, solutions from the Mixed Layer brine and burkeite liquors are returned to the lake. The Lower Salt brine is treated separately at the Westend plant to

recover borax and sodium sulfate. Figure 3 shows a flow diagram of the Argus soda ash process.

Wyoming Trona Process. The two techniques to refine soda ash from trona ore are the sesquicarbonate process and the monohydrate process. Both use the same procedures but in different sequences. It takes approximately 1.8 t of trona ore to make 1.0 t of finished soda ash. The monohydrate method is the primary process used today to make soda ash. Figure 4 shows a flow diagram of both technologies.

FMC Corp. developed the monohydrate process in 1960. Although it patented and licensed the technology to other producers, FMC did not use the technique until 1972. In the monohydrate process, trona is crushed and calcined in rotary gas-fired calciners at 150°–300°C to remove water and carbon dioxide from the ore, which reduces the weight of the ore by 27%, leaving an impure product containing 85% sodium carbonate and 15% insolubles. The thermal decomposition of trona involves the following reaction:



The calcinate is dissolved with hot water and the clear, hot solution containing about 30% sodium carbonate by weight is sent to evaporative multiple-effect crystallizers or mechanical vapor recompression (MVR) crystallizers, where sodium carbonate monohydrate crystals ($\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$) precipitate at 40°–100°C, which is below the transition temperature of monohydrate to anhydrous soda ash. The insoluble portion of the ore containing shale and shortite is collected by clarifiers, filtered, and then washed to recover any additional alkali before being piped in a slurry to tailing ponds or injected under ground in abandoned sections of the mine. Some companies pass the liquor through activated carbon beds before crystallization to remove trace organics solubilized from the oil shale so that the organics do not interfere with crystal growth rate and crystal habit in the crystallizers. The crystals are sent from the crystallizers to hydrocyclones and dewatered in centrifuges to between 2% and 6% free moisture. The centrifuge cake is conveyed to steam tube dryers where the crystals are dehydrated into anhydrous soda ash at 150°C, screened, and sent to storage or shipment. The final product made by the monohydrate process is dense soda ash with a bulk density of 0.99–1.04 g/cm³ and an average particle size of about 250 µm.

The sesquicarbonate process produces light to intermediate grades of soda ash crystals with a bulk density of about 0.89 g/cm³. The trona is crushed, dissolved in hot (95°C) mother liquor, clarified, filtered, and passed to cooling crystallizers, where crystals of sodium sesquicarbonate ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$) precipitate. Activated carbon is added to filters to control the organics that interfere with crystal growth. The sodium sesquicarbonate is hydrocycloned, centrifuged, and calcined at 110°–175°C using gas or indirect steam heat. Dense soda ash can be made by calcining the sodium sesquicarbonate at 350°C.

Synthetic Soda Ash

Synthetic soda ash can be made by one of several chemical reactions that use common raw materials for feedstock, such as limestone, salt, and coal. Other technologies produce soda ash as a by-product of a process.

Leblanc Process. Nicolas Leblanc developed the Leblanc process in 1791 in the first effort to commercially synthesize soda ash. Common salt was combined with sulfuric acid to produce sodium sulfate and hydrochloric acid. The sodium sulfate was heated in a rotary furnace with coal and limestone (or charcoal and chalk) to produce a black ash, which contained sodium carbonate, calcium sulfide, and some unreacted coal. The mixture was leached with

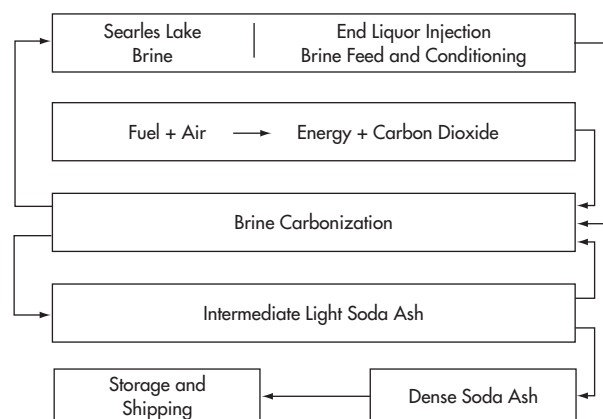


Figure 3. Argus soda ash process

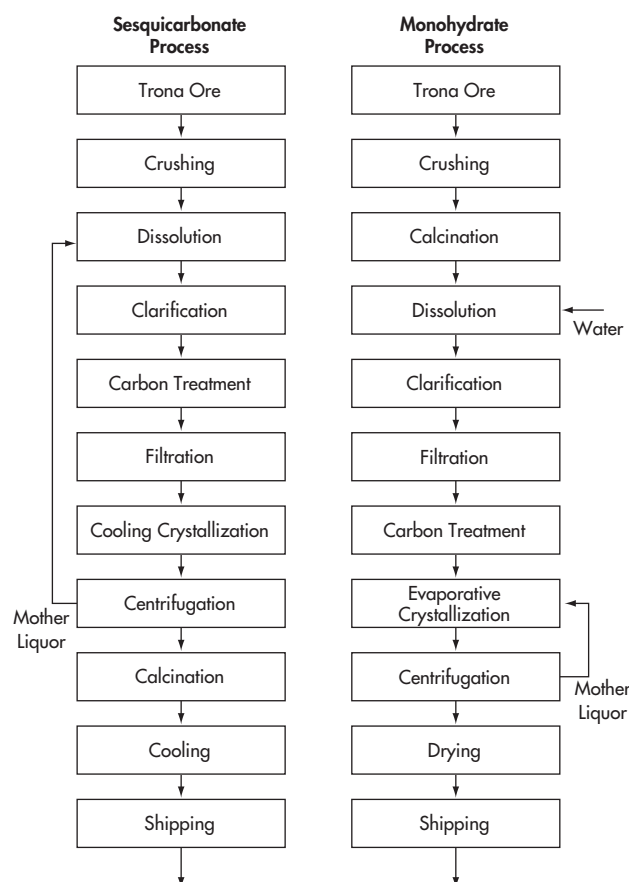
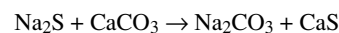
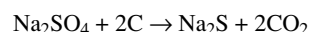


Figure 4. Two methods of producing soda ash from trona ore

cold water, which was evaporated or dried to obtain crystalline sodium carbonate. The chemical reaction was



The Leblanc process was used primarily in France and England. In about 1915, it was displaced by the Solvay ammonia-soda process; one plant in China, however, reportedly was producing

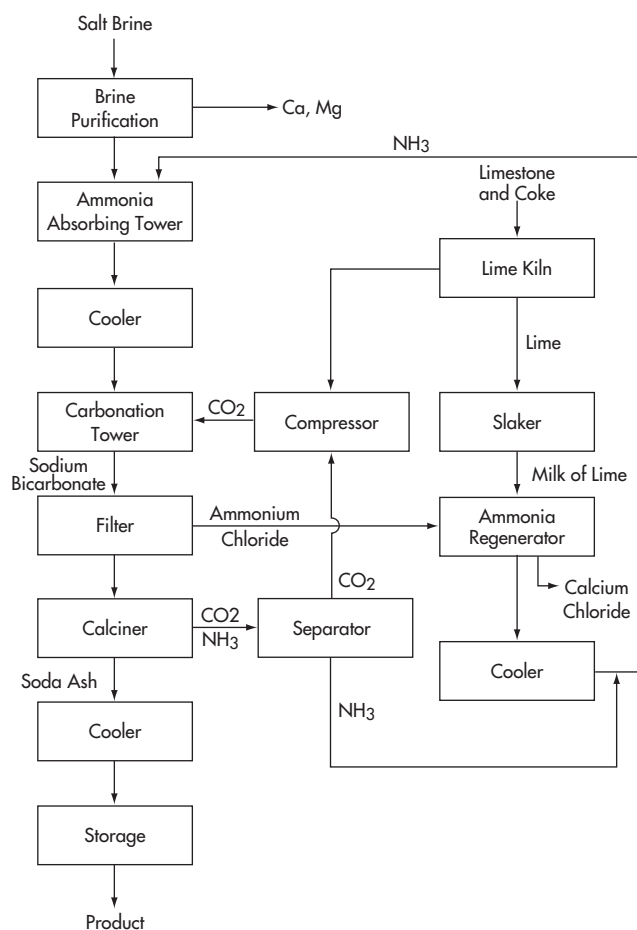
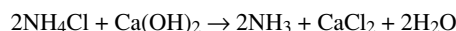
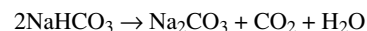
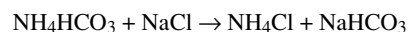
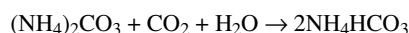
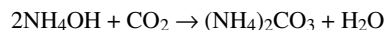
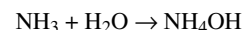
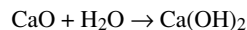
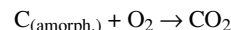
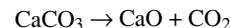


Figure 5. Flow diagram of the Solvay ammonia-soda process

about 250 tpy of soda ash as of 1950. The Leblanc technology was not used successfully in the United States except during a short period from July 1884 to January 1885 at a plant in Laramie, Wyoming.

Solvay Process. Also known as the ammonia-soda process, the Solvay process was developed by Alfred and Ernest Solvay in 1861 as an inexpensive way to manufacture soda ash on a large scale. Manufacturing 1.0 t of synthetic soda ash requires about 2.8 t of steam; 1.7 t of salt; 1.4 t of limestone; 0.6 t of coal for the boilers; and about 0.2 t of coal for the dryers. The process discharges approximately 1.7 t of waste products that include sodium chloride and calcium chloride. In the process, a sodium chloride brine is treated with milk of lime to remove magnesium ions and with soda ash to remove calcium ions. The brine is then saturated with ammonia, which acts as a carrier, and carbon dioxide gas in an absorption tower to produce ammonium bicarbonate, which reacts with the salt in solution to form sodium bicarbonate and ammonium chloride. The sodium bicarbonate precipitates, after which it is filtered and calcined at 175°–225°C to light soda ash (based on its bulk density of 0.51–0.62 g/cm³), and the gases produced are recycled back to the liquid phase. The solution containing ammonium chloride is reacted with milk of lime to recover the ammonia for reuse and to produce by-product calcium chloride for either sale or disposal. Limestone and coke are required to make the milk of lime. Dense soda ash (bulk density of 0.96–1.06 g/cm³) is made by hydrating

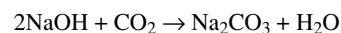
light soda ash to change the bulk density. The chemical reactions in the Solvay process are



The Solvay process is the dominant method used in the world today to manufacture synthetic soda ash. Approximately 70% of the total world output of soda ash is synthetic, the majority of which is from the Solvay process and the remainder from the ammonium chloride, New Asahi, and caustic carbonation processes. Figure 5 shows a flow diagram of the Solvay ammonia-soda process.

Electrolytic Process. Electrolytic soda ash is produced by introducing an electric current through a cell containing a saturated solution of sodium chloride. Sodium hydroxide forms at the cathode, and as carbon dioxide gas is passed through the solution around the cathode, sodium bicarbonate precipitates. The material is collected and dried to produce soda ash. In 1939, three electrolytic plants owned by the West Virginia Pulp and Paper Co. were in operation in Tyrone, Pennsylvania; Covington, Virginia; and Luke, Maryland. The plants also used the coproduct chlorine from the cells for bleaching applications.

Caustic Carbonation Process. Dow Chemical Co. operated the only caustic carbonation plant in the United States from 1955 to 1970 in Freeport, Texas. This plant, and a few others in the world, converted sodium hydroxide obtained as a coproduct from chlorine manufacture into soda ash. The sodium hydroxide in the electrolytic cell is treated with flue gas. The basic reaction is



Higher energy costs associated with the electrolytic process that produces both chlorine and caustic soda normally result in higher market prices for caustic soda compared with soda ash; therefore, this technique is not used extensively in the world.

Caprolactam Pyrolysis. This process involves pyrolyzing caprolactam residue to obtain a 95% sodium carbonate and 5% carbon product. A 40-tpd plant began production at Salamanca Guanajuato in 1989. The soda ash-carbon material was being sold to a pulp-and-paper operation that converted the soda ash to caustic soda. The small quantity of carbon in the soda ash reportedly was not a problem (Garrett 1992).

Ammonium Chloride (AC) Process. The Asahi Glass Co. of Japan developed the AC process in 1949 at the Kitakyushu Factory. It is essentially a modification of the conventional Solvay process. Because salt for synthetic soda ash manufacture must be imported, and therefore is expensive, a new technique was developed to improve the use of salt. In the Solvay process, about 70% of the sodium content in the salt is converted to soda ash with the remaining 30% and all of the chlorine discharged as waste. Only 28% (by weight) of imported salt was used to produce soda ash; the remaining 72% was lost as waste. The AC process uses more than 90% of the sodium from the salt. In the Solvay process, the ammonium

chloride produced is converted to ammonia and recycled; in the AC process, however, it is crystallized by cooling. Ammonium chloride is an excellent nitrogenous fertilizer used in Asia mainly for paddy rice; experimental applications, however, indicate it has beneficial uses for wheat, sugarcane, cotton, coconut and palm oil trees, bananas, and jute (Tsunashima and Nakaya 1982). Another difference between the Solvay and AC methods is that the AC method uses solid salt rather than salt brine as feedstock. In addition, the mother liquor is recycled to dissolve additional salt.

New Asahi (NA) Process. The NA process was developed in the early 1970s to improve on the AC and Solvay processes by reducing energy consumption, labor requirements, and equipment maintenance. The process has two variations that can be used, depending on the AC demand situation, and the NA monoproduction and coproduction processes. In the first variation, solid ammonium chloride reacts with a lime slurry to release the ammonia, which is recycled with a 25% calcium chloride solution (compared with a 10% solution in the Solvay process) discharged as waste or recovered for sale. In the other variation of the process, by-product solid ammonium chloride is produced by direct contact cooling crystallization when the facility has an ammonia plant. The NA coproduction process has lower production costs compared with the NA monoproduction technique.

Akzo Process. Akzo Zout Chemie of the Netherlands developed a process to make vinyl chloride and soda ash from salt using an amine-solvent system catalyzed by a copper-iodide mixture (Akzo N.V. 1981). Van Andel (1983) indicated that the method was an alternative to salt electrolysis, direct ethylene chlorination, and oxychlorination techniques. It produces soda ash rather than caustic soda and uses steam instead of electricity, reducing total energy consumption about one half that of the conventional process.

Ormiston Mining Process. Although Ormiston Mining and Smelting of Canada developed this process mainly to produce sodium hydroxide, it can be altered to produce soda ash. The method involves electrolysis of a sodium sulfate solution in an electrolytic cell that generates sulfuric acid. Ammonia is added to neutralize the acid and the process ultimately produces sodium hydroxide and ammonium sulfate. The caustic soda can be reacted with lime and converted to soda ash. Although the operating economics appear to be cost-prohibitive, some nations without soda ash resources but with abundant sodium sulfate deposits may find this process promising (Thompson and Genders 1992).

Hüls Process. The Hüls process produces soda ash and hydrochloric acid from salt using an amine-solvent system (Rauh 1991). The technique was developed by Chemische Werke Hüls AG, which was awarded a U.S. patent in 1982. The by-product hydrochloric acid may be easier sold than other by-product chemicals recovered from other processes, depending on market conditions.

END USES

Soda ash obtained from either natural or synthetic production processes serves a variety of end-use markets. The markets in developed nations are mature and are not expected to grow appreciably but will generally parallel the population growth rates of those nations. In developing countries, where the glass, chemical, and industrial sectors are emerging, consumption is expected to grow more significantly as the demand for consumer products increases.

Soda ash has been used in glass and soap manufacture for more than 5,500 years and these continue to be important end uses today. Older uses for soda ash, such as embalming the dead, treating colic pains, and making bread, gave way to newer uses in the 20th century, such as pH control in swimming pools, flue gas desulfurization for cleaner air, and glass fiber insulation for homes. Although sur-

rounded every day by many consumer products that contain soda ash, most people are unfamiliar with what soda ash really is. Based on reported industry sales in 2004, the manufacture of glass products represented about 50% of domestic soda ash consumption, with the glass container and beverage sector as 49% of this end use; flat glass, 36%; fiber glass, 9%; and specialty glass, 6% (i.e., glass tumblers, medicine bottles, incandescent bulbs, etc.). The other end uses were chemicals (mainly sodium bicarbonate, sodium chromates, sodium phosphates, and sodium silicates), 26%; soaps and detergents, 11%; distributors (which buy soda ash directly from the producers and resell it to various downstream consumers), 5%; miscellaneous uses, 4%; flue gas desulfurization, 2%; and pulp-and-paper and water treatment, 1% each.

Glass

The glass industry is the largest consumer of soda ash, especially the glass-container sector. Soda ash is a source of sodium oxide that is used as a fluxing agent in container, flat, fiber, and specialty glass manufacture to reduce the temperature at which the raw materials melt. Soda ash decomposes into sodium oxide and carbon dioxide, which rises through the glass melt and helps mix the ingredients.

Soda-rich glass is softer than other more refractory types of glass; therefore, forming is easier. The quantity of soda ash added to glass batches varies with the type of glass being manufactured and the percentage of recycled glass (also known as *cullet*) being used. Glass containers, for example, may require more than 180 kg of dense soda ash for every 450 kg of silica sand. A typical batch for clear glass containers may consist of 155 kg soda ash; 172 kg limestone; 145 kg feldspar; and 5 kg sodium sulfate. Flat-glass batches require about 115 kg of soda ash per 450 kg of silica sand used. The growing nationwide effort to recycle glass has benefited many of the domestic glass-container manufacturers because cullet substitutes for part of the raw material requirements in a glass batch. Cullet also melts at lower temperatures (about 20%–25% lower), thereby reducing glass-production costs. The increased use of cullet has conversely affected soda ash consumption. The U.S. soda ash consumption in the glass-container industry has also declined because of increased use of polyethylene terephthalate (PET) plastic containers.

Chemicals

The inorganic chemicals industry is the second largest user of soda ash, comprising 26% of total domestic demand. Although many sodium-based compounds are indirectly produced from soda ash, the primary chemicals that are directly manufactured from soda ash feedstock are discussed in the following subsections.

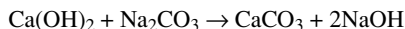
Sodium Bicarbonate

Sodium bicarbonate, or baking soda, is manufactured by percolating CO₂ gas through a carbonation tower containing a saturated soda ash solution. The sodium bicarbonate precipitate is collected, filtered, centrifuged, dried, screened, and packaged. Approximately 0.68 t of soda ash is required to make 1 t of sodium bicarbonate. The major uses of sodium bicarbonate are household consumer products, animal feed, foods for human consumption, baking products, beverages, plastics, chemicals, pharmaceuticals, personal-care products, fire extinguishers, soaps and detergents, flue gas scrubbing, and other miscellaneous end uses. Five producers operating six plants have a combined annual production capacity of about 708 kt. Two of the companies are also soda ash producers.

Sodium Hydroxide (Caustic Soda)

Caustic soda is mainly produced as a coproduct with chlorine gas in the electrolysis of salt brine in mercury, diaphragm, or membrane

cells. Nonelectrolytic caustic soda, however, also known as *chemical caustic soda*, has been produced in the last decade by several of the Green River soda ash producers. The lime-soda process was the primary method of caustic soda manufacture at the beginning of the 20th century before the electrolytic process gained favor. Chemical caustic soda is produced by the following reaction:



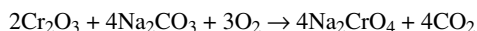
The lime is slaked—CaO converted to Ca(OH)₂—and added to 1.33 t of dissolved soda ash to produce 1.0 t of chemical caustic soda. Calcium carbonate is precipitated from the reaction, calcined back to lime, and recycled.

Sodium Sesquicarbonate

Sodium sesquicarbonate is a hydrated compound containing soda ash and sodium bicarbonate. Trona ore is first crushed and dissolved to separate the insoluble impurities. The sodium compounds in solution are then clarified, filtered, crystallized, centrifuged, calcined, and recovered as long, needle-shaped, monoclinic crystals of sodium sesquicarbonate. FMC Wyoming Corp. has a 50-ktpy sodium sesquicarbonate facility in Wyoming that sells mainly to the detergent industry.

Sodium Chromates

Chrome ore is roasted with soda ash in a rotary kiln to produce sodium chromate or sodium bichromate; these are used to produce other chromium compounds such as chromic acid and chromic sulfate. The chemical reaction is



For every ton of sodium bichromate produced, 0.79 t of soda ash is required. The end uses of sodium bichromate are chromic acid, chromium oxide, leather tanning, pigments, wood preservatives, drilling mud additives, and other uses (metal finishing, water treatment, textiles, catalysts).

Sodium Phosphates

The phosphate chemicals, and the corresponding quantity of soda ash required to make 1 st of the chemical, are as follows: sodium tripolyphosphate (Na₅P₃O₁₀), 0.76 st; mono sodium phosphate (NaH₂PO₄), 0.45 st; disodium phosphate (Na₂HPO₄), 0.747 st; trisodium phosphate (Na₃PO₄), 0.68 st; sodium metaphosphate (NaPO₃), 0.557 st; sodium acid pyrophosphate (Na₂H₂P₂O₇), 0.478 st; and tetrasodium pyrophosphate (Na₄P₂O₇), 0.84 st. The sodium phosphates have exceptional cleaning properties, especially sodium tripolyphosphate, and are also used in baking powder, carbonated beverages, milk products, dental materials, fire-resistant products, metal surface treatments, and water treatments.

Sodium Silicates

Sodium silicate is produced from silica sand and soda ash in a process similar to glass manufacture except that the sodium silicates are water soluble and glass is not. The two raw materials are melted at 2,450°C in an open-hearth furnace. The melt is withdrawn, cooled, crushed, and dissolved under pressure with steam. The three types of sodium silicate s, and the corresponding quantity of soda ash needed to produce 1 st of the chemical are sodium orthosilicate (0.8 st); sodium metasilicate pentahydrate (0.33 st); and water glass (0.37 st). Sodium silicates are used in soaps and detergents; silica-type catalysts and gels; pigments; paper adhesives; water, paper, and ore treatment; and other miscellaneous end uses.

Other Sodium Chemicals

Many other sodium-based chemicals are derived from soda ash. Sodium aluminate, sodium cyanide, sodium fluoride, and sodium sulfite are just a few examples.

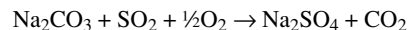
Soaps and Detergents

The third largest end use of soda ash is in soap and detergent manufacture, accounting for 11% of total domestic consumption. Soda ash is used directly and indirectly in this sector with different functions. First, soda ash is added directly to different detergent formulations to serve as an agglomerating aid, surfactant carrier, and source of alkalinity. Second, soda ash is the feedstock to make other sodium-based chemicals known as *builders*. Builders are agents that enhance the cleaning action in the liquid washload by tying up the calcium and magnesium ions to improve surfactant activity. The builders include sodium tripolyphosphate (which is an excellent builder but contributes to the environmental problem of eutrophication), sodium silicates, and synthetic zeolites. One or a combination of these is used in various detergent formulations. Lastly, soda ash is used to soften laundry water.

The end-use data presented pertain to the direct use of soda ash in soap and detergent manufacture; the quantity of soda ash used to produce other sodium chemicals used in formulations are included in the chemicals sector, which is the primary, first-tier consumer. Soda ash is used in powdered home and industrial detergents but not in the newer liquid detergent formulations. Many states have legislation to restrict or ban the use of phosphatic detergents because of environmental considerations; therefore, detergent companies have modified product formulations to accommodate regional market restrictions. As a result, national sodium tripolyphosphate consumption has been decreasing, thereby reducing soda ash usage. To compensate for the decline, additional soda ash has been added to detergents as alternate medium-strength builders, such as in synthetic zeolites and in sodium silicates. Despite the growth of liquid detergent use, the net effect is that soda ash consumption in the soap and detergent sector remains strong.

Flue Gas Desulfurization

Flue gas desulfurization reduces SO₂ emissions in stack gases from the burning of fuel. Soda ash and other soda ash-based compounds such as sodium bicarbonate and sodium sesquicarbonate are very effective dry sorbents of sulfur and nitrogen compounds. The reaction is as follows:



Compared to calcium-based compounds such as lime and limestone, scrubbing reagents based on soda ash have been proven to be more effective scrubbers because of their greater surface area, which enhances the reaction with sulfur and nitrogen. Soda ash, however, remains more expensive and geographically restrictive than calcium materials. Most of the power plants that burn high-sulfur coal are east of the Mississippi River, where there are plentiful limestone quarries that can be mined more economically and the product transported shorter distances than soda ash produced in the West. Therefore, the quantity of soda ash sold for this end use is restrictive because of the economic advantages of lime and limestone. Some soda ash, however, is blended with lime for use in the dual-alkali process. The flue gas desulfurization market is 2% of total domestic soda ash sales.

Distributors

Distributors offer a variety of services to many soda ash consumers that may not be available from a soda ash producer directly, such as

buying in bags, small volumes, or on an infrequent basis. Soda ash sold to distributors for resale comprised 5% of domestic reported consumption in 2004.

Pulp and Paper

Soda ash is used in pulp digestion and bleaching operations and in water treatment and paper-coating formulations. Its main use is in making the sodium sulfite buffer solution used in the neutral sulfite pulp-manufacturing process, in which the soda ash neutralizes the corrosive effects of the recovered black liquor. Although many pulp mills had used caustic soda because of its high sodium oxide content and its strong alkalinity, high prices and supply shortages of caustic soda prompted several mills to switch to soda ash, which was less expensive and more available. The total market represented about 1% of U.S. soda ash sales in 2004.

Water Treatment

Soda ash is used to chemically alter the pH of municipal and industrial water supplies and as a precipitant to remove impurities in brine and industrial process water. In the basic water treatment process, soda ash is added to adjust acidity or alkalinity. Generally, it is added to acidic water to raise the pH and reduce the corrosivity of the water and the accumulation of mineral scale, thereby extending the life of metal pipes and equipment. One example of this application is in swimming pool chemicals where soda ash is added to adjust the pH of the water.

As a precipitant, soda ash removes calcium and magnesium ions and other contaminants from water, which decreases the hardness of water. Most chlorine and caustic soda manufacturers pretreat the sodium-chloride-rich brine feedstock with soda ash to remove any calcium and magnesium impurities, thereby improving feedstock composition and product quality.

Since 1987, when the U.S. Bureau of Mines began collecting reported soda ash consumption data, a certain quantity of soda ash equivalent contained in purge liquors, soda liquors, and mine waters has been sold to coal-fired power plants for process water treatment. These data are included under the water treatment category rather than under flue gas desulfurization.

Another unique soda ash application in water treatment involves treating surface waters (e.g., lakes and rivers) contaminated from acid rain or natural causes. Although soda ash is a more expensive alkaline compared with less expensive calcium-based reagents such as limestone, it reportedly is more effective than lime in neutralizing the effects of acidification. The concept has been conducted in lakes in Sweden and New York with positive results; the practice has been criticized, however, for merely treating the result of acid rain rather than attempting to prevent the spread of pollution from the source, which would involve flue gas desulfurization. The total quantity of soda ash used for all water treatment applications is about 1% of total soda ash demand.

Miscellaneous Uses

Although soda ash is used in several minor applications, specific end-use data are unavailable; the total category, however, is 4% of domestic reported consumption. The uses include agriculture, brine treatment, corn syrup manufacture, drilling mud additives, dyes and pigments, enamels, food processing, leather tanning, metal refining, perfume, pharmaceuticals, and textiles.

ECONOMIC FACTORS

Transportation and Packaging

Soda ash is packaged in 23–46 kg paper bags and 1-t supersacks. Large quantities are shipped in bulk, often using unit trains (~100-t

railcars). Producers use dedicated port facilities and chartered vessels that allow soda ash, a low-unit-value product, to be exported around the world. Smaller shipments of both bulk and bagged soda ash are to domestic customers.

Prices

For three quarters of the 20th century, the synthetic soda ash industry with several nationwide plants established the lead for setting the soda ash selling price, leaving the smaller natural soda ash industry to follow by paralleling any price movement made by the former. Rising fuel costs after the 1973 energy crisis, coupled with pollution-abatement equipment required by environmental legislation, adversely affected the synthetic industry more than the natural operators, thereby creating a two-tier sales price—one for natural soda ash and another for synthetic soda ash.

The posted list price of natural soda ash differs from the value that is reported to and by USGS annually. The value may or may not correspond to the published list price for the commodity. The values that tend to be synonymous with the average market price are the combined total revenue of Wyoming and California natural bulk, dense soda ash sold on an f.o.b. (free-on-board) basis at list prices, spot prices, discount, long-term contracts, and for export, divided by the aggregate quantity of soda ash sold. Bagging, handling, and insurance costs are not included. The average annual value for bulk, dense soda ash, f.o.b. Green River, Wyoming; Searles Valley, California; and Parachute, Colorado (now dormant); was \$70.27/t in 2004. On July 1, 2004, the list price for Wyoming bulk dense soda ash was raised from ~\$116/t to \$139/t. The California price for the comparable product was increased from ~\$144/t to \$150/t.

Foreign Trade

Before the startup of synthetic soda ash manufacturing in the United States in 1884, and apart from limited natural soda ash production in the West, imported soda ash supplied most domestic supply requirements for the glass and detergent industries. As domestic soda ash production capacity expanded, the United States rose from being import dependent to a net exporting nation.

Imports

England had been a major source of soda ash imports in the late 19th and into the 20th century. Synthetic soda ash plants were built in Canada and Mexico primarily to satisfy those countries' requirements; because of their close geographic location, however, these nations began trading with the United States to solve supply shortages or to provide alternate soda ash grades. The Solvay plant in Amherstburg, Ontario, has now been closed, and only one facility remains in Mexico. Imports of soda ash in 2004 increased by 20% to 6,000 t from 2003. In 2004, about 41% of imports were from the United Kingdom and 37% from Mexico. The remainder was from Belgium, Bulgaria, China, Germany, India, Japan, Taiwan, and Turkey.

Exports

U.S. soda ash exports have grown significantly in the last two decades because of increasing world demand, favorable currency exchange rates, lifting or easement in foreign tariffs and embargoes, and synthetic soda ash plant closures. Another important factor has been the creation of the domestic export association known as the American Natural Soda Ash Corporation (ANSAC), which was reorganized in 1983 from the Soda Ash Export Trading Association assembled in 1982. ANSAC has been very successful in raising export sales by consolidating the efforts of four individual U.S.

soda ash producers in the world market. In 1981, before the creation of ANSAC, exports were only 13% of U.S. production, but by 2004 it had risen to more than 43% of total production. Exports of soda ash in 2004 were 4.67 Mt. In 2004, U.S. exports to 44 countries, on a regional basis, were as follows: Asia, 36%; North and South America, 22% each; Europe, 11%; the Middle East, 4%; Oceania, 3%; Central America and Africa, 1% each; and the Caribbean, less than 1%.

FUTURE OUTLOOK

The outlook for U.S. soda ash for the next 5 years is optimistic, despite competition from Chinese soda ash producers (Kostick 2004). According to the USGS, the market for domestic soda ash is expected to grow by about 0.5% per year, and the world demand is forecasted to range from 2% to 2.5% per year for the next several years. Asia and South America are the two areas that will continue to have increased soda ash consumption in the near future. In contrast, ANSAC estimates world demand for soda ash will grow about 4%–4.2% per year for the next few years.

ACKNOWLEDGMENTS

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Sodium Sulfate Resources

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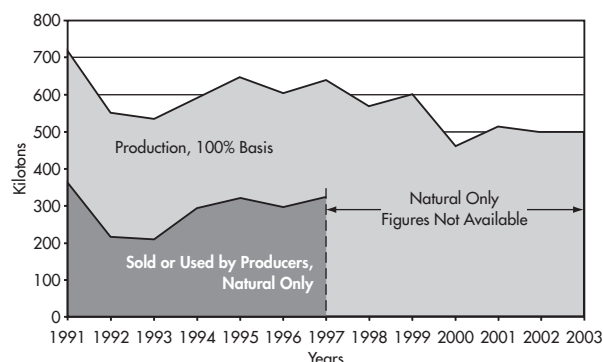
INTRODUCTION

Sodium sulfate is an important industrial chemical. As recently as 25 years ago, it was produced and consumed in the United States in quantities exceeding 1 Mtp y. Since then, both its production and use have declined; approximately half the production, however, still comes from natural sources. Figure 1 illustrates the history of production of natural sodium sulfate (up to 1997) and manufactured sodium sulfate in the United States. Production of natural sodium sulfate from various types of deposits is the main source of this chemical in Canada, China, Mexico, and Spain, and probably in Argentina, Chile, Iran, Spain, and the Russian republics.

In the United States, more than one half of the total output is a by-product of various manufacturing processes or products including ascorbic acid, battery reclamation, cellulose, rayon, and silica pigments (Kostick 2005). In addition, there is sizable production of sodium sulfate from other chemicals (primarily salt and sulfuric acid), called “salt cake” (Garrett 2001). The U.S. Geological Survey (USGS) does not separate natural sodium sulfate from synthetic sodium sulfate in reporting production (Kostick 2005).

MINERALOGY AND PHYSICAL PROPERTIES

Sodium sulfate is widespread in occurrence and is a common constituent of many mineral waters and seawater. Atmospheric precipitation contains sulfate; it is one of the major dissolved constituents of rain and snow (Davis and De Wiest 1966). Many of the saline lakes throughout the world contain varying amounts of sodium sulfate. Because sodium is usually the dominant cation, some make an anionic distinction, referring to lakes containing predominantly sulfate as bitter lakes and those containing predominantly carbonate as alkali or soda lakes (Bateman 1950). Sodium sulfate in its natural form is found in two principal minerals, mirabilite and thenardite. Mirabilite, the hydrous form, is commonly called Glauber’s salt. It was discovered by the German chemist J.R. Glauber (1603–1668), who derived its name from the Latin, *sal mirabile*, meaning wonderful salt. Thenardite, the anhydrous variety, was named for the French chemist Louis Jacques Thenard (1777–1857) of the University of Paris (Mitchell 1979). The largest quantities occur in the form of mirabilite. Sodium sulfate is found in varying degrees of purity, from theoretically pure efflorescent crystals of mirabilite to combinations and admixtures of other salts and impurities. It is a common constituent of some brines; from this source, much is extracted commercially.



Adapted from McIlveen and Cheek 1994.

Figure 1. Sodium sulfate production in the United States, manufactured and natural until 1997. Only total sodium sulfate production has been published since 1997.

Sodium sulfate also is found in compounds such as the minerals glauberite, the double-salt of anhydrous sodium and calcium sulfate; bloedite, the hydrous double-salt of sodium sulfate and magnesium sulfate; and burkeite, the anhydrous double-salt of sodium carbonate and sodium sulfate.

More than 40 minerals contain sodium sulfate in varying proportions; many are of special interest because of their frequent occurrence.

Table 1 lists some sodium sulfate bearing minerals. The reader is referred to other publications (Grabau 1920; Cole 1926; Dana 1932; Dietrich 1969) for descriptions of these minerals. Only mirabilite and the nardite will be described in this chapter. Mirabilite, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, contains 55.9% water of crystallization. It is noted for its efflorescence or spontaneous loss of water. On dehydration, it changes to the anhydrous form, Na_2SO_4 . Mirabilite is an opaque to colorless, water-soluble mineral that tastes first cool, then slightly bitter. It has a specific gravity of 1.48. It frequently forms as efflorescent, needlelike monoclinic crystals but generally is found in the massive form.

Thenardite, the anhydrous mineral Na_2SO_4 , contains 43.68% Na_2O and 56.32% SO_3 . It ranges from colorless to white and may be tinted shades of gray or brown. It is a water-soluble mineral with a

Table 1. A list of minerals that contain sodium sulfate

Mineral	Composition	% Na ₂ SO ₄
Thenardite (anhydrous)*	Na ₂ SO ₄	100
Hanksite	9Na ₂ SO ₄ •2Na ₂ CO ₃ •KCl	81.7
D'ansite	9Na ₂ SO ₄ •MgSO ₄ •3NaCl	81.2
Leontite	(Na,NH ₄ ,K) ₂ SO ₄ •2H ₂ O	<79.8
Vanthoffite	3Na ₂ SO ₄ •MgSO ₄	78
Hectorfloresite	4Na ₂ SO ₄ •NaClO ₃	74.1
Sulphohalite	2Na ₂ SO ₄ •NaCl•NaF	73.9
Burkeite	Na ₆ (SO ₄) ₂ (CO ₃)	72.8
Eugsterite (Fritzsche's salt)	2Na ₂ SO ₄ •CaSO ₄ •2H ₂ O	62.3
Darapskite Na	NO ₃ •Na ₂ SO ₄ •H ₂ O	58.0
Hydro-glauberite	5Na ₂ SO ₄ •3CaSO ₄ •6H ₂ O	57.9
Glauberite	Na ₂ SO ₄ •CaSO ₄	51.1
Loeweite	MgSO ₄ •Na ₂ SO ₄ •2½H ₂ O	46.2
Ferrinatrite	3Na ₂ SO ₄ Fe ₂ (SO ₄) ₃ •6H ₂ O	45.6
Mirabilite (Glauber's salt)	Na ₂ SO ₄ •10H ₂ O	44.1
Bleodite (astrakanite)	MgSO ₄ •Na ₂ SO ₄ •H ₂ O	42.5
Kroehnkite	CuSO ₄ •Na ₂ SO ₄ •2H ₂ O	42.1
Nickelbleodite	Na ₂ Ni(SO ₄) ₂ •4H ₂ O	40.3
Sideronatrite	Na ₂ Fe(SO ₄) ₂ (OH)•3H ₂ O	38.9
Caracolite	Pb(OH)Cl•Na ₂ SO ₄	35.4
Palmierite	(K,Na) ₂ Pb(SO ₄) ₂	<31.9
Tychite	2MgCO ₃ •2Na ₂ CO ₃ •Na ₂ SO ₄	27.2
Aphthalite (glaserite)	(K,Na) ₃ Na(SO ₄) ₂	21–38
Tamarugite	Na ₂ SO ₄ •Al ₂ (SO ₄) ₃ •12H ₂ O	20.3
Natrochalcite	Cu ₄ (OH) ₂ (SO ₄) ₃ •Na ₂ SO ₄ •2H ₂ O	18.8
Almeriite	Na ₂ SO ₄ •Al ₂ (SO ₄) ₃ •5Al(OH) ₃ •H ₂ O	15.9
Mendozite (soda alum)	Na ₂ SO ₄ •Al ₂ (SO ₄) ₃ •24H ₂ O	15.5
Natrojarosite	Na ₂ Fe ₆ (OH) ₁₂ (SO ₄) ₄	14.7
Noselite	3Na ₂ Al ₂ Si ₂ O ₈ •Na ₂ SO ₄	14.3
Slavikite	(Na,K) ₂ SO ₄ •Fe ₁₀ (OH) ₆ (SO ₄) ₁₂ •63H ₂ O	<4.6

* Salt cake is anhydrous sodium sulfate with a purity lower than 98%.

slightly salty taste. Its specific gravity (2.67) and hardness (2.5 to 3) exceed those of mirabilite. It commonly occurs in the massive form without visible crystals. Its crystals are frequently tabular pyramids of the orthorhombic system.

Sodium sulfate also occurs as a heptahydrate, containing seven molecules of water, but this is unstable and has not been found in the natural environment.

The solubility of sodium sulfate has an important effect on the crystallization of the salt in nature, as well as in its production. Its solubility in water generally increases as a nonlinear function of temperature. Below 1.2°C, ice and mirabilite form. As the temperature increases above 0°C, increasing amounts of sodium sulfate become soluble. At 32.4°C, a transition point on the solubility curve is reached as the decahydrate melts in its own water of crystallization and the anhydrous form crystallizes. With increasing temperatures, solubility decreases somewhat. The presence of other dissolved salts changes the transition temperature and solubility characteristics of sodium sulfate.

CLASSIFICATION OF DEPOSITS

Essentially all commercial deposits of sodium sulfate resulted from accumulation and evaporation of surface water and groundwater in basins with interior drainage called *playas*. They are found in arid to semiarid regions. Thus these deposits fall within the broad classification of evaporites. They can be further classified into two categories: (1) those occurring as crystalline beds of mirabilite or glauberite and/or brines within or underlying playalakes; and (2) those found as buried beds of thenardite, glauberite, and associated minerals. The first category includes the principal deposits of the world. Notable among these are the lake deposits of western Canada; Great Salt Lake, Utah; the vast mirabilite-glauberite deposits of the Kara Bogaz Gulf on the eastern shore of the Caspian Sea; and the brine deposits of the western United States and Mexico. These require pumping, dredging, or reservoiring for exploitation.

Commercial deposits of the second category are relatively rare. Deposits of thenardite and glauberite are being mined in Spain, and thenardite was mined at Camp Verde, Arizona, and at Rhodes Marsh near Mina, Nevada. Conventional mining techniques are used for extraction.

ORIGIN OF SODIUM SULFATE DEPOSITS

Evaporation of surface waters, with consequent concentration of salts, is the principal agent in the formation of alkali and bitter lakes from which sodium sulfate and other salts are extracted. Because of the great difference in composition between sea water salts and those of playalake deposits, it is generally accepted that the se deposits are recent accumulations from nonmarine sources.

The brines of playalake deposits are more diverse in composition than seawater because each deposit contains soluble salts from discrete sources within its drainage area. The salinity of the brines is much greater because of the high rates of evaporation characteristic in arid interior basins where the deposits occur.

The evolution of brine and subsequent precipitation of minerals involve complex geochemical factors. These include the weathering of solutes from the watershed, their transport to the playa basin, and their evaporative concentration. Jones (1966) pointed out the importance of lithology and weathering processes to the dominant anion in playalakes of the western United States. Krauskopf (1967) discussed the fate of various elements and radicals during transport and the eventual arrival of sodium as the dominant cation, and either sulfate or chlorides as the chief anion. McIlveen and Cheek (1994) reported that in 1970 Hardie and Eugster discussed the evolution of dilute waters in closed basins, placing them into four groups: Group A (Na-CO₃-SO₄-Cl brines), Group B (Na₂SO₄-NaCl brines), Group C (Na-Mg-Ca-Cl brines), and Group D (Na-Mg-SO₄-Cl brines). The precipitations of calcite, sepiolite, and gypsum are important points of bifurcation during the evolutionary process.

In nature, two processes—evaporation and cooling—cause the deposition of sodium sulfate. Evaporation decreases the volume of water, and cooling decreases the solubility of the salt. Below the freezing point of water, ice decreases the available water for solution and the solubility of sodium sulfate minerals, causing mirabilite to form. This natural phenomenon accounts for the accumulation of intermittent beds of crystalline sodium sulfate in the bitter lakes of Canada, Russia, and the United States from which sodium sulfate may be harvested during the winter. Crystallization from cooling also results from day and night temperature changes, particularly at high elevations where these changes can be extreme.

In warmer climates, evaporation is the principal agent of precipitation of sodium sulfate. In those climates, natural cooling is not employed in the production of sodium sulfate, but concentrated

brines are pumped to the surface and cooled by refrigeration to yield mirabilite crystals.

Most sodium sulfate deposits of commercial significance contain permanent crystalline beds and brines at or near the surface. The crystalline beds can range in thickness from a few millimeters to several meters. They usually are interstratified with other salts, clays, silts, and organic matter. The impervious clays and silts help preserve a portion of the intermittent beds from redissolving. Brines generally occur with in crystal beds, but in some deposits crystal beds are lacking.

In most deposits, sodium sulfate predominates, with sodium and magnesium chlorides, magnesium sulfates, and carbonates also present. In more complex deposits, concentrations of potassium chloride and borates can be appreciable, depending on the location of the deposit in relation to the source of soluble salts.

The origin of sodium sulfate deposits has prompted many theories. Variations in these theories mainly concern the source of alkalic salts that make up the deposits. Other factors considered are the origin of the basin and the agent of transportation and deposition of the sodium sulfate (Ruffel 1970).

Early theories generally attributed the source of the salts to decomposition of granitic rocks. It was assumed that the feldspars in granites yielded soluble salts that were transported by surface waters, and that pyrite and other sulfides in these rocks were oxidized to sulfuric acid, which immediately dissolved some of the basic oxides to produce soluble sulfates (Wells 1923).

Following an extensive study of the deposits of western Canada, L.H. Cole (1926) considered four possible sources of the sodium sulfate: (1) underlying sands and shales, which contain small amounts of alkalis, and interbedded volcanic-ash beds, which contain an appreciable percentage of these salts; (2) connate waters in underlying strata; (3) springs in or near the deposits; and (4) surface deposits of bentonitic glacial drift. Cole concluded that the probable source was the salts contained in the bentonites, which are widely distributed in the glacial drift. Surface waters carrying calcium salts in solution react by base exchange with the alkali silicates, releasing the salts contained in the bentonite in the form of soluble sulfates, and so forth. These in turn are concentrated and deposited in undrained lake basins.

More recent investigators have attributed the source of some sodium sulfate to the decomposition of rocks and sediments, such as bentonite, that also contain sulfates, and from the leaching of buried beds of sulfates. Organic-rich clay and shale also would produce sulfate through the oxidation of pyrite and marcasite (Davis and DeWiest 1966). A subaerial means of transport is provided because many playa lakes are hydrologically coupled with the surrounding water table. Sulfides are found in the organic-rich muds (containing stromatolites, etc.) and vegetative debris of some playa lake sediments. The fermentation of organics under anaerobic conditions would produce hydrogen sulfide, which could oxidize to sulfate (Reeves 1968).

McIlveen and Cheek (1994) reported that Grossman studied the sodium sulfate deposits of the Northern Great Plains of Canada and the United States in 1968 and attributed the origin of those deposits to the solution of deeply buried marine evaporites. In his model, groundwater from the Rocky Mountains moved downward and eastward into the Saskatchewan Subbasin during the Quaternary, leaching the buried evaporites of the Prairie Formation (Devonian). Ascending mineralized groundwater during the late Pleistocene discharged into stratified drift where freezing segregated pure crystals of sodium sulfate in micrometric (chemically stratified and stagnant) lakes.

In a later study, Last and Slezak (1986) questioned the dissolution of deeply buried Paleozoic evaporites as the ultimate source of the salts based on the incompatible brine chemistry. Their paper describes the origin of the basins, in addition to the hydrochemistry, mineralogy, sedimentology, and diagenesis of the deposits in western Canada.

The USGS studied the saline lakes in west Texas to investigate the hypothesis that the source of salts in the basins originated from connate waters or brines migrating from deeply buried Paleozoic evaporites or from Cretaceous rocks that crop out in the lake basins. They concluded that the origin of the deposits was, and is, by evaporative concentration of the runoff of potable groundwater discharging from the shallow High Plains Aquifer. Their study dealt with an analysis of hydraulic heads and pore volume flushing in addition to evaluation of solute ratios and isotopic chemistry (Wood and Jones 1990).

A subsequent article (Wood and Sanford 1990) dealt with the ratio of groundwater outflow to inflow (flux ratio) in hydrologically open basins and the resultant mineralogy and volume of precipitated salts. In addition, possible mechanisms by which brine could escape from the system are discussed. The authors developed a groundwater model, PHRQPITZ, to define the effects of various flux ratios on the mineralogy and thickness of deposits. Another paper (Sanford and Wood 1991) investigates two typical waters, seawater and Na-HCO₃ groundwater, to demonstrate the importance of basin leakage on brine evolution.

OCCURRENCE, RESERVES, AND PRODUCTION

Several countries have sodium sulfate deposits of sufficient size and purity for commercial mining (Figure 2). The principal producing countries are Spain, Mexico, Canada, the United States, China, Turkey, Iran, and Chile. Of lesser importance are Argentina, Egypt, South Africa, and the former U.S.S.R. (Garrett 2001). Although data on mine production for natural sodium sulfate are not available, total world production is estimated to be about 4 Mt, and total world production of by-product sodium sulfate is estimated to be between 1.5 and 2.0 Mt (Kostick 2004).

Spain

Spain appears to have some of the largest glauberite-thenardite deposits in the world. They contain an estimated 2.5 billion t of equivalent sodium sulfate, of which the recoverable reserves are about 272 Mt. The majority of these reserves are in the Madrid Basin or Tajo Basin in the central part of the country, about 50 km south of the country's capital, and the Ebro Basin in northeast Spain (Garrett 2001). Spain's four sodium sulfate producing companies are FMC Foret, S.A.; Sulquisa S.A.; Crimidea, S.A.; and Minera de Santa Marta S.A. (Recursos Minerales 2003).

In the Madrid Basin, the principal mines are the El Castillar and Sulquisa. The El Castillar deposit is located in Villarrubia de Santiago, Toledo Province, where beds of thenardite 5 to 8 m thick are mined by the underground room-and-pillar method. The ore horizon contains only a small amount of glauberite but rests on a thin glauberite layer with a clay marl and halite underneath. The horizon extends more than 30 km² and contains probable reserves of 200 Mt of Na₂SO₄. Composition of the ore is reported as 70% to 75% sodium sulfate, 11% to 17% calcium sulfate, 0.4% to 0.6% sodium chloride, 3% to 9% clay, and 1% to 5% moisture (McIlveen and Cheek 1994). FMC Foret operates the mine and a plant producing anhydrous sodium sulfate.

Near Villacónes, the Sulquisa deposit consists of thicker, higher-grade glauberite deposits. About 20 m of thoroughly leached overburden overlies a high-grade glauberite bed 25 to 45 m thick

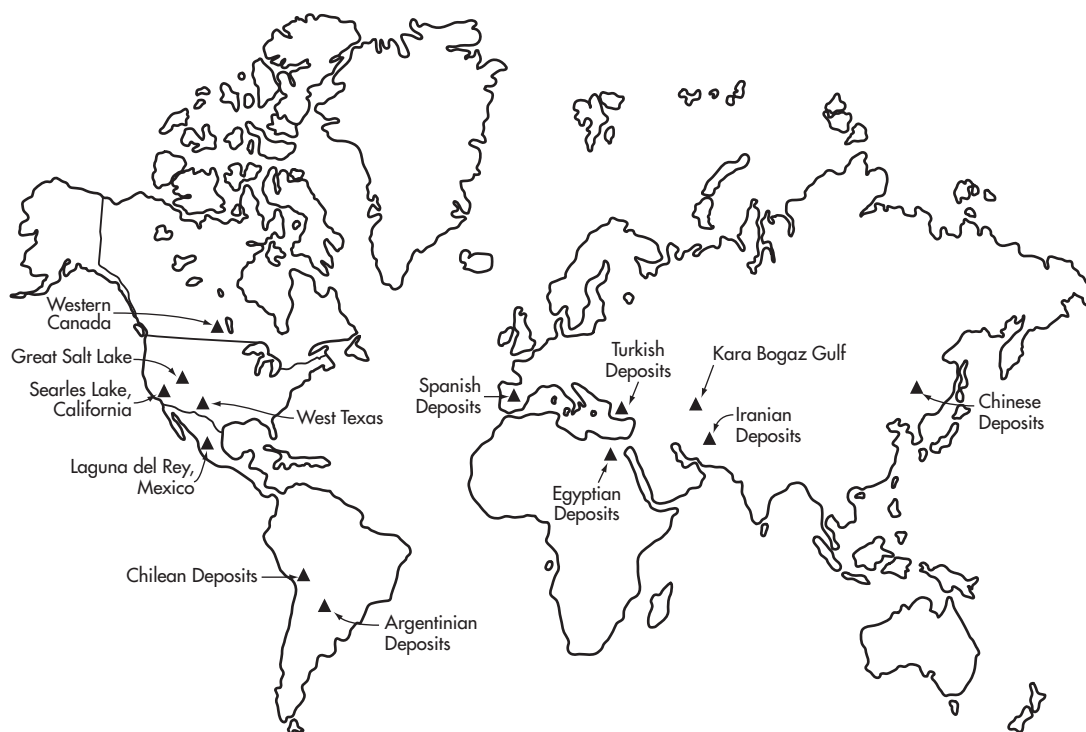


Figure 2. Principal sodium-sulfate-producing deposits of the world

containing some centimeter-thick interlayers of crystalline magnesite and magnesian shale. The ore is basically quite pure, averaging 40% to 42% Na_2SO_4 .

The Ebro Basin is an elongated and conformed depression of approximately 50,000 km^2 . The basin's lacustrine fill is Tertiary, and its important sediments range in age from Early Oligocene to Late Miocene. The sediments are up to 3 km thick, with zones that are predominately gypsum, interlayered with fine-grain siltstones and mudstones. There are three sub-basins containing glauberite: Rio Tiron-Belorado, Alcanadre-Arrubal, and Remolinos-Zaragoza (Salvany and Orti 1994). As the depocenter shifted from Zaragoza (the eastern and oldest) to Rio Tiron-Belorado (the western and youngest), the glauberite changed character from having considerable halite and some thenardite to being very pure with only a small amount of halite in the underlying clay. There is open-pit production at Cerezo del Rio Tiron by Crideros Minerales y Derivados, S.A. (Crimidesa), in Burgos Province and at Belorado by Minera de Santa Marta (MSM). These operations are rated at capacities of 500 and 240 ktpy, respectively.

The Calatayud Basin also contains very large deposits that are less well studied and are not known to be developed commercially.

Total production of natural sodium sulfate from Spain has increased. For 1999, it was estimated to be 600 kt, ranking it first in world production (Garrett 2001). In 2003, the estimated production was 907 kt, of which 728 kt was from glauberite and 179 kt was from thenardite (Recursos Minerales 2003).

Mexico

In 1999, Mexico produced 600 kt of natural sodium sulfate (Garrett 2001), making it the second largest producing country in the world. One of the world's largest sodium sulfate deposits, and the world's largest production of sodium sulfate in 1999, occurred at Laguna

del Rey in northern Coahuila, approximately 160 km north of Torreon (Garrett 2001). The evaporite lens consists of glauberite (averaging 50%; $\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$) and bloedite (averaging 20%; $\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$), the latter as thin beds and irregular aggregates.

The crystal bed is 10 km long and 4 km wide, with 35 m thickness at the center. Its area is 40 km^2 , its volume is 560 million m^3 , and it contains approximately 350 Mt of sodium sulfate. The main concentration of bloedite, which occurs as short prismatic, monoclinic crystals or as extremely fine-grained masses, is found as a layer 1 to 2 m thick, located about 8 m below the top of the evaporite mass. Mirabilite and epsomite occur in minor proportions. The formation underlying the crystal bed is impervious clay and silt containing some sodium chloride. Glauberite occurs as thin tabular crystals and bloedite is found in massive concentrations. The intercrystalline spaces, amounting to as much as 25% of the evaporite mass, are partially filled with clay, and the rest with a brine in equilibrium with the solid phase.

A composite average analysis of brine from a depth of 20 m from several wells in the lake bed showed 18.46% sodium sulfate, 5.91% sodium chloride, and 5.28% magnesium sulfate. Analysis of several cores of the crystal bed showed 35% to 36% sodium sulfate and only 1.5% to 1.8% sodium chloride. Magnesium sulfate ranged from 4.7% to 12.7%. Estimated reserves are approximately 160 Mt of anhydrous sodium sulfate.

Sodium sulfate is produced at Laguna del Rey by Quimica del Rey, S.A. de C.V., a subsidiary of Industrias Penoles, S.A. de C.V. The plant was built in 1963 with a capacity of 30 ktpy. In 1988, the plant was expanded to its present capacity of 510 ktpy.

Other deposits are known to occur in northern Coahuila and in the state of Chihuahua, but in size and sodium sulfate content, they are smaller than the deposit at Laguna del Rey.

Sulfate de Viesca recovers 22 ktpy of sodium sulfate as a by-product from production of sodium chloride from natural brine. The plant is near Viesca in the southwestern part of Coahuila.

Deposits of thenardite occur in the state of Sonora near the municipality of Bacardahuachi, some 190 km northeast of Hermosillo. Outcroppings of thenardite and efflorescences in the soil occur discontinuously along the east side of the Bacardahuachi Valley in an area approximately 6 km long and 4 km wide. The deposits occur within the Baucrit Group (Oligocene). The outcroppings are covered by unconsolidated surface material, which varies in thickness between 10 and 30 m. Four workings have been developed within this area. In the largest pit, the Oro Blanco, the thenardite is reported to attain a thickness of 20 m. Analyses of selected samples from the Oro Blanco ran between 95% and 99% Na₂SO₄ (Anon. 1981).

During 1982, Para Mex, the Mexicanized affiliate of the Spanish company Tolsa, had conducted some exploration of the Oro Blanco and was evaluating the commercial possibilities of producing sodium sulfate from this area.

In 1999, Quimica del Rey, the country's main producer, had a plant capacity of 620 ktpy with about 250 wells at Laguna del Rey with only 70 to 80 needed to supply the plant (Garrett 2001).

Canada

Numerous saline lakes containing sodium sulfate are known on the western plains of Canada. Seventeen deposits contain more than 1 Mt each. Only one of the large deposits is in Alberta; the remainder are in Saskatchewan. Their commercial exploitation began in 1918 at Mukiki Lake, near Saskatoon, Saskatchewan (Last and Slezak 1986). At present, only Millar Western near Palo and Saskatchewan Minerals near Chaplin produce sodium sulfate.

An interesting occurrence of sodium sulfate has been reported at Castleguard Cave, which drains the Columbian Icefields of the Canadian Rocky Mountains. The mirabilite occurs in association with gypsum and epsomite (Younge and Krouse 1987). Though of geological interest, this occurrence is apparently noncommercial.

Commercial deposits of sodium sulfate are located in the Prairie Provinces of Canada where they occur in basins and depressions in glacial drift that lack apparent outlets. In general, the deposits are crystalline beds that underlie saturated brine lakes containing a few millimeters to approximately 1 m of brine in the spring and summer. The deposits contain two recognizable phases of crystalline beds—intermittent and permanent.

The intermittent beds form on the bottom and along the shores of the lakes. They crystallize and redissolve with fluctuations in temperature. This can occur in a matter of hours, but as winter sets in, less solution of the crystals occurs, causing the beds to become thicker and more compact.

The permanent beds underlying the lake usually are interstratified with thin layers of mud, clay, and organic matter. These beds range in thickness from less than 1 m to several meters. At Ingebrigt Lake, permanent beds are reported (Cole 1926) to cover 2.7 km with an average thickness of 6.7 m. In one part of the deposit, a thickness of 42.4 m was measured. Cole estimated the tonnage of hydrous salt in Ingebrigt Lake to be 22.7 Mt. A more recent evaluation is 8.2 Mt of anhydrous sodium sulfate (Broughton 1977).

Most of the deposits currently in production contain several million tons of sodium sulfate. The one deposit in Alberta contains 2.7 Mt (Watson 1980); estimates of total reserves in Saskatchewan range between 54.4 and 181 Mt. Another evaluation places the total anhydrous sodium sulfate reserve at 54.4 to 63.5 Mt and evaluated commercial reserves at 27.2 to 36.2 Mt (Broughton 1977). An

updated estimate of reserves would account for the tonnage mined since then.

Current capacity is reported at approximately 613 ktpy though production has never been close to reported capacity. The termination of Agassiz's production reduced this figure to an effective capacity of approximately 453 ktpy. This could presumably increase by 160 ktpy should a new owner reopen the Agassiz operations. About 253 ktpy of capacity belongs to Saskatchewan Minerals, which is owned by Dickenson Mines, Limited (Goldcorp, Inc.).

In 1999, Canada produced about 350 kt of natural sodium sulfate and a significant amount of by-product and synthetic sodium sulfate (Garrett 2001). At that time, natural sodium sulfate was produced by Saskatchewan Minerals from their Chaplin Lake and Ingebrigt Lake properties and by Millar Western from their Whiteshore Lake property. All three are in Saskatchewan. In 2002, the Ingebrigt Lake property was closed (CIM 2001). In 2005, the Saskatchewan government listed the annual production of sodium sulfate in the province at about 530 kt and from five plants, but apparently two plans produce only sodium sulfate—Saskatchewan Minerals and Millar Western (Saskatchewan Industry and Resources 2005).

United States

Deposits of sodium sulfate are found in Arizona, California, Colorado, Idaho, Montana, Nevada, New Mexico, North Dakota, Oregon, Texas, Utah, Washington, and Wyoming. At the present time production is chiefly from brine deposits at Searles Lake, California, and in west Texas. Small quantities have been produced from saline lake deposits in Wyoming. Most of the southwestern brines are in dry lakes or playas underlain by beds of mirabilite, thenardite, and other evaporite salts. In the northwestern United States, the deposits associated with saline or intermittent dry lakes are similar in origin and composition to the Canadian deposits. Except for the brine deposits in west Texas, the deposits of the Southwest are chemically more complex than the northern deposits.

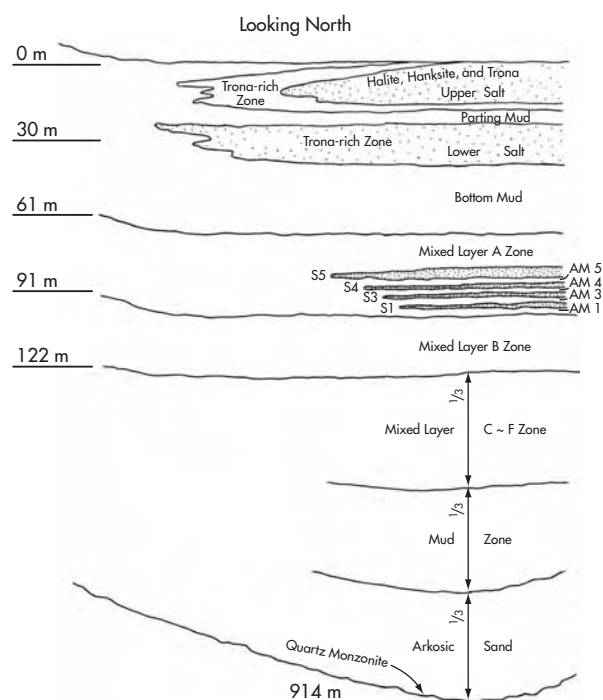
California

California has several sodium sulfate deposits. Dale Lake, Durmid Hills, Soda Lake, and Danby Lake have a record of past production but are not now producing (Smith 1966). Owens Lake has reserves of 10.9 Mt but has not produced any sodium sulfate (Kostick 1980).

At Searles Lake, minerals have been extracted from brines since 1873. Sodium sulfate was first produced in 1914. Searles Lake currently is the leading source of natural sodium sulfate in the United States (Moulton 1980). It probably has produced more sodium sulfate than any other deposit in the world. The Kerr-McGee Chemical Corporation operated the deposit for many years, but in November 1990 the operation at Trona, California, was purchased by the North America Chemical Company (Kostick 1990) and then by I MC Chemicals Inc., now known as Searles Valley Minerals Inc.

Sodium sulfate and other usable salts are produced at Searles Lake from brine underlying a large playa. The surface of the playa covers an estimated 155 km², but the central part, which forms the main deposit, is about 30 km² (Graubau 1920). A hole drilled by Kerr-McGee Corp. in 1968 encountered 930 m of basin fill and bottomed in quartz monzonite (Moulton 1980). Figure 3 shows the salt deposits in cross section.

Brine occurs in the interstices of the salt deposits. Ions present in the brine are sodium, potassium, carbonate, bicarbonate, sulfate, chloride, and borate. The upper salt, lower salt, and mixed layer are the productive zones, each contributing a distinctive brine to meet



Adapted from North American Chemicals Inc. company materials

Figure 3. Cross section of Searles Lake, California

the individual requirements the plants. In some instances, solar concentration of the produced brine is used to improve plant efficiency (Moulton 1980).

A plant expansion under way in 1977 was to bring capacity to 590 ktpy (Parkinson 1977). The plant never operated as planned and, in fact, in 1982 Kerr-McGee shut down about half of their sodium sulfate capacity, so output dropped to about 200 ktpy.

Utah

Sodium sulfate is no longer produced from natural brine at Great Salt Lake, Utah. Thick beds of mirabilite, intercalated with thin clay layers, have been found beneath the lake at several localities. Mirabilite crystallizes and sinks to the bottom of the lake during the winter. A layer of mirabilite 0.15 to 0.30 m thick occurs seasonally over large areas of the lake. Under favorable conditions, it is carried by winds and currents to the shore where it accumulates to a depth of 0.3 m or more. Strand deposits as thick as 3 m have been observed.

The Great Salt Lake is estimated to contain 3.8 Gt of salt, 342 Mt of which are sodium sulfate (Cohenour 1966). Great Salt Lake Minerals and Chemical Corp., an affiliate of North American Chemical Co., estimated that the playa contains 408 Mt of sodium sulfate (Kostick 1980).

On the north end of the lake, near Ogden, Great Salt Lake Minerals and Chemicals Corp. operates 69 km of evaporation ponds and a plant complex for producing potassium sulfate and magnesium chloride. Although sodium sulfate is no longer produced, common salt continues to be produced. The first production of sodium sulfate was reported in 1970. The operation had a sodium sulfate capacity between 22.7 and 32.9 ktpy.

Texas

The Ozark-Mahoning Company operated four sodium sulfate deposits in west Texas until 1987 when three of them—Rich,

Mound, and Brownfield lakes—were shut down and mothballed because of economic and climatologic conditions. The company had produced sodium sulfate from brine in west Texas continuously since 1933. The Texas deposits underlie playas and occur as brine and crystalline mirabilite. The brine contains mainly sodium chloride and sodium sulfate, with lesser amounts of magnesium and potassium salts, and is produced from wells 30.5 m deep. A fifth deposit, Soda Lake, near Monahans in Ward County, was abandoned in 1970 after nearly 40 years of continuous operations, during which time more than 1 Mt of anhydrous sodium sulfate were produced.

Cedar Lake deposit, near Seagraves, covers a surface area of about 21 km². It is the only deposit currently in production. Beds of crystalline salts are minimal, but strata containing saturated brines are found from near the surface to a depth of 30.5 m. The shallower strata contain brines of low salt content and are less productive. Richer brines come from beds 12 to 30.5 m below the surface. Brines from the Cedar Lake deposit contain about 10.5% sodium sulfate, 14% sodium chloride, and 1% each of magnesium and potassium.

The Brownfield Lake deposit, 16 km east of Brownfield, covers an area of about 4 km². The main deposit lies outside the boundary of the present dry lake surface. Saturated brine was produced from crystal beds at depths from 9 to 30.5 m. These beds, which contain thin layers of clay and silt, range from 1 m to as much as 4 m in thickness. The brine contains 15% sodium sulfate and 10% sodium chloride. A solution mining project to extract the crystalline reserve was developed.

The Rich Lake deposit, 19 km north of Brownfield Lake, produced sodium sulfate-bearing brine from a crystal bed averaging 2 m in thickness. The brine was transported by pipeline to the Brownfield Lake plant for processing. Ozark-Mahoning operated plants at Brownfield Lake and Cedar Lake. The combined capacity of the two plants was 159 ktpy.

A fourth deposit, Mound Lake, is located 13 km north of the Brownfield Lake plant. The lake has an area of 5 km², and lacustrine sediments occur to a depth of 24 m. The major portion of the reserve is brine similar in composition to that of Cedar Lake. A significant tonnage of mirabilite also exists. Mound Lake began producing in April 1981, and the brine also was transported to the Brownfield plant for processing.

The Brownfield plant, in addition to its sulfate deposits at Rich and Mound lakes, is being kept on a care-and-maintenance basis and could be reopened pending an improvement in the sodium sulfate market.

Arizona

At the Camp Verde deposit in Yavapai County, Western Chemical Co. mined solid beds of thenardite of varying thickness for many years. The deposit is unusual, because pure anhydrous sodium sulfate occurring in solid crystal form is rare. The deposit consists of layers of thenardite and other sodium salts interbedded with clay, which form a part of the Verde Formation. The total thickness of the beds is at least 46 m. Mining was done in a large quarry by underground room-and-pillar methods. The last mining was done by Arizona Chemical Co., a subsidiary of American Cyanamid Co., in 1934 (Ralston 1949).

Nevada

Nevada's principal producing deposit in years past was Rhodes Marsh, near Mina in Mineral County. The deposit covers 28 km². Production was confined mainly to the central portion of the deposit, where a bed of solid thenardite 1 to 2 m thick was mined (Ralston 1949).

New Mexico

A sodium sulfate deposit is known near Alamogordo in Doña Ana County. In Eddy County, near the potash mines, brine wells containing appreciable amounts of sodium sulfate and magnesium sulfate have been reported (Lang 1941). These wells were produced by Ozark-Mahoning from 1951 through 1957; the brines were trucked to Ozark's plant near Monahans, Texas, for processing. The wells depleted rapidly and were abandoned.

North Dakota

The sodium sulfate deposits of northwestern North Dakota are in Divide, Williams, Mountrail, and Ward counties. They are a southeasterly extension of the deposits in Saskatchewan. The Lewis and Clark Expedition first noted the sodium sulfate in North Dakota. Several lakes are known. The Federal Emergency Relief Administration (FERA) investigated and prospected most of them in 1934. The U.S. Bureau of Mines (USBM) in 1948 made an important reevaluation based on drilling (Binyon 1952).

The sodium sulfate content is generally high; sodium chloride, magnesium sulfate, and calcium sulfate are the main impurities. The USBM reported tonnages occurring in 18 lakes. They estimated that nine of the largest each contain more than 1 Mt of Glauber's salt. The major portion of the reserve occurs in the permanent and intermittent crystal beds, and only a minor portion occurs in the form of brine. Total reserves are reported to be 25 Mt of Glauber's salt or 11 Mt of anhydrous sodium sulfate (Binyon 1952; Crosby 1973).

The Grenora Lakes area contains three medium-sized sodium sulfate deposits—Grenora No. 1, Grenora No. 2, and Stink—with combined reserves of 6.9 Mt of Na_2SO_4 (Murphy 1996; Garrett 2001). Grenora No. 2, the largest deposit, covers 2 km². FERA drilling showed the maximum thickness of the permanent crystal bed to be 24 m and the average thickness to be 3.66 m. USBM estimated that the deposit contained 5 Mt of Glauber's salt or 2.2 Mt of anhydrous sodium sulfate (Binyon 1952). Drilling conducted by Ozark-Mahoning in 1977 generally corroborated the Bureau's estimate. Ozark-Mahoning owns Grenora No. 2 but it is not favorably located for economical exploitation.

Other States

A number of deposits in Montana, Washington, and Wyoming are not considered economically important because of their location and size, even though their composition is similar to the Canadian deposits.

China

Information on sodium sulfate in China, though available, is not readily attainable; therefore, not much is known about the geology of deposits. One known occurrence is a salt lake at Yuncheng, north of the Zhongtiao Mountains in Shanxi, which has been a source of salt for centuries. Chemical plants around the lake use brine containing significant amounts of boron, bromine, calcium, and iodine in addition to sodium sulfate and other sulfur compounds. Production from Yuncheng reportably accounts for 60% of China's output of mirabilite (Chin 1986).

An aquifer brine with high concentrations of sodium sulfate occurs 10 to 15 km west of Pengsham City, Szechuan Province, on the western bank of the Minkiang River. The brine occurs at a depth of 18 to 50 m primarily in a band about 20 km long and 1 to 6 km wide that is roughly parallel to the river, with a second small band 0.5 by 2 km just north of the city. The brine is pumped from hundreds of wells into solar evaporation ponds where mirabilite is crys-

tallized in winter and then dehydrated to form an anhydrous product. The brine occurs in Cretaceous and Middle Triassic limey clay that contains anhydrite crystals. It averages 97.8 g/L Na_2SO_4 , and reserves are reported to be 4.65 Mt of sodium sulfate (Hou and Yang 1938; Garrett 2001).

Mirabilite has been reported at the 200,000-km² Qaidam Basin, in Qinghai, which contains 20 major salt lakes. Mineralization in the basin includes mirabilite, boric acid, and lithium, in addition to sylvite and salt (Chin 1983; Garrett 2001).

Sodium sulfate also occurs with several of China's large soda ash deposits, such as at Chaganor. The Pleistocene deposit is located in the central part of the Inner Mongolia Autonomous region, 80 km south east of Erlianhot. The deposit covers 21 km², with nine porous brine-filled beds of salts containing about 11.3 Mt of sodium carbonate and 4.5 Mt of sodium sulfate (Garrett 2001).

In 1999, China produced an estimated 300 kt of natural sodium sulfate, 27 kt of sodium sulfate as a by-product, and 30 kt of synthetic sodium sulfate (Garrett 2001).

In 2003, a new anhydrous natural sodium sulfate operation with an annual capacity of 200 ktpy came onstream near Xishunhe in Hongze County, Jiangsu Province. The plant uses mirabilite from the only large sodium sulfate deposit in east China. A second facility in the area owned by a Chinese chemical company and a Spanish sodium sulfate producer has an annual capacity of 600 ktpy, making the region the world's largest natural sulfate production base (Kostick 2004).

Turkey

Natural sodium sulfate is produced in Turkey, although output is not large. First production recorded was in 1963, when 1.264 kt were produced. Output has increased steadily, and production in 1990 was about 80 kt, making it seventh in world production (Kostick 1991).

Several saline lakes in southwestern Turkey contain appreciable amounts of sodium sulfate. Tersakan Lake is about 160 km south of Ankara, near the town of Cihanbeyli. The lake, 13 km long and 4 km wide, covers 52 km². Its sodium sulfate content is greater than 8%. Sodium chloride and magnesium sulfate are present in amounts less than 5% and 2%, respectively, and because the calcium lake water has been impounded to induce evaporation, the sodium sulfate content of the brine increases. In the bottom of the ponds, crystalline layers more than 95% pure have formed.

At Aci Gol, a large lake 56 km east of Denizli, the saline content is similar to that of Tersakan Lake, although the sodium content is slightly lower and the content of sodium chloride slightly higher. Aci Gol is more than 26 km long, nearly 10 km wide, and has a surface area of about 200 km².

Production of sodium sulfate has come from Aci Gol: Alkim Alkali Kimya (in addition to two small lakes), Sodas Sodyum Sanayi, and Otuzbir Kimya Ltd. (Karayazici 1988). In 1999, Turkey produced 183 kt of natural sodium sulfate, 79 kt of by-product, and 71 kt of synthetic sodium sulfate for a total of 333 kt of product (Garrett 2001).

Iran

Iran produced 185 ktpy of sodium sulfate in the year ending March 1990; down somewhat from their peak production of 265 ktpy in the year ending March 1988. In 1990, production was from 13 mines in the provinces of Markazi, Semnan, and Teheran (L. Antonides, personal communication). Considerable sodium sulfate is produced as a by-product or coproduct of Urmiah (Reziieh) Lake's K_2SO_4 production. In 1999, Iran produced an estimated 180 kt of natural

sodium sulfate, 214 kt of sodium sulfate as a by-product, and 39 kt of synthetic sodium sulfate (Garrett 2001).

Chile

Small amounts of natural sodium sulfate are produced from playa deposits in northern Chile. The deposits are in the Atacama Desert, which lies along the west side of the Andes between the mountains and the Pacific Ocean, at an elevation of about 1,067 m. Some additional output is by-product from the nitrate industry. In 1999, Chile produced an estimated 150 kt of natural sodium sulfate, 16 kt of sodium sulfate as a by-product, and 20 kt of synthetic sodium sulfate (Garrett 2001).

Argentina

Many salt lakes and playas, some of which contain rich deposits of sodium sulfate, are located in Argentina, on the arid plateaus and in the intermontane valleys of the Andes (Wells 1923).

A large playa deposit of mirabilite and other salts is located in northwestern Argentina in Jujuy Province. The deposit is in the Andes at an elevation of 3,353 m. A permanent bed of mirabilite covering 53 km² occurs in the middle of a dry lake bed. The permanent bed, covered by a thin layer of sodium chloride, calcium sulfate, and sand, is reported to be 4.6 m thick at the center of the deposit and gradually thinner toward the edges. Subsurface waters from melting snow in the surrounding mountains feed into the lake and thus furnish a supply of brine year-round.

Production of natural sodium sulfate in Argentina decreased from 32 kt in 1986 to 15 kt in 1999. In that same year (1999), by-product sodium sulfate was 15 kt, and synthetic sodium sulfate was 43 kt (Garrett 2001).

Africa

A series of salt pans, some of which contain sodium sulfate, occur in the deserts and velds of the South African uplands. To date, none have been commercially exploited. In 1968, however, Associated Sulfate (Pty.) Ltd. was established to build a plant to produce sodium sulfate using raw materials from solar salt pans and effluent from the Rustenburg platinum plant.

Many alkali lakes and playas found in South Africa contain brines and a mixture of salts, such as Britten and Hagenstad pans. Some contain mirabilite-thenardite deposits and a high-sulfate brine, but as of 1999, there was only modest sodium sulfate production from these lakes. Most of the production potential is for sodium sulfate as a by-product from sodium chloride production (Garrett 2001).

About 110 Mt of sodium sulfate reserves exist in the Makgadikgadi Basin of Botswana (Massey 1973; Kostick 1980). For more than 40 years, various parties have considered developing, or attempted to develop, this large deposit, which covers more than 900 km².

In March 1991, a plant was completed at Sua Pan by Soda Ash Botswana (Pty.) Ltd., owned 52% by a South African consortium and 48% by the government of Botswana.

Production of 300 ktpy of soda ash and 650 ktpy of common salt was predicted to occur some 2 years after the initial startup of the plant. Garrett (2001) reported that as of 1999, no sodium sulfate production had occurred. Sodium sulfate and potassium chloride are mentioned as possible by-products (Antonides 1988).

Sodium sulfate deposits are found in the northern part of the Western Desert of Egypt, some 80 km west of the Nile Delta. Twelve principal lakes occur for 25 km along the axis of Wadi El Natrun, a minor tectonic depression. Some of the larger lakes remain permanently flooded, whereas the smaller lakes dry up seasonally.

Upon exploration, one of the latter, Beida Lake, was discovered to contain probable reserves of the B category, exceeding 1.1 Mt of thenardite and about 100 kt of halite. In 1999, Egypt produced an estimated 25 kt of natural sodium sulfate, 42 kt of sodium sulfate as a by-product, and 3 kt of synthetic sodium sulfate (Garrett 2001).

Commonwealth of Independent States

Production of sodium sulfate from bedrock and playa deposits has steadily been decreasing since the demise of the former U.S.S.R., from a high of more than 350 kt in 1989 to less than 50 kt in 1999. In the same period, production of sodium sulfate as a by-product and synthetic material both maintained production rates of more than 350,000 tpy (Garrett 2001).

Many deposits containing sodium sulfate occur in the CIS, in a large area from the Black Sea to western China and farther north into west-central and eastern Siberia. The economically important deposits are in the Aral and Caspian depressions and in the Kalunda Steppe in Kazakhstan. Although literature on sodium sulfate deposits in the Russian republics is reportedly fairly extensive, it is not readily available and requires translation. The reader is referred to a paper by Dort and Dort (1970) that contains a summary of several publications on Russian deposits.

The largest known occurrence of sodium sulfate in the world is in the Kara Bogaz Gulf (Kara Bogaz Gol), an embayment on the eastern side of the Caspian Sea. It is separated from the Caspian by a bar with a narrow strait through which water flows from the sea into the embayment. In 1927, the gulf covered 18,000 km² and the average brine was about 8 to 9 m. The first salts were crystallized about 500,000 years ago. Three separate layers are present: the upper layer is at a depth of 0 to 0.3 m and is up to 3 m thick; the middle layer is at a depth of 5 to 8 m; and the lower layer is at a depth of 14 to 18 m. Gypsiferous-carbonate muds separate the salt layers by 2 to 5 m. Beginning in 1934, a drying cycle and lowering of the Caspian Sea resulted in less water entering the gulf (Garrett 2001).

Kolosov, Pustyl'nikov, and Fedlin (1974) reported that the Kara Bogaz Gulf experienced a final phase of intense desiccation between 1939 and 1948. Seawater then moved across the bar from the Caspian Sea at a reduced rate of 9 to 10 km per year. For a time, the movement of seawater into the bay apparently reached equilibrium with evaporation. After 1957 or 1958, no decline in water level or constriction of the bay's area or appreciable change in brine composition was observed. Gypsum and glauberite were being precipitated out of the saturated brine throughout the bay. Bloedite (astrakanite) and halite were being deposited locally. Some carbonates were being deposited in the zone of mixing adjacent to the strait.

As a result of concern over the declining water levels in the Caspian Sea, a dam was constructed in 1980 across the strait that had once replenished the Kara Bogaz Gulf with Caspian seawater. This accelerated the severe desiccation of the gulf and, by 1983, no surface brine remained. Winds carrying sulfate dust traveled hundreds of kilometers, causing severe ecological problems (Levine 1988). Seawater was released to the gulf in 1984 at about 2 km³/yr (Kurilenko, Ruday, and Shvarts 1988). This, however, was apparently inadequate to solve the problem. Soviet scientists predicted that 80% of the minerals in the gulf would be irretrievably lost without adequate recharge from the Caspian Sea (Levine 1988).

The first commercial utilization of salts at Kara Bogaz Gulf, which began in 1929, used surface waters as a source of raw material. This source was abandoned, however, in 1953, because of the fluctuating hydrological and hydrochemical regimes of the gulf, and the operators began pumping the interstitial brines of the buried salt deposits as a feed source. Four recognizable salt horizons occur

to a depth of 18 m, each with distinct hydrological and mineralogical characteristics. Recent hydrological proposals by scientists from Leningrad State University and the All-Union Research Institute of Halurgy have recommended the following changes to the local brine industry: locating and developing production wells based on optimum hydrogeology and stratigraphy, lowering the brine output of each well from 500 to 250 m/hr, and using the end liquors from the plants to recharge the pay horizons (Kurilenko, Ruday, and Shvarts 1988).

In 1924, Kara Bogaz Gulf was estimated to contain 1 billion t of sodium sulfate (Grabau 1920). Later estimates of 2 billion t were reported (Goudge and Tomkins 1960; Hemy 1969). More recently, Russian sources indicate that reserves at Kara Bogaz Gulf may be lower than was previously thought (Kurilenko and Frolovskii 1982).

The Aral Sea is considered to be another rich source of sodium sulfate but the diversion of water from its two major tributaries, the Amu Darya and the Syr rivers, for agricultural purposes has resulted in a severe constriction of the Aral. Unless replenishment can be reestablished to counteract the evaporation loss, it has been predicted that the Aral Sea could be gone within another 30 years (Ellis and Turnley 1990). Although there have been later schemes to change this trend, *SurfWax Geography News* (2005) notes that the Aral Sea, once the world's fourth largest lake, is now the tenth largest, having shrunk by 39,994 km² since an atlas of the region was produced in 1967.

Some sulfate is produced in the central Asian republics that adjoin it. Lakes in western Siberia and in Kazakhstan are good sources but are not known to be currently producing except on a local scale. The steppe region around Kalunda, in Alta Kray, has a number of lakes rich in sodium sulfate. A sulfate combine was established on Lake Kuchuk, the largest of these (Hemy 1969).

Sodium sulfate and magnesium salts are produced from Kara Bogaz Gulf by Karabogazgolsulphate Combine. In 1990, the CIS ranked fourth in world production, producing an estimated 365 kt of natural sodium sulfate (Kostick 1990), mostly from the Kara Bogaz Gulf deposit. A 37.5-ktpy sodium sulfate unit was commissioned there in 1988 (Levine 1988). In 1999, Garrett (2001) estimated that the CIS produced 40 kt of natural sodium sulfate, 375 kt of by-product, and 365 kt of synthetic sodium sulfate for a total of 780 kt of sodium sulfate from all sources.

Antarctica

Because mirabilite is the first mineral, after ice, to appear in freezing seawater, it is not surprising that several occurrences have been noted in Antarctica. Mirabilite efflorescences commonly occur on the surfaces of rocks, glaciers, and sea ice; some occurrences are also reported farther inland.

Sodium sulfate has been described in coastal lakes that have been elevated and separated from the sea because of isostatic rebound. Other occurrences are reported in impoundments behind glaciers. The inland deposits are probably a result of seawater-derived salts transported with snow and accumulated in local depressions.

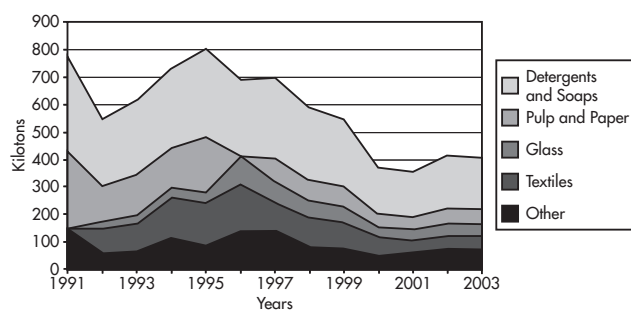
Though these occurrences are not economic, they are of geological interest. The reader will find them described in a paper by Dort and Dort (1970) along with a discussion of the low-temperature origin of sodium sulfate.

SYNTHETIC SODIUM SULFATE

Synthetic production was formerly grouped together under the by-product listings, which are still the predominant segment. It includes one of the faster growing segments of sodium sulfate production—that of reclaiming sodium sulfate from waste streams. For

many years, synthetic sodium sulfate has been a by-product or coproduct from the production of other chemicals. Now, because of its importance, synthetic sodium sulfate from reclamation processes has been added to this list of synthetic sodium sulfate sources. Important sources follow.

- *Manufacture of viscose rayon.* Sodium sulfate is generated in an acid spin bath by the neutralization of sodium hydroxide used to prepare the viscose solution. In the past, this source has been of almost equal importance with natural sodium sulfate on a worldwide basis. Growing popularity of other synthetic fibers coupled with environmental concerns, however, has resulted in reduced production. Of particular significance has been the replacement of rayon tire cord by other synthetic fibers, fiberglass, and steel. Nevertheless, rayon manufacturing continues to be an important source of supply. Avtex Fibers, Inc., a major manufacturer with nameplate capacity of 77 ktpy, ceased operation in November 1989 after encountering difficulty meeting environmental standards (Kostick 1990). Liberty Fibers Corp., Lowland, Tennessee, is the only rayon producer in the United States. They have a capacity to produce 38 tpy.
- *Manufacture of hydrochloric acid from sodium chloride and sulfuric acid in the Mannheim furnace and similar processes.* In the Hargreaves process, sulfur, steam, and air are substituted for sulfuric acid. Many years ago, the Mannheim furnace was the main source of sodium sulfate, and this chemical was truly a coproduct rather than a by-product. Because the salt discharge from the furnace tended to form cakes, it was named salt cake. This name remains as a trade designation for low-grade sodium sulfate. Large amounts of hydrochloric acid are produced today as a by-product in the manufacture of chlorinated hydrocarbons. As a result, the Mannheim furnace process is generally considered to be obsolete; in certain geographical areas, however, and in particular raw material situations, it continues to be an economically significant source of sodium sulfate.
- *As a by-product in numerous other processes* wherein certain sodium salts are converted to acids by reaction with sulfuric acid, or sodium alkalis are neutralized with sulfuric acid as part of the process. Current operating (or under construction) examples are the processing of chromium ores to produce sodium dichromate and the production of lithium salts, vanadium pentoxide, boric acid, ascorbic acid, phenol, formic acid, silicic pigments, and various catalysts. One aspect of several of these producers, both in this category and the preceding, needs to be noted: their ability to change the by-product. In the Mannheim furnace, for instance, if potassium chloride is substituted for the sodium chloride, then the by-product is potassium sulfate instead of sodium sulfate. It is an economic decision and might have to include some changes in some of the processing equipment. But, it is not just limited to this one process, and should the market become extremely depressed, or perhaps if alternative opportunities arise, there could be further switching by the by-product and coproduct manufacturers.
- *Reclamation.* This newly added category includes reclamation of sulfate values with final form of sodium sulfate from liquid waste streams and from flue-gas desulfurization (FGD) units, and reclamation of lead from discarded batteries. In the former, there have been a number of articles about the Aqua-Tech process by Allied-Signal, Inc., which treats sulfate-bearing streams from pulp mills, thus generating sodium sulfate for internal process use or sale to other pulp mills and with excess available for sale to the open market.



NOTE: For 1991, glass was combined with "other." For 1996, pulp and paper was combined with "other."

Figure 4. Sodium sulfate consumption in the United States since 1991

In 1985, USBM published its pilot work with the citric process for the FGD that has been installed in several coal-fired electric power generating plants. Engineering firms have made a number of inquiries about the processing from the Glauber's salt phase, the final product shown in the report, to a final anhydrous material for sale on the open market. If left with Glauber's salt as a final form, most areas at present would permit it to go to a landfill. An annual report by USBM shows two small producers with FGD as sources, which perhaps incorporate the citric or a similar process. It may be that this process is more attractive than FGD units which generate gypsum.

Natural sodium sulfate remains the source for about half the market in the United States and has remained important worldwide during the past decades. Although vast resources are available, producers of the natural material currently are aware of the threat from by-product sources. The outlook for the natural sodium sulfate business is certainly not the most promising it has ever been.

END USES

Detergents

In the United States, the detergent industry has displaced the pulp and paper industry as the leading market for anhydrous sodium sulfate (Figure 4). As used by the detergent industry, sodium sulfate is an inexpensive filler and diluent, because it is white, noncorrosive, and neutral. In addition, it is claimed to have very mild detergent properties. Formerly, about one third of dry home laundry detergent was sodium sulfate. Now it is much less than that, perhaps one sixteenth or even as low as one sixty-fourth. Dry laundry detergents are now losing ground to liquid home laundry detergents. The liquids now make up as much as 50 % or more of the home laundry detergent market.

Kraft Paper

At the beginning of the 1980s, the manufacture of kraft paper pulp was the principal use of sodium sulfate. It has now dropped to a distant second place, being almost the sole segment of decline for the consumption of sodium sulfate. In the early part of the decade, the substitution of emulsified sulfur and caustic soda, which was much cheaper than salt cake, first made an impact on salt cake usage. Synthetic suppliers who had formerly produced truly a salt cake—notably the rayon industry and similar by-product producers—had to upgrade their facilities to produce higher-purity material. This decline trend began in 1982 and continues because of more efficient kraft recovery systems and environmental rules and regulations. The potential for this industry to be a net producer of sodium sul-

fate was mentioned in the Synthetic Sodium Sulfate section of this chapter.

Glass

Another important consumer of sodium sulfate is the glass industry. Sodium sulfate has two favorable effects in the glass melter: it promotes early reaction with unmelted batch and it has an influence in the early stages of glass formation. Harben (1991) noted that a batch of container glass has about twice as much sodium sulfate as flat glass, at about 1% and 0.5%, respectively. This tracks to the concept that because sodium sulfate is an aid to the pliability of the glass, the more complicated the shape of the glass mold, the more sodium sulfate is used. It does appear that flat glass is much more demanding in certain aspects such as particle size and limits of certain chemical contaminants. Both commodities demand the least variation possible for all their raw materials, and sodium sulfate is definitely included.

Other Uses

The textile dyeing industry was once a large consumer of sodium sulfate in the United States; this industry, however, is mostly gone because offshore labor is less expensive for the textile industry. Without U.S.-produced textiles, there is little need for a domestic textile dyeing industry. The world's leading manufacturer of dyeing equipment, Gaston County Dyeing Machine Company, reports that using sodium sulfate reduces corrosion of the stainless-steel equipment used in the industry. A big impetus for the switch over from common salt to salt cake has come from the recent formulation of dyes that allow sodium sulfate to be as efficient as common salt in penetrating the dye to the center of the thread.

A number of other uses for sodium sulfate still are important, though the consumption is spread out to many small users rather than the few large users of the previous industries. It is used, for example, as an ingredient of stock foods and remedies, in the manufacture of inks, in tanning of leather, and in the manufacture of synthetic sponges.

The literature abounds with articles and patents for the use of Glauber's salt as one of the main ingredients in passive solar energy devices. The advantage it offers is that, with appropriate other salts, its phase change is at room temperature. It absorbs significant amounts of energy in the process of crystallizing and then as it melts it gives off energy at the same temperature. Thus, with the appropriate phase-change temperature and the appropriate salts in the mixture, it can moderate the heat load in warming an environment or, conversely, moderate the cooling load in keeping an enclosure cool. No commercial applications have made a lasting effect though. The problems (no single source is cited) stem from the mixture surviving only a finite number of phase changes and then having to be either recharged or replaced. New and better mixtures are claimed, but they have not as yet made their way to the marketplace with any success.

It is difficult to estimate worldwide consumption patterns because of great variations from one country to the next. Canada, Sweden, and Finland are large producers of kraft paper pulp, and perhaps 95% of the sodium sulfate consumed in those countries is used for this purpose. Environmental concerns are having effects overseas similar to those being experienced in the United States. In the United Kingdom, France, Germany, Japan, and many other countries, paper production is small, so the major consumption of sodium sulfate is in detergents, glassmaking, production of other chemicals, dyeing processes, and miscellaneous uses. Worldwide consumption patterns probably are not far from the estimate shown for the United States (Figure 4).

PRODUCT SPECIFICATIONS

Because there are no industry standards for designation of grades, types, or specifications, there is a proliferation of designations, most of which are not fully applicable throughout the industry they are supposed to describe. Detergent grade, for instance, has in common only purity—and even that is not completely uniform. A product that is 99.7% pure, yet has a trace of coloring, would not be acceptable to most detergent manufacturers. Those manufacturers in the detergent industry are further differentiated by their tolerance for varying amounts of common salt, iron, and also have individual particle-size considerations, sometimes completely at different ends of the spectrum from each other.

When perusing the literature, or perhaps when discussing the uses of sodium sulfate with those familiar with the industry and members of the fraternity of producers, it is not rare to hear or see the term *salt cake* applied loosely to mean all production of sodium sulfate. This term technically applies to sodium sulfate that is discolored, is lumpy, or has contaminants; these attributes preclude its use except by the pulp and paper industry or other industries that can tolerate such attributes and where it is sold at reduced prices. Salt cake in this latter, and more accurately narrow, connotation can range in purity from 90% to 99% Na_2SO_4 . As mentioned in the earlier discussion of the Mannheim process, the sodium sulfate produced was relatively impure and discolored, and it came out in the form of cakes—thus the term *salt cake*. It is synonymous with low-purity sodium sulfate. Only a few natural resource producers have selected this grade for production, most of the time as captive sources for the pulp paper industry. They are able to accomplish this production with very little refining required in the beneficiation process.

High purity, also referred to as technical grade, refers to anhydrous sodium sulfate with a purity of 99% or greater. Different consumers for the same end use may have quite different specifications. Particle size and strict limits on trace contaminants are important to almost all consumers of this grade of material. The glass industry, in particular, can be very strict about iron, copper, or any of the noble metals, with limits in the parts per million. Most production from the natural resource producers can meet these stringent limitations, but only with some earnest effort.

Glauber's salt (mirabilite), the decahydrate of sodium sulfate, was once an item of commerce. Because Glauber's salt has a melting point only slightly above room temperature and it effloresces when exposed to ambient conditions, anhydrous is preferred for most volume usage. Small quantities of Glauber's salt are still sold, however, for some special uses.

PROCESSING

No two operations are exactly alike for any of the natural producers. It is only after the point where Glauber's salt is delivered to the evaporative process that strong similarities are apparent. Even within the same company, or different companies operating in the same vicinity, the stages up to and sometimes through the crystallization of Glauber's salt are different. It ranges from minor, though notable, differences to extreme differences. After the Glauber's salt is fed to the evaporative system, however, the systems could be interchangeable for the same final product being desired. That is, paper-grade systems could be interchanged with each other or technical-grade (high-purity) systems might be interchanged and have little or no effect on the end product. It is the mining and extraction procedures up to this point that differentiate the producers. This is true worldwide. Each deposit differs somewhat in composition. Some of the deposits, such as those in Saskatchewan and Texas, are simple salts with only one product extracted. Those of

the Great Salt Lake and Searles Lake host a complex set of minerals, and a number of them are extracted in sophisticated processes in various forms and varieties. Yet, once the Glauber's salt is extracted, not too much difference remains in the final steps.

Canada

A number of structural changes have been made in the Canadian industry since the sixth edition of this book. Saskatchewan Minerals, formerly a Province Corporation, is now owned by Dickenson Mines, Limited (Goldcorp, Inc.). The Francana Operations at Metiskow, Capri, and Alsaska have all closed. At present, only two of the natural producers' locations are in production. These are Saskatchewan Minerals' plant at Chaplin, Saskatchewan, and Millar Western Industries Ltd., formerly Midwest Chemicals, at Palo, Saskatchewan. Both Canadian producers use seasonal temperature differences to assist in processing the sodium sulfate deposits. Brine accumulates on the lake bed and becomes nearly saturated in the late summer months. Then it is pumped to large reservoirs that may be more than 3 m deep. As cold weather sets in, Glauber's salt crystallizes from the saturated brine. The residual mother liquor, containing most of the magnesium and sodium impurities, is drained off. After draining, the Glauber's salt remains in the reservoirs until the coldest part of the season, usually January or February, when it is harvested and accumulated in stockpiles at the plant site.

A dredging system, pioneered by Orminston, was used in the 1990s at two of the lakes to supplement the stockpiled supply during the warmer season. Besides Orminston, Saskatchewan Minerals at Chaplin used a dredge in the warm weather. No Canadian company is using this process, however, in 2005.

Obviously, the Canadian plants are somewhat dependent on nature to produce the crystals of Glauber's salt. Drought or other unusual conditions can affect the production cycle. The plants try to keep more than 1 year's supply of Glauber's salt in their stockpiles to keep production from being interrupted by such conditions. This method has proved very successful in Canada, producing a salt cake of high quality.

To prepare a salable anhydrous product, the Glauber's salt must be dehydrated. Because of the inverse solubility of sodium sulfate (i.e., less soluble at higher temperatures), this is not a simple, straightforward operation. In the early days, dehydration was done in large rotary kilns, some of which were fired by lignite. None of the operating producers are using this method.

When Glauber's salt is melted, the solubility of anhydrous sodium sulfate in the water of crystallization is exceeded, causing precipitation. The balance of the water must be evaporated to produce an anhydrous product. Ozark-Mahoning's submerged combustion evaporators are used for this purpose by Millar Western Industries. The Saskatchewan Minerals plant at Chaplin uses a multiple-effect vacuum evaporator.

The choice of evaporative system is an economic issue, hinging mainly on two issues: initial capital cost and energy efficiency. The choice is either low capital cost, such as for submerged combustion evaporators and other direct-fired units with high operating cost for energy and maintenance, or high-energy-efficiency evaporators, such as the multiple-effect or mechanical vapor recompression evaporators, which have higher initial capital cost but enjoy low energy and operating costs. If high energy efficiency is chosen, a second issue is choosing between multiple-effect and mechanical vapor recompression evaporators. Then the selection criterion is the relative cost of electricity and gas or other heating fuel. The multiple-effect evaporators use more heating fuel and less electrical energy than the vapor recompression evaporators but can be more

cost-effective depending on the relative cost. It was the relative cost of fuel that prompted Saskatchewan Mineral's Chaplin plant to choose the multiple-effect over the vapor recompression evaporators when they replaced their Holland evaporator in 1983.

At all plants, the anhydrous salts precipitated in the evaporators can be separated from the saturated solution by mechanical means, including centrifuges and hydrocyclones, and the wet salt is finally dried in direct-fired rotary kilns. Parallel-flow dryers are now preferred for ease of control and fuel economy, whereas in the older processes countercurrent flow was used in the dryers.

Mexico

The brine processed at Quimica del Rey, S.A. de C.V., is very strong and probably saturated. It contains more than 26% sodium sulfate and appreciable amounts of chlorides and magnesium. About 65 wells produce the brine from a depth of approximately 12 m. The brine temperature is 25°C before precooling with the spent brine. The cooled brine is fed to a vacuum crystallizer where it is cooled to 9°C by evaporative cooling, causing Glauber's salt to crystallize. The slurry is thickened, filtered, and melted. Evaporation is accomplished in multiple-effect evaporators. Final drying is in co-current-fired rotary kilns. Part of the mother liquor is processed further for recovery of magnesia products and the balance goes to waste.

United States

The United States has also seen changes in corporate ownership. Kerr-McGee sold its Searles Lake plant to North American Chemicals Inc. in 1990. This is now owned by Searles Valley Minerals, Inc. (IMC Chemicals Inc. is an affiliate of Great Salt Lake Minerals and Chemicals Corp.). The largest production of natural sodium sulfate in the United States still comes from Searles Lake, California, even though output is much less than in the past. Before 1982, the Kerr-McGee Chemical Corp. plants made about 500 kt of sodium sulfate annually. The Trona plant, representing about half of the total sodium sulfate capacity, was shut down in 1982. Similarly, the Argus plant, which is the newest addition in the area, is not currently operating. The Westend plant now is Searles Valley's only source of sodium sulfate.

The Searles Lake brine is complex, and a number of salable products are extracted. At the Westend plant, sodium sulfate is recovered along with soda ash and borax. Mixed brines are first carbonated with carbon dioxide to precipitate sodium bicarbonate, which is removed by filtration. The decarbonated brine is cooled to crystallize borax. This borax is separated from the brine, which is then cooled further to produce a crop of Glauber's salt. After it is removed, a final cooling recovers a second crop of borax. Heating converts the sodium bicarbonate to soda ash and the borax is either crystallized as a hydrate or dehydrated to anhydrous form. The Glauber's salt is washed, melted, and recrystallized as anhydrous sodium sulfate. The following description of the Trona plant is included because it is of interest, even though the sodium sulfate part is shut down.

The Trona main plant cycle had three major process plants. The brine from the lake was cooled to produce a crop of Glauber's salt that was removed and dried to sodium sulfate. The resultant mother liquor from this step was processed further to recover potash and borax. A different brine was treated in a liquid-liquid solvent extraction plant to recover boron values as boric acid. After it was removed, mixed sodium and potassium sulfates were precipitated by evaporation, and these mixed sulfates were fed to the potassium sulfate plants. The Trona carbonation plant was somewhat similar to the Westend plant in that carbon dioxide precipi-

tated sodium bicarbonate, which was filtered and removed. Cooling then precipitated borax. Finally, burkeite, a double salt of sodium sulfate and sodium carbonate, was recovered and fed to the Argus process.

In the Argus plant, brines from the lake were mixed with burkeite solutions and streams from other plants to recover additional soda ash. Nothing has been published since Moulton (1980), so the details of plant practice at Trona are not available.

Cooper Natural Resources is the nation's second largest natural producer of sodium sulfate. Cooper Natural Resources operates the Dry Gulch plant (also known as the Seagraves plant) in Terry County, Texas, which has a capacity of 141 kt and has the Brownfield plant with a capacity of 64 kt on standby. Both plants use a refrigeration process to crystallize the Glauber's salts that had been developed in the early 1930s for a plant near Monahans, Texas. The Monahans plant closed in 1970 because the deposits were essentially exhausted. The Ozark submerged combustion burner used in the evaporative section of the old Monahans plant probably represented the first commercial application of submerged combustion in the United States.

The Texas brine contains both sodium chloride and sodium sulfate, as well as smaller amounts of magnesium and potassium salts. At the Brownfield plant, a portion of the brine was pumped through the Permian salt bed to introduce sodium chloride. The high sodium chloride content depressed the solubility of sodium sulfate, improving its extraction. At the Seagraves plant, sufficient sodium chloride is present in the brine; additional salt is not needed. The Texas climate does not lend itself to the production of Glauber's salt by atmospheric chilling, so mechanical refrigeration and heat exchange are required. The Glauber's salt formed in this manner is filtered and washed, yielding a product of high purity.

Melting and dehydration of Glauber's salt is accomplished by a mechanical vapor recompression evaporation system, which has much improved fuel efficiency over the former submerged combustion units, even after the Seagraves plant had been updated with a heat recovery system in conjunction with the submerged combustion units. Hydrocyclones and centrifuges separate the anhydrous crystals from the saturated solution, which is returned to the evaporators. The crystals are dried in parallel-flow rotary kilns.

Other Countries

Other than for Spain, little is published about processing in other countries. The little that has been seen is consistent with the earlier statement that the mining portion differs, extracting by incorporating some form for crystallization of Glauber's salt, and the evaporative portion is in line with the techniques applicable for the particular end use of the material. It can be reasonably assumed that methods used are similar to those used in the United States, Mexico, and Canada, wherein chilling by natural or mechanical means precipitates Glauber's salt, allowing separation from other salt. The Glauber's salt would then be dried to anhydrous sodium sulfate.

In Argentina, saturated brine from a lake bed is pumped to crystallization tanks where great night and day temperature variations result in precipitation of Glauber's salt. This is possible because the plant site is at an elevation of 3,353 m. The Glauber's salt is melted by heating; the precipitated anhydrous sodium sulfate is then separated and dried. There is no evaporation of water, so the saturated solutions probably are recycled through the system.

Deposits in Spain, one of the few countries where thenardite is the starting material, are mined underground and present special problems because the minerals contain an appreciable amount of calcium sulfate in the form of glauberite ($\text{Na}_2\text{SO}_4 \cdot \text{CaSO}_4$). Countercurrent leaching at temperatures between 35° and 40°C dissolves

most of the sodium sulfate, leaving calcium sulfate undissolved. The solids, which probably contain other insoluble impurities, are settled in large Dorr thickeners. A second leaching step with water at 29°C results in maximum recovery of sodium sulfate. Evaporation is carried out in a single-effect vacuum evaporator with forced circulation. Final drying is done in a fluid bed dryer with hot air heated by steam (McIlveen and Cheek 1994).

PRICES

Published price information for sodium sulfate usually only approximates the true market price. In the United States, prices usually are based on quotations from by-product sources located near consuming points. Because producers of the natural salt are located at great distances from most customers, the free on board (f.o.b.) plant value for natural material may be much less than the published price. On the other hand, in periods of shortages and rising prices, published information often lags behind actual selling levels.

In 1998, the terms “Most-Favored Nation” and “Non-Most Favored Nation” were discarded and “Normal Trade Relations” and “Non-Normal Trade Relations” came into use. By 1999, “Non-Normal Trade Relations” was no longer applicable and was not used. A few rogue nations without normal trade relations with the United States, however, face significantly higher tariffs. In 2003, the sodium sulfate (100% Na₂SO₄, bulk, f.o.b. works, in the East) was \$114 per 0.9 t. In regard to tariffs, crude (salt cake) was free, but anhydrous sodium sulfate had a 0.4% ad valorem tariff.

For tax purposes, a depletion allowance of 14% for both domestic and foreign deposits is permitted by the Internal Revenue Service.

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Decorative Stone

George S. Austin, James M. Barker, and Scott C. Lardner

INTRODUCTION

Stone, one of the oldest building materials, today remains a well-established material used throughout the construction industry. It is still widely considered to be the most aesthetically pleasing, prestigious, and durable building material. The use of natural stone is much less prevalent now than in the past, though demand is rising. New and reopened quarries are coming online to meet increased demand related to new building technology and increased residential use of stone. Natural stone is becoming a key design element in modern homes. Buyers prefer low-maintenance natural materials inside and outside the home.

CLASSIFICATION

No classification can completely eliminate overlap between dimension stone, aggregate, and decorative stone because most stone is multipurpose. Much stone used for decorative purposes is not produced specifically for that end use. About 50% of the rock quarried for dimension stone becomes waste, which can be sold as decorative stone coproducts (Figure 1) composed of the exact stone used in the dimension stone side of the business. Thus, dimension stone and decorative stone are intimately intertwined. Many uses require a compromise between decorative and structural qualities (O. Bowles, personal communication).

Shipley (1945) used the term *decorative stone* interchangeably with *ornamental stone*. Gary, McAfee, and Wolf (1972) defined decorative stone as that used for architectural decoration, such as mantels, columns, and storefronts, but added that it is sometimes set with silver or gold in jewelry as curio stones. Bates and Jackson (1987) and Jackson (1997) also restricted decorative stone to that used for architectural decoration. Murhovich and others (2002) proposed doing away with the term “decorative stone” in favor of *decorative rock materials*. Meanings of otherwise identical terms used in the stone industry differ between geologists, engineers, and quarries; they often carry a much broader meaning for quarriers and engineers compared to their very specific use by geologists (Makens, Dobrell, and Kennedy 1972).

Geologist define decorative stone, including ornamental stone, more broadly as any stone used primarily for its color, texture, and general appearance. It is not used primarily for its strength or durability, as is construction stone, or in specific sizes, as is dimension stone. The decorative stone industry uses a much wider range of stone types, such as naturally rounded pebbles, compared

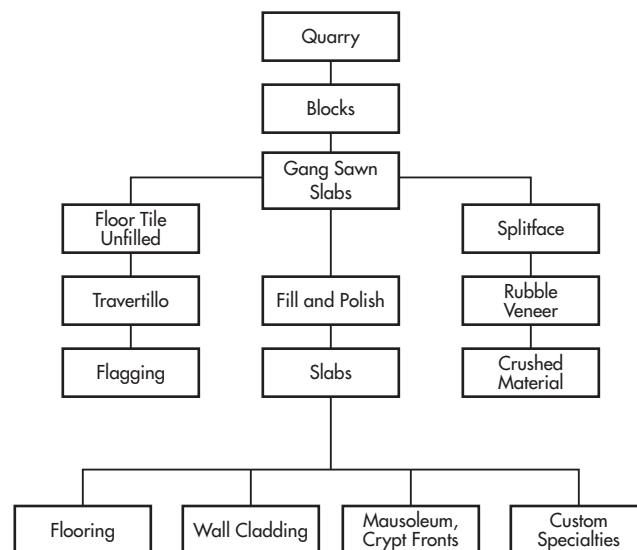


Figure 1. Materials flow from quarry (top) to numerous products, produced by New Mexico Travertine west of Belen, New Mexico. Travertillo is travertine tile with rounded corners similar to ceramic saltillos produced in Mexico.

to the dimension stone industry. Decorative stone usually serves some structural purpose, but it is not load-bearing to any great extent. Weak or costly stones that are attractive serve in solely decorative applications.

The basic types of decorative stone are rough stone, aggregate, cut or dressed stone, and synthetic stone:

- Rough stone (unprocessed or slightly processed)
 - Fieldstone (moss rock)
 - Flagstone
- Aggregate (lightly processed; screened or not)
 - Uncrushed stone
 - River rock
 - Scoria and cinder
 - Fused argillaceous rock

- Crushed stone
 - Rubble
 - Exposed aggregate
 - Dash
 - Terrazzo
- Cut or dressed stone (moderately to highly processed; no set size)
 - Statuary and objet d'art
 - Fireplace rocks and hearthstones
 - Ashlar
 - Monuments and memorials
 - Tile and paving blocks
 - Veneer and wall cladding
 - Miscellaneous
- Synthetic stone (made from various raw materials)

STATISTICS AND END USES

Decorative and dimension stone data are difficult to separate because the U.S. Geological Survey keeps statistics only on dimension stone, sand and gravel, and crushed stone. The value of domestic dimension-stone production in 2004, which includes some decorative stone, was about \$257 million compared to imports of about \$1.49 billion and exports of about \$64 million. Production in 2004 was 1.30 Mt, of which about 35% was for decorative uses (Dolley 2005). The principal uses are rough blocks in building construction (41%) and monument stone applications (25%). In 2004, dimension stones used or sold were granite (35%), limestone (28%), sandstone (13%), marble (5%), slate (1%), and miscellaneous stone (18%), by tonnage. Dressed stone was mainly sold for flagging (25%), ashlar or partly squared pieces (24%), and curbing (22%), with the rest miscellaneous or unspecified (29%), by tonnage (Dolley 2005).

Crushed stone was valued at \$9.7 billion in the United States in 2004. Imports were 15 Mt and exports were 2 Mt. About 1.61 billion t of crushed stone was consumed. Of the 806 Mt identified by use, 82% was construction aggregate, 15% for cement and lime and chemical or metallurgical manufacturing, 2% for agriculture, and 1% for miscellaneous uses. Crushed stone used for decorative purposes is scattered throughout several of these categories. Limestone and dolomite constitute about 86% and granite 8% of crushed stone in the United States. About 6% is sandstone and quartzite, miscellaneous, marble, calcareous marble, slate, volcanic cinder, scoria, and shell (Tepordei 2005).

Rough Stone

Rough stone is used as it is found in nature with very limited processing such as minor hand shaping, edge fitting, and size or quality sorting. This stone type is often marketed locally in relatively small tonnages and includes fieldstone and flagstone. The primary end uses of rough stone are landscaping, edging, paving, and large individual stone landscape or interior accents (Figure 2).

Fieldstone

Fieldstone is picked up or pried out of the ground (gleaned) without extensive quarrying and includes garden or large landscaping boulders (Hansen 1969; Austin, Barker, and Smith 1990). Boulders and cobbles can be split or roughly trimmed for use in rubble walls and veneers, both interior and exterior. Popular fieldstone rock types include sandstone, basalt, limestone, gneiss, schist, quartzite, and granite, but many others are suitable. Individuals or small companies



Figure 2. Medium-to-large stone, for use as accents, on display in a New Mexico stone yard



Figure 3. Slabby sandstone moss rock used in a retaining wall. The blocks are mottled by attached lichens.

collect much of the fieldstone because the industry is labor intensive and markets are small. Shipping costs often preclude selling fieldstone far from where it is collected. The stone can be sold in small quantities from the backs of vehicles (Austin, Barker, and Smith 1990). Fieldstone includes many rock types, sizes, and shapes, with the only common denominator that it must be set by hand and be durable (W.R. Power, personal communication).

Moss rock is fieldstone partially covered by algae, mosses, lichens, and fungi, which give the rock an aged and variegated patina (Austin, Barker, and Smith 1990). The plants are supported by moisture and nutrients in the stone. Moss rock is used for landscaping, walls, and fireplaces. Although almost any durable rock can be moss rock, most are slabby or rounded sandstone and limestone (Figure 3).

Flagstone

Flagstone or flagging consists of thin, irregular slabs used for paving, walkways, and wall veneers. Random-shaped flagging is produced widely in the United States. Suitable stone breaks very easily in one direction, producing flags. Any fissile stone can be

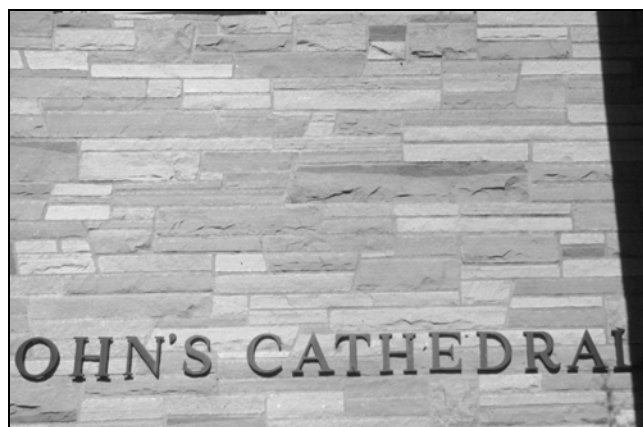


Figure 4. Ashlar blocks of Coconino Sandstone (Jurassic) used as a veneer for a wall of St. John's Cathedral, Albuquerque, New Mexico

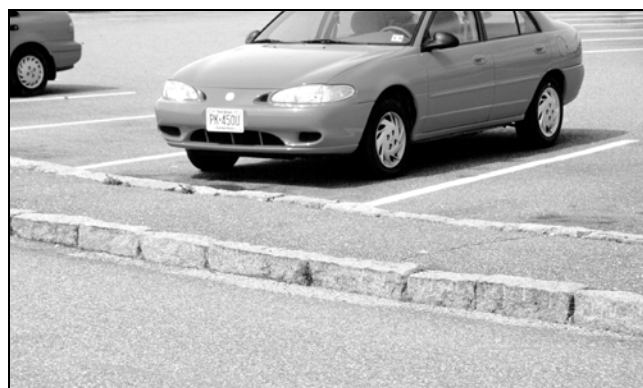


Figure 5. Granite blocks used for curbing in a parking lot near Bar Harbor, Maine

used, but sandstone (bedding planes) and slate (cleavage surfaces) are best and dominate the market. Limestone and dolostone are quarried as flagstone in the Great Lakes area of the United States (A.M. Johnson, personal communication). The Coconino sandstone is quarried extensively in Arizona and produces very high quality, red-to-pink-to-white flagstone (Townsend 1962). Sandstone flags up to 0.5 m² can be split to a thickness of 3 cm or less. Flagstone slabs 3 to 10 cm thick are used for walkways in high-traffic areas; they must be resistant to abrasion and have low relief on the wear surface to minimize tripping. If used in walkways, these thin slabs must be set on a very firm base. Thicker flags of sandstone or granite can be used in walls (Figure 4) or set on edge as curbing (Figure 5).

Aggregate Uncrushed Stone

Natural aggregate is lightly processed, usually by washing or screening, yielding products suitable for decorative use. Fragments can be either rounded or angular and must be resistant to weathering. Many types of decorative stone aggregate can be used for rock lawns or area covers in virtually unlimited colors. Typically, local materials are used, which limits choice but lowers cost. The aggregate is placed on UV-resistant black, impermeable or semipermeable poly-

Table 1. Typical coverages by size for decorative stone aggregate

Aggregate Type	Size, in.	Size, cm	Depth	Coverage, ft ² /st	Coverage, ft ² /t
Rock	1/4	0.64	2 in. (5.08 cm)	115	126
	1/2	1.27		150	165
	3/4-1	1.91-2.54		120	132
River rock	1-3	2.54-7.62	1 rock	90	100
	3-6	7.62-15.24		60	66
Riprap	1-3	2.54-7.62	1 rock	90	100
	3-8	7.62-20.32		60	66
	6-12	15.24-30.48		30	66
Pea gravel	3/8	0.95	2 in. (5.08 cm)	110	121

Adapted from Arizona Trucking and Materials brochure, Tucson.



Figure 6. Small river rock and volcanic cinder used for a xeriscape lawn

ethylene (most often 4 mils thick) covering a prepared surface treated with weed killer. A wide variety of sizes are used at an application rate of at least 50 kg/m². The rate varies depending on aggregate size and layer thickness (Table 1).

River Rock. River rock constitutes distinctive water-rounded pebbles, cobbles, and boulders commonly used as an area cover (Figure 6). White to gray is typically specified, but other colors are available. River rock most commonly is granite or gneiss, but any durable rock can be used. The rounding usually is done in a river or coastal marine environment. In Pennsylvania, white-to-buff vein quartz is a popular river rock for landscaping (S.W. Berkheiser, Jr., personal communication).

A diverse market has arisen worldwide in rounded stones sold typically by weight (\$0.07 to \$1.65/kg) or bag. The stones are often polished, not always naturally, and may be fairly exotic rock types like jade, but more common stones are also widely sold.

Scoria and Cinder. Scoria or volcanic cinder is a lightweight, vesicular equivalent of basalt (Figure 6) or other basic volcanic rocks. It is used primarily for desert landscaping in the southwestern United States; it is less common elsewhere but is available in most parts of the country. Scoria is sold as either red-to-brown or black-to-gray varieties, but both are otherwise similar. Reddish hues are more popular and, hence, more valuable than other hues



Figure 7. Rock lawn with accent pieces in Belen, New Mexico



Figure 8. Large exposed aggregate panel on a commercial building

(Osburn 1980). The color differences of cinder are a result of the presence (red) or absence (black) of oxygen during volcanic eruption and emplacement.

Fused Argillaceous Rock. Natural fires in North Dakota lignite produce fused interbedded claystone and sandstone (E.C. Murphy, personal communication). In New Mexico, natural coal fires produce a similar material locally called “red dog” (Hoffman 1996). Red baked and fused shale related to coal fires is mined in the northern Powder River basin of Wyoming (Harris 1991; Heffern and Coates 1997). These materials are used as low-quality aggregate in areas lacking better materials or in landscaping.

Crushed Stone

Crushed stone is the most common decorative aggregate and can be produced from virtually any pleasing stone. It is broken mechanically and usually screened before use; larger sizes are often called rubble. Harris (1991) uses the term *decorative aggregate* to describe crushed and sized stone used for landscaping such as area cover, rock lawns, walkways, and borders around plants or gardens (Figure 7). This chapter describes rubble, exposed aggregate, dash, and terrazzo here under crushed stone, although exposed aggregate, dash, and terrazzo are used with a binder such as cement.

Rubble. Rubble consists of large rough stone or blocks produced in quarrying, often as waste, and used for retaining walls, seawalls, bridgework, and landscaping. Only landscaping rubble is considered decorative stone because it is used primarily for its color, texture, or general appearance. In New Mexico, large boulders of pegmatite are used in landscaping as accent pieces (Austin, Barker, and Smith 1990).

Smaller rubble is popular as wall facing in homes and commercial buildings. The primary purpose is aesthetic—it replaces brick or other veneer—but ease of installation, weather resistance, light weight, and ability to bond well with mortar are also important. Rubble can be set in random patterns across 0.05 to 4 m² of exposed rock. Low-density rocks, such as pumice, have several advantages: shipping costs are lower, setting is easier for the stone mason, and few, if any, anchors are required to tie the stone veneer to the wall (Power 1994). In Minnesota, waste rock from processing granite dimension stone, called *grout*, is used as decorative stone, including sawn, split, and even polished slabs (A.M. Johnson, personal communication; Jackson 1997).

Exposed Aggregate. Exposed aggregate is one of the most common methods of using crushed stone (Figure 8). Stith (1970) found the most important properties to be color, hardness, soundness, absorption, shape, size distribution, and impurities.

Many colors and shapes are available, making exposed aggregate compatible with almost any architectural scheme. Color should be uniform and permanent because it is the architect's main criterion. Observation of weathered and fractured outcrops of the proposed aggregate can be useful in determining how the stone will react (Cutcliffe and Dunn 1967). Spalling and other forms of physical deterioration should be noted. The color should vary only slightly, if at all, between weathered and fresh outcrops. Variations in color from exposure to sunlight or weather should be noted to minimize color differences across the faces of a structure (Cutcliffe and Dunn 1967). Color segregation of stone by quarry procedures, blasting, stockpiling, blending, batching, and weathering should be avoided (Cutcliffe and Dunn 1967; Evans 1993).

The ability to cast exposed aggregate in complex shapes and with background coloring (dash) of cement gives the architect great freedom. Aggregate, mixed with white or gray cement in a 2:1 ratio, can be precast into panels or cast in place in walls and floors or walkways, with the aggregate dispersed or concentrated in the facing layer (Stith 1970). The aggregate is exposed by sand blasting, bush hammering, wire brushing, or acid washing the surface of the aggregate/cement mixture (Cutcliffe and Dunn 1967), and then it is sealed.

Dash. Dash, either coarse (for texture) or fine (for color), is added to exposed aggregate, stucco, or concrete. Sand dash is added to stucco and small-scale, exposed-aggregate surfaces for color. Very fine dash is added to concrete or cement as a permanent pigment instead of more expensive mineral pigments that may react with the cement compounds. Well-mixed, nonreactive dash material avoids blotchiness or shade variation common with artificial or mineral pigments and can be used in conjunction with stucco dash or exposed aggregate.

Terrazzo. First produced by the Romans more than 1,500 years ago, terrazzo floors provide quality at low original and maintenance cost and have a very long life. Terrazzo, a mixture of sized, crushed stone, and cement, offers variety in color and design (Figure 9). This mixture is poured into a prepared floor area, hardened, ground smooth, sealed, and polished (Reed 1978;

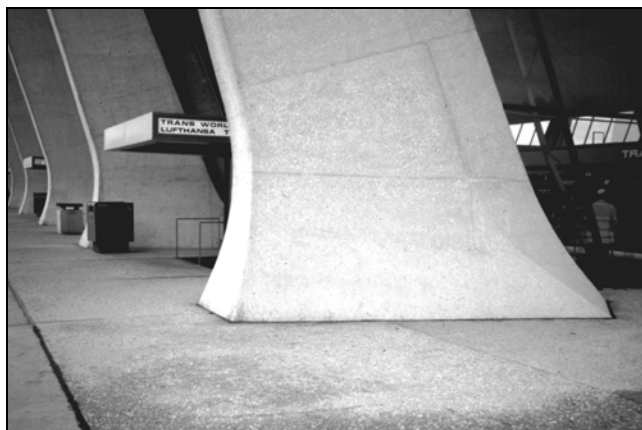


Figure 9. Terrazzo flooring (polished) at the Dulles International Airport, Washington, D.C. Lighter area near lower center in front of pillar is a reflection off the highly polished surface. Exposed aggregate forms the surface of the pillar.

American Geological Institute 1997). The stone aggregate has low porosity and low absorption. The portion of the terrazzo that needs protection is the portland cement matrix, which is porous and will absorb stains. The primary application of terrazzo is in high-traffic, public areas and buildings. Relatively soft stone—usually limestone, dolostone, or marble—is preferred for terrazzo, but granite is also used. Quality control is paramount during quarrying so that color can be matched across batches. Maintaining consistent color during processing ensures quality, color continuity, and freedom from impurities. The Terrazzo, Tile and Marble Association of Canada (www.ttmac.com) recommends a thin-gauge epoxy or polyacrylate for sealing.

Cut or Dressed Stone

Cut or dressed stone is finished on one or more sides by various methods and is used where uniform surfaces are needed. Typical uses are in walls, monuments, sculptures, waterfalls, or other relatively small, very detailed artistic renderings. Many stones are fashioned into structural or decorative adornments such as capitals, veneers, friezes, cornices, corbels, coping, and ribbing. Nonstructural statuary and art, along with stones too soft or brittle for structural use, are used in some parts of buildings, although in low volume.

Statuary and Objets d'Art

Artists use stone for carving, sculpting, or producing objets d'art (Figure 10). Carvable stone is commonly soft and uniform, such as marble, limestone, soapstone, and alabaster. Some sculptors carve commercial granite and jadeite, though those stones are hard. Color, texture, softness, and the ability to take a polish are important for statuary stone. Carvable stone commands the highest price but accounts for the smallest sales volume of any of the stone categories. Many small firms and artisans cut and polish semiprecious gems and ornamental stone from hard stone such as jade, agate, quartz, jasper, chalcedony, chert, and petrified wood (Burchett and Eversoll 1991), or softer stone such as tuff, talc (soapstone), serpentine (verde antique), marble, travertine, and gypsum (alabaster).

Fireplace Rocks and Hearthstones

Many types of stone are used in fireplaces. Commercial use is restricted to relatively few types compared to the many used by



Figure 10. Renowned sculptor Allan Howser, of Taos, New Mexico, surrounded by statues and rock ready for his chisel

individuals. Although rough stone and aggregate are often used in rustic fireplaces, dressed stone is more typical. Moss rock, flagstone, river rock, scoria, and ashlar are often used as a decorative facing on a fireplace. Argillite or millstock slate is cleaved or rough-finished and used as hearthstones and mantles (Carpenter 1983). Polished travertine is often strengthened with epoxy or cement and is very popular for hearthstones.

Ashlar

Ashlar consists of rectangular, nonuniform stones with at least two smooth parallel sides, set randomly or by design in a wall. The exposed surface of each piece is generally $<0.4 \text{ m}^2$, laid exposing the sawn or naturally smooth face or the rough (broken) face (Figure 4). Ashlar blocks are prepared either from natural slabs that split and fracture into usable shapes or by sawing the required two parallel sides usually about 7 to 15 cm apart. The remaining sides have an attractive broken appearance that, when exposed, is called split-faced ashlar. Natural or sawed blocks are broken in a hydraulic guillotine to assorted sizes, palletized, shipped to the job site, and laid by hand in courses similar to brick.

Monuments and Memorials

Stone is cut and polished for tombstones, historical markers, and similar monuments and memorials. A typical stone used for monuments and memorials is pure white, statuary-grade marble. Monument stone must be hard, take a high polish, and be resistant to weathering. Tombstones are most often one of the varieties of granite.

Tiles and Paving Blocks

Tiles are cut or split stones with one very thin dimension that can be polished (Harris 1991). Typically they are 0.3 m^2 or 0.5 m^2 (12 in. \times 12 in. or 18 in. \times 18 in.) and 10 to 15 mm thick and can be used in many ways on all interior surfaces, including floors and walls (Figure 11). Tiles can be made from many types of stone, but most are slate, granite, marble, limestone, basalt, or tuff. Travertine is also cut into tiles.

Bluestone, slate, and argillite (Carpenter 1983; Power 1983), as decorative stone, are used primarily as flagging and floor tiles, but are also used for sills, stair treads, risers, shower and toilet



Figure 11. Various sizes of flagstone and floor tile composed of red Lyons Sandstone (darker color) of Permian age and other flagstone (lighter color) in stone yard near Lyons, Colorado

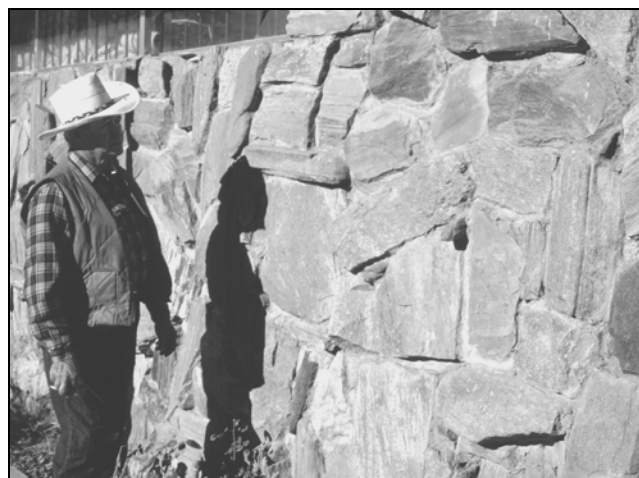


Figure 12. Precambrian Vadito schist used as veneer wainscoting in Santa Fe, New Mexico

stalls, and exterior spandrels and facings. They are available in various shades of green, gray, purple, red, black, or variegated. Slate finishes vary from the natural split surface to knife-shaved, sand rubbed, and honed or semipolished (Harben 1990).

Tiles and paving blocks made of tuff generally are called cantera stone but include adoquin, sillar, tufa, tuff, calduro, and others (Kuiper 1988). Most of these are imported to the United States from Mexico.

Veneers and Wall Cladding

A veneer is any rock that can be laid up on a wall. Wall cladding is composed of larger sheets, often filled and polished, of travertine, serpentine (verde antique), marble, and others. Schist (Figure 12), which cleaves along preferred directions, yielding relatively flat stones, is also used.

Miscellaneous Uses

Nonforested areas of the United States use stone in the manner that other areas of the country use wood, such as limestone fenceposts in Kansas (D. A. Grisafe, personal communication). An Internet search reveals many unusual uses for stone around the world, including lamps with bases of rough stone. In some lamps from Bali, even the lamp shade is carved from stone. Intricately carved stone furniture with latticework backs is for sale on Web sites from India. Stone dishes and lidded boxes from ancient cultures can also be purchased, in addition to modern examples, particularly from Southeast Asia. A number of sites sell “healing” stones and are devoted to stone therapy, and soap-shaped deodorant stones are also available. These are but a few examples illustrating the widespread use of stone across the ages.

Synthetic Stone

Cast stone is defined as a refined architectural concrete building unit manufactured to simulate natural cut stone, used in unit masonry applications. The earliest known use of cast stone was in AD 1138 (Cast Stone Institute 2005). Cast stone is a masonry product used as an architectural feature, trim, ornament, or facing for buildings or other structures. Cast stone can be made from white or gray cement, manufactured or natural sands, carefully selected

crushed stone, or well-graded natural gravels and mineral coloring pigments to achieve the desired color and appearance while maintaining durable physical properties that exceed most natural cut building stones. Cast stone is an excellent replacement for natural cut limestone, brownstone, sandstone, bluestone, granite, slate, keystone, travertine, and other natural building stones (Cast Stone Institute 2005). Some cast stone, however, can suffer deleterious effects from prolonged exposure to sunlight (T.P. Dolley, personal communication).

Stone or slag, usually crushed, is the main ingredient in the production of manufactured stone by melting and frothing. Basalt is melted and cast into various forms (Kuzvart, Woller, and Hora 1992). Irregularly shaped boulder- and cobble-sized masses are used as artificial scoria or cinder. Manufactured stone can be used in floor and wall panels.

Crushed marble is combined with a binding polymer, and perhaps a coloring agent, to produce cultured-marble tiles. Ground limestone is mixed with organic resins to produce cultured marble molded into a variety of shapes. Quartz stone is a relatively new product made from pure quartz and polymer binders, creating a countertop or flooring material that has properties similar to those of natural granite.

GEOLOGY AND DISTRIBUTION OF MAJOR DECORATIVE STONES

Hundreds if not thousands of types and varieties of stone are used in the decorative stone industry. The terms used in the stone industry vary widely between countries, the professions involved in the stone industry, and segments of the industry. In Scandinavia, the stone industry differentiates hard stone from soft stone. The latter includes limestones and marble that, if siliceous, may be harder than some igneous rocks like tuff that are called hard (Shadmon 1988). Complete coverage of all local industry classifications is nearly impossible. Consequently, only the dominant commercial rock types are discussed here as an overview.

Granite

Commercial granite, which has a wider meaning than geological petrographic definitions, includes all feldspathic intrusive rock with

visible grains and all metamorphic rocks with gneissic texture. It includes true granite plus other intrusive igneous rocks (Murphy et al. 2002) and their metamorphic equivalents—syenite, monzonite, gabbro, anorthosite, amphibolite, and gneiss. Commercially, dark fine-grained igneous rocks, even of diabase or basalt composition, are often called black granite (Power 1983). Commercial granite, whether light or dark, has high strength and durability and is relatively impervious to water and weathering.

Commercial granite in the United States is quarried at more than 100 sites in 20 states. The dominant companies are Cold Spring Granite, Rock of Ages Corp., and Coggins Granite Industries. Major production centers (Harben 1990) include Georgia (Elberton), North and South Carolina, New York, Massachusetts, Vermont, New Hampshire, Minnesota (St. Cloud), South Dakota, Wisconsin, and Texas (Burnet and Llano counties). Near Elberton, Georgia, about 100 companies quarry and sell granite as rough blocks or finished products such as memorial markers.

Prominent European igneous decorative stones are Scandinavian red granite (rapakivi type in Finland), norite, diabase, and larvikite (an orthoclase-syenite, labradorite). Rossa (red) Aswan granite and red porphyry (*porfido rosso antico*) is produced in Egypt. Green porphyry (*porfido verde antico*) is produced in the Peloponnese region of Greece (Kuzvart 1984). Spain, India, the Republic of South Africa, Australia, and Brazil are also noted sources of granite in the world market.

Pegmatite

Most pegmatites have about the same chemical and mineralogical composition as granite, but pegmatites are typified by very large, interlocking crystals. Most pegmatites have a coarsely crystalline granite composition with abundant quartz and orthoclase feldspar. Other minerals, notably muscovite or white mica, may be abundant. Boulders are preferred to highlight this coarse texture. Many stone or landscaping companies stock large pegmatite boulders, which are moved to the building site by flatbed truck. In Quebec, amazonite pegmatite from Saint-Ludger-de-Milot and Lac Saint-Jean is used for decorative stone aggregate and for small decorative objects (J.-L. Caty, personal communication). Michigan architects surveyed by Johnson (1983) highly favored coarse pegmatite. Although not extensively quarried today, old mines operated when sheet muscovite was mined in the past are inviting to enterprising stone dealers.

Basalt and Traprock

In the western United States, Tertiary and Quaternary basaltic rocks are exposed over thousands of square kilometers. Basalt is fine-grained, hard, tough, dense, and durable. It is composed of pyroxene and calcic plagioclase and is well suited for use as a decorative stone for landscaping.

Traprock is a common term for basaltic dikes or flows. Power (1994) states the correct petrologic term for traprock is diabase or dolerite. When sold as cut building stone, it is commonly called black granite.

Tuff

The main use of tuff is as cantera stone floor tiles and wall cladding (Figure 13). Some Mexican tuff is sculpted into statuary. The tuff varies in color, with pastels predominating. The stone is characterized by many inclusions of large pumice fragments (up to 30%) and phenocrysts, up to 50 mm in diameter, of quartz, biotite, feldspar, magnetite, and rock fragments such as granite or basalt (Kupper 1988). The high porosity of tuff makes this rock suitable where low weight is a factor. In addition, the porosity gives the stone a texture that is visually appealing for rustic application (Figure 14).



Figure 13. Volcanic tuff (cantera stone), cut with a chain saw, was used as the primary building stone at The Lodge (built circa 1930) at Los Alamos, New Mexico. Although containing voids and depressions, the cantera stone hardens somewhat with time to produce a more durable veneer.



Figure 14. Cantera stone blocks used to form a wall at Bandelier National Monument, New Mexico

Marble and Travertine

Geologically, marble is a metamorphosed carbonate and travertine is a sedimentary carbonate deposited from flowing water, usually in a spring system. Commercial marble is an crystalline rock composed predominantly (>50%) of calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), or serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$). Serpentine with white calcite or dolomite stringers forms verde antique. Commercial marble must take a polish and may include crystalline limestone, travertine, and serpentine in addition to metamorphic carbonate. Crystals range in size from fine (easily polished) to coarse. The ability to take a polish is important, but the color and crystalline character can be more important.

Limestone, Dolostone, and Marble

Carbonate rocks, usually marine in origin, are found in many parts of the United States and many other nations. The Bloomington–Bedford District of southern Indiana has produced a well-known dimension limestone (commonly called Indiana Limestone) for more than a century. Limestone and dolostone are usually gray, but can be white, buff, tan, or black. White marble is composed of nearly pure calcite. Dolostone is composed predominantly of dolomite. Mineral impurities that darken limestone and dolostone include iron carbonates, iron oxide, iron sulfide, chert, silica, clay, graphite, and carbonaceous matter (Power 1994). Crystallinity, bed thickness, ease of polishing (3 to 3.4 on the Mohs hardness scale), and the presence of fossils, stylolites, or other textures and structures make limestone and dolostone attractive decorative stones. Bedding can vary from thin to massive and is important in determining the end use of commercial marble and travertine. Limestone imported into the United States comes primarily from Spain and France.

The Georgia Marble Company in Georgia and the Vermont Marble Company in Vermont quarry the bulk of U.S. commercial marble production. Marble, particularly white marble, is commonly crushed and sized and sold in lots ranging from carloads to bags of <45 kg. White marble from Georgia (Power 1994) and varicolored travertine from New Mexico (Austin and Barker 1990) are premium decorative stones. The Yule quarry in Gunnison County, Colorado, which supplied white marble for the Lincoln and Jefferson Memorials in Washington, D.C., has recently operated intermittently after being closed for many years. Marble imports come principally into the United States from Italy, Portugal, Spain, and Turkey.

Travertine

Commercial travertine is hard, dense to vuggy, finely crystalline, compact, massive to concretionary or fibrous limestone that takes a polish (Austin and Barker 1990). Impurities in travertine impart colors ranging from white to pink, red, tan, yellow, green, gold, brown, or black. Variations in impurities can cause multicolor banding of layered travertine. Travertine may be called tufa (within the industry; tuff is used to describe cantera or volcanic tuff, but never travertine), calcareous sinter, marble, Mexican onyx, or onyx marble. New Mexico Travertine produces most of the domestic travertine (Barker, Austin, and Sivits 1996).

Sandstone and Conglomerate

Sandstone suitable for cutting, flagging, and curbing has been produced worldwide for thousands of years. Commercial sandstone consists of both sandstone and siltstone. Color variations are due largely to iron oxide. Moss rock is a popular sandstone found in many areas as loose fieldstone on surface outcrops. Picture rock is sandstone that exhibits complex color (liesegang) banding from variations in weathering and which is sold as slabs cut to simulate landscape paintings.

Slate, Schist, and Gneiss

Slate is a fine-grained metamorphic rock with pronounced, relatively smooth, and flat cleavage surfaces that is used mainly for roofing. Stair treads, floor tile, flagging, wainscoting, trim, chalkboards, billiard and laboratory tables, plaques, and signs are also produced. Slate can be purple, gray or black (reduced), red or green (oxidized), or mottled. These colors can alter or bleach on exposure (called semiweathering), but roofing slate should have permanent colors (called unfading) or at least alter evenly to a pleasing shade and be from the same lot. Most slate is initially split by hand from

quarry blocks (Sweet 1990) with further punching by foot treadles and machine shaping.

Slate production in the United States is concentrated in New York, Vermont, Virginia, and Pennsylvania, where it is centered at Pen Argyl and Slatedale. Slate production techniques have changed little with time. Quarrying must be done slowly with little blasting because it would split the slate. Wire and chain saws are also used. Cold weather limits the quarrying season in many places; the stone is ruined if it is freeze-thawed while in large blocks, so none can be quarried ahead without careful storage. Slate is still largely hand split and punched with foot-driven treadles. Because of the assistance of nature in prying weakened surfaces apart by alternating freezing and thawing, flagstone quarries tend to be small and close to the surface.

Sale of slate in the United States is particularly strong in the South, Southwest, and California (Harben 1990) because of its resistance to color change over years in direct sunlight. Slate is growing more important in world markets for its natural unpolished appearance, nonslippery and multicolored durable surfaces, and relatively low price (Vagt 2003).

Quartzite

Quartzite is metamorphosed quartz sandstone that breaks through the grains rather than around them. Commercial quartzite is a hard siliceous rock commonly white to light-gray to bluish-gray or pinkish. Gneiss is often marketed as quartzite. In Virginia, thin-bedded to massive quartzite of the Cambrian Weverton Formation has been quarried since 1893 (Sweet 1990).

Quartzite is marketed for flagstone, veneer facing stone, and other decorative uses. Fern stone is quartzite containing dendritic limonite along bedding planes. Idaho also produces quartzite used as both flagging and building stone.

PRODUCTION

Decorative stone operations range from very small to very large. Many large quarries producing dimension or building stone also produce large quantities of waste rock, although their preferred output is large, sound, rectangular blocks. This waste material is normally crushed to aggregate, screened, and sold as decorative stone. It may alternatively be processed into ashlar (Figure 15). Aggregate quarries produce rock that can be used as higher-value landscaping stone as easily as lower-value concrete aggregate. Demand, appearance, and cost of the stone are most commonly the deciding factors in the choice between these two alternatives.

A number of finishes can be applied to a stone on an edge (E), a surface (S), or both (B):

- Natural cleft—natural, nonuniform finish (S)
- Sawn—dull, smooth finish created by a diamond or wire saw (E/S/B)
- Split—split with the natural grain (E/S)
- Honed—smooth, formal look, no shine (E/S/B)
- Polished—smooth, mirror finish (E/S/B)
- Flamed—slightly pebbled, medium relief (E/S/B)
- Sandblasted—slightly textured finish, light relief (E/S/B)
- Rocked—hand-cut, chiseled finish, heavy relief (E)
- Bush hammered—small pyramidal indentations, medium relief (E)
- Tumbled—rotated in a drum; rocks semirounded (B)

Only two producers are active at this time. Georgia Marble produces only their white marbles, which under French ownership



Figure 15. Breaking and palletizing ashlar from dimension stone waste at New Mexico Travertine in Belen, New Mexico

will expand over the next 5 years using imported stone. New Mexico Travertine produces several colors of travertine from its quarry but has expanded to use more than 12 limestones from other domestic quarries. Tennessee Marble Company produces tiles and slabs but primarily markets the stone for cut-to-size projects and has limited access to stones other than Tennessee pink, which is difficult to produce and is limited in slab size (Matthews 2002).

Quarrying

Quarrying decorative stone uses the same general techniques used in the production of other types of stone, but details are adjusted depending on the desired finished product. For example, blasting is minimized using small charges of low-velocity explosives for slab blocks. Stone quarries use diamond wire saws, belt saws, chain saws, and air wedges that allow rapid, more accurate quarrying and produce thinner products than in the past. Great care and considerable hand dressing (Figure 16) are necessary for high-quality wall capstone, flagstone, or slate. Accent pieces used in landscaping, such as large pegmatite boulders, require preservation of the coarsely crystalline surface during transport to the final site. Cranes may be needed to lift pieces, and padding is used to prevent damage in transit. Contrast this to the production of crushed stone, which requires almost no protection.

Stratification in rock produces zones of weakness called rift by producers. These are important because they determine the direction in which the stone splits most easily. Spacing of the rift determines the thickness of the quarried layer. Bed seams, joints, cutters, reeds, and runs are additional terms used in the sandstone industry to describe other natural planes or directions in which the stone splits or can be cut (Bowles and Barton 1963).

Processing

By the early 1900s, the muscle power of earlier ages had given way to steam, electricity, and compressed air. In recent years, carbides and diamonds for cutting and higher grade steels for drills have allowed for more efficient cutting of stone, but the basic equipment was similar to that of the past. Since the Browning torch was developed, it has been widely used in the granite industry and has revolutionized channel cutting (Meade 1986a). Channel cutting with



Figure 16. Limestone capstone being carefully hand-dressed at the finishing plant of New Mexico Travertine, Belen, New Mexico

diamond-studded belt saws is doing the same to limestone and marble production (Harben 1990). High-pressure water jets are also being used to quarry granite in North Carolina.

Automation that allows affordable production is being introduced rapidly, but much waste is still produced, leading to coproducts. Products include tiles and other decorative pieces such as kitchen counters, table or desk tops, bathroom counters and basins, and fireplace mantels. The trend is toward thinner slabs, specialty surfaces (polished or flame textured), and new applications such as coordinated lines of furniture in homes. Production of large volumes of crushed stone is ensured by modern drilling equipment, blasting techniques, and crushing and processing machinery.

SPECIFICATIONS

Formal specifications exist through the Marble Institute of America for most stones used in the dimension stone industry. Specifications are less developed in the decorative stone industry, where color and texture are of principal importance, along with the surface treatment used. The ability to be split into flat slabs is important in the production of flagstone, of less importance in fieldstone and moss rock, and of no importance for river rock.

Strength, porosity, adsorption, and durability are important in some decorative stone end uses and of little importance in others. Durability and strength are significant in crushed stone used for some decorative purposes, such as terrazzo and exposed aggregate (Ault 1989). The Aggregates and Dimension Stone chapters in this book cover physical properties in detail.

Flagstone

Irregularities on a flagstone wear surface must be <1 cm in height (Harris 1991) to minimize tripping. A standard test for abrasion resistance of stone subjected to foot traffic is given in American Society for Testing and Materials (ASTM) Standard C241.

Tiles and Paving Blocks

Slate for floor tiles sold in the United States comes in four basic square or rectangular sizes from 15 × 15 to 46 × 46 cm (Figure 17). Size is limited only by the curvature of foliation, which can cause tripping in tiles more than 1 m across. Tile thickness varies from



Figure 17. Processing line for square floor tiles at New Mexico Travertine

6 mm for light-duty and housing use to 9 mm for heavy-duty use in public areas (Harben 1990). Flexure testing of slate is covered by ASTM C120. A minimum abrasion resistance (ASTM C241) of 10 is required for carbonate floor tile. Where two or more marbles are combined, there should be a maximum difference of 5 points of abrasion resistance. For stairways, floors, and platforms subject to heavy foot traffic, a minimum abrasion resistance of 12 is recommended.

Exposed Aggregate

In general, tests for exposed aggregate are variations of those used for cement and road building or construction-aggregate end uses. Standard evaluation techniques for such end uses may have severe shortcomings when applied to exposed aggregate. Highway service records, acceptance tests, and government ratings of stone do not correlate with its quality as exposed aggregate (Cutcliffe and Dunn 1967).

Hardness is determined by Los Angeles abrasion, ASTM, or Micro-Deval tests. The aggregate should be hard enough to minimize replacement of faulty exposed aggregate because repair costs are extremely high, if repair is possible at all (Cutcliffe and Dunn 1967; Stith 1970). Abrasion resistance is less significant in exposed aggregate, but softness or brittleness may cause excessive fines during batching (Cutcliffe and Dunn 1967).

Soundness is the main criterion that determines the durability of exposed aggregate during temperature and humidity cycles, weathering, and erosion. Several sides of an exposed aggregate particle often are not encased in cement, making poor-quality stone very susceptible to weathering. A variety of tests involving freeze-thaw cycling and exposure to solutions are applied to exposed aggregate as discussed by Stith (1970) and Cutcliffe and Dunn (1967).

Water absorption should be <1.5% because high absorption promotes weathering and staining (Shergold 1954; Stith 1970). Average pore space and percentage saturation also influence soundness. Completely saturated rocks, small pores, and capillaries are more deleterious than larger, better-drained pores (Verbeck and Landgren 1960; Yedlosky and Dean 1961; Stith 1970).

Particle shape and size distribution are less important factors for exposed aggregate. The two main criteria are few thin or platy particles and minimal dust or fines. Impurities to avoid are shale, clay, iron sulfides and pyrite, chert, gypsum, bituminous materials,

dolomite, limestone, or any reactive material >1% by weight (Cutcliffe and Dunn 1967; Stith 1970).

Dash

Dash is fine-grained (up to 9 mm) exposed aggregate, and the basic principles and specifications previously described for exposed aggregate apply. Stone grains as small as 1.5 mm are used as concrete block facing (Ladoo and Myers 1951).

Terrazzo

Aggregates for terrazzo use are tested by methods applicable to aggregates for other uses. These include ASTM Standards C33, C88, C131; Los Angeles abrasion; and sodium sulfate tests. Terrazzo is essentially exposed aggregate with only one side exposed, so the criteria previously described for exposed aggregate generally apply. Specifications and data on terrazzo are available from the Terrazzo, Tile and Marble Association of Canada or the National Terrazzo and Mosaic Association.

Veneer and Cladding

Modern use of interior decorative stone as veneers and cladding does not require the high ASTM standards for compressive or flexural strength called for in structural stone. Exterior veneer and cladding stone is hung, using a variety of support and anchor systems, to the structural wall behind. Stone that meets the minimum ASTM criteria for flexural strength, modulus of rupture, and density is usually suitable for exterior veneer.

The standard specification for marble dimension stone (exterior) is ASTM Standard C503. Marble in this context includes calcite, dolostone, travertine, and serpentine. Marble for exterior use must be sound and free of spell cracks, open seams, pits, or other defects that would affect its strength, durability, or appearance. Molded, cast, or artificially aggregated units are discussed under the section on Synthetic Stone in this chapter.

Cantera Stone

The criteria established by ASTM for cantera (consolidated volcanic tuff) stone are as follows: bulk specific gravity (C97), 1.336 to 1.88; absorption (C97), 9.9% to 22%; modulus of rupture (C99), 435 to 1,520 psi; compressive strength (C170), 1,800 to 9,960 psi; and an abrasive hardness (C501) of 3.3 (Kuiper 1988).

ECONOMIC FACTORS

The decorative stone industry tends to be vertically integrated in the United States, although a dealer/distributor network is also in place. Many producers market both through their own sales operation and through various representatives. This is due in part to the desire of clients to view the stone before purchase. Developers of large projects often visit the quarry, but it is often advantageous to have examples of the stone available regionally at distributors.

The decision to use a particular stone in a project is made by architects who, as a group, are the greatest single influence on demand in the decorative stone industry. The reputation and trade name of the stone are the principal factors rather than test results used by architects to determine durability. Architects rated factors affecting their choice of stone (Johnson 1983) from most important to least as follows: (1) appearance (overwhelmingly), (2) durability, (3) cost, and (4) availability. Appearance of stone depends on color, texture, and uniformity. Limestone was the most frequently selected stone with granite second, but exposed aggregate panels were preferred for small commercial buildings. Stone is specified often for government buildings, sometimes for churches, and increasingly for commercial or residential structures.

Costs

Decorative stone ranges from a moderate cost, high-bulk commodity to a high cost, low-bulk one. Crushed stone for landscaping (ranging from \$15 to \$90/t) is an example of the former, whereas stone for sculpture (perhaps \$6,000 for a large block of Carrara marble) represents the latter. Decorative stone often commands a higher price than identical stone used where aesthetics are not considered.

In 2005, costs for decorative stone in Tucson, Arizona, ranged from \$22 to \$42/t for sized, bulk, landscaping materials in various colors. Tumbled stone was \$88/t and standard boulders were about \$0.18/kg. Specialty boulders ranged up to \$0.88/kg. Transport was \$15 to \$70 per load in the greater Tucson area with large orders trucked free to the jobsite (K. Santini, personal communication).

Transportation

All major forms of transport are used for decorative stone. Truck transport of aggregate (86%) predominates over rail (6%) or inland/coastal water transport (barge 2% and lake <1%), whereas sea transport (<1%) is least common (Anon. 1988). Any transport by water, barge, or ship is the lowest cost. Truck transport is very effective, though usually more costly per unit shipped, because of flexibility and orientation toward individual irregular shipments and low capital outlay (Hayes 1991). The stone is shipped in bulk or palletized (Figure 18) and is loaded onto the truck at the production site to be carried directly to the end-use site with no intermediate handling. Delivery by truck is prompt, and damage is minimal even for polished or slabbed stone. In contrast, rail transport may cost more because it is oriented to large predictable shipments, is capital intensive, and has high fixed costs. High railcar coupling speeds may damage more stone than road vibration during truck haulage. Rail rates often are set according to the finish rather than simply by the type of stone. Timing is important because most consumers need rapid delivery once a decorative stone is ordered. Distribution yards closer to consumers than production facilities are often used for flexibility and rapid delivery (Hayes 1991).

In Michigan (Johnson 1983) in the early 1980s, transport costs ranged from 20% to 100% more for highly finished stone than for the same stone when unfinished, rough, split, or sawn. Crushed stone transport cost was only about 40% of that for unfinished stone. Shipping of decorative stone on the Great Lakes was not readily available then, although its cost would have been about 10% of rail rates. Lake transport was reserved for large volumes from established producers with regular shipments, such as coal or iron ore (Johnson 1983).

Most factors applicable to construction aggregate transport apply to decorative aggregate. Decorative stone aggregate carries significantly more value than construction aggregate, even if they are the same rock, so higher transport costs are justified. Decorative stone includes a wide variety of products requiring transportation. Although much stone is used locally, certain segments of this market will support higher cost transport offshore and worldwide. Decorative stone is often sold in relatively small lots, so bulk transport cost advantages cannot often be realized, although they are substantial if the shipment is large.

End uses of decorative aggregate such as landscaping rock are the most sensitive to transport cost and thus travel the least distance, although this distance can be significant. Aggregate has been imported into the United States (Timmons and Harben 1987) to areas accessible to ships such as the eastern, Gulf, and southeastern coasts of the United States, and large portions of the Midwest by barge. This is particularly true for low-volume retail sales where small lots may be shipped long distances because the per-ton retail



Figure 18. Various rock types sorted by size, shape, and surface coating (such as moss rock); palletized, and ready for shipment by truck in New Mexico Travertine's yard

value is high. Polished or slabbed decorative stone, a high-value commodity, can be shipped any distance if well protected. In contrast, decorative aggregate is resistant to exposure and shock and needs minimal protection during transport.

Substitutes

All decorative stones have competition from substitute materials, and more are appearing. Examples include concrete, enameled porcelain, stainless steel, aluminum, brick, plastic, synthetic stone, crushed glass and slag, and recycled materials. The aesthetic appeal, prestige, and durability of stone are exceeded by few substitutes. For this reason, substitutes simulate stone, often at lower cost. Stone substitutes are often designed as prefabricated modules or precast panels, as recommended for much of the potential decorative stone in Michigan (Bourque and Associates 1999). Some decorative stone such as terrazzo or exposed aggregate is also used in panels.

TARIFFS AND DEPLETION ALLOWANCES

Complex tariffs on imported dimension stone also apply to dimension stone used as decorative stone. In the United States, the tariffs in 2003 varied from free to 6.5% for Normal Trade Relations (NTR) status according to type, size, value, and degree of preparation (Dolley 2005). Tariffs on crushed or rough stone, including that used for decorative purposes, are 3.0% ad valorem (Dolley 2005).

In the United States, the depletion allowance for domestic or foreign decorative stone depends on the form of the stone and its end use. For dimension stone, it is 14%. For slate used or sold as sintered or burned lightweight aggregate, it is 7.5%. For stone used for rubble and other non structural purposes, the depletion allowance is 5%.

MARKETS AND TRENDS

The use of steel, glass, aluminum, plastic, and reinforced concrete made stone non essential in construction and caused a long-term decline in use of large structural blocks (Johnson 1983). Sales of stone for exterior paving and curbing have decreased because of increased use of asphalt and concrete. In the last few decades, the beauty, heat and sound insulation, and permanence of stone have led to its use for exterior cladding (sheets or panels) of many commercial buildings (Hora 1994).

Stone acceptance and usage in the United States have grown in recent years. In Europe, use of decorative and roughly dressed stone dropped from 50% to 0.25% relative to crushed stone during the 20th century (Kuzvar 1984). Recently the aesthetic appeal of stone and the development of thinner stone in lightweight panels and frames have offset this to a degree (Johnson 1983) and have increased the use of stone veneers and cladding. Thin-stone slab applications are favored by architects because of lower cost relative to glass and steel (Sweet 1990). Dimension stone is being used more commonly in the residential markets. Improved quarrying, finishing, and handling technology, as well as greater variety of stone and the rising cost of alternative construction materials, are among the factors that suggest a continuing increase in demand for dimension stone during the next 5 to 10 years (Dolley 2005). Domestic crushed stone production appears to be stable or increasing slightly. While crushed stone free on board (f.o.b.) prices are not expected to increase significantly, the delivered prices are expected to increase, especially in and near metropolitan areas, mainly because more aggregates are being transported longer distances (Tepordei 2005).

Veneer style has shifted to smaller pieces of stone assembled in panels for unit construction, giving a cubic look, particularly for granite buildings. Extensive engineering and testing led to precasting of stone and concrete panels, epoxy bonding of finished stone panels before installation on site, and most recently, bonding of ultra-thin stone veneer to expanded aluminum backing (Meade 1986b). Use of stone increased for decorative interiors with various shades and colors of marble in lobbies and foyers. Residential use of thin stone tiles and countertops, particularly granite, has increased. Decorative stone panels and tiles made from agglomerated stone such as Chilean lapis are bonded into tiles for high-contrast colored trim (L.P. Meade, personal communication). Over time, taste in stone architecture changes and some stones fall out of favor, such as the brownstone fronts once popular on urban residences (Ladoo and Myers 1951).

The trend in North America is for specialized use of stone for architectural purposes. The trend in stone use is away from blocks and toward veneer and cladding in larger thin panels that, depending on stone type, may need to be backed by glass fiber/epoxy or other strengtheners. Wider spans may need to be thicker or use special anchors depending on wind load or other factors. A trend in architecture is toward smaller, thinner preassembled stone panels set in larger panels for rapid installation onto steel frameworks or exterior walls to yield a look as if built with large stone blocks.

The broader residential market that uses a wider variety of stone is growing, particularly in the Southwest, but demand is not great enough to create demand for all quarry waste. This contrasts with Italy, where virtually all stone quarried is used, so U.S. costs remain higher for stone and also for fabrication. The European participation in the Marble Institute of America shows that the U.S. market is viable for importers. Multinational participation in the U.S. stone industry is helping establish acceptable standards for suspension systems and artificial supports. The U.S. stone industry carries much higher product liability, and environmental, safety, and health costs, compared to foreign producers (Meade 1986a).

The stone industry remains labor intensive, which limits markets for relatively costly U.S. stone. Technology improvements, particularly widespread diamond (Harben 1990) or flame cutting, partly offset this. Improvements in mechanical fasteners and cements have fostered the decorative stone panel market, which is also being standardized to improve competitiveness. Increased panel sales means increased sales of exposed aggregate, often turning quarry waste into a product. Chemical treatment to increase

durability of stone is making a wider variety of stone types available (Johnson 1983).

Zoning and alternative land use are constant concerns of the stone industry. Federal agencies and sometimes state or local agencies regulate stone quarries and sand and gravel operations. The decorative stone industry in the United States is subject to the same safety, health, and environmental pressures and regulations as the aggregate and dimension stone industries. Much decorative stone is produced as a coproduct of urban stone quarries that are under extreme pressure to relocate farther from growing population centers and to impact less on wetlands. Many inoperative quarries are being converted into scenic and high-value commercial and residential developments. Shortages of aggregate in most urban areas are likely because of local zoning restrictions and land development alternatives. The stone industry will continue to be concerned with environmental restrictions and safety factors.

Matthews (2002) characterized and summarized trends in the North American dimension stone and the largely derivative decorative stone markets as follows:

- Domestic stone production is unable to meet increasing demand; >97% is imported.
- Besides Italy, Turkey and Mexico are supplying stone.
- Per capita use of stone is less than half that of Europe, so market growth is likely.
- Increased stone use during the 1990s was in residential fireplaces (stone), bath rooms and entryways (tile), and kitchen countertops (granite).
- Colors in demand are beige, yellow, and white; green and black are still high in demand.
- Limestone is the stone of choice, and buyers want honed, sandblasted, water jet, flamed, or antique finishes. Granite and marble are declining in market share against limestone. Slate, quartzite, and sandstone demand is increasing. Cross-cut travertine will lead demand. Indiana limestone, available only in buff-beige or gray, will decline.
- The latest finish for granite is water-blast, which is evenly textured while maintaining color, and will partly replace flamed granite. Textured finishes that do not alter the characteristics or color of the stone are preferred.
- The demand for tile, including natural stone tile and tile decorative accessories is displacing ceramics and hard floor coverings, the dominant domestic market. The carpet industry is competing by consolidating carpet sales with ceramic and stone. This will lead to increased demand for natural stone tiles.
- Stone marketing is often domestic and local in scope. Most producers are regional and neither promote nor sell nationally. They do not use outside distribution channels.
- The lack of vertical integration in stone production and marketing is eroding. Many fabricators are becoming installers and importers, making stone use more affordable. Many contractors or developers directly import stone.
- Producers typically operate a quarry serving a small fabrication plant capable of producing only cubical work sold to contractors for commercial or residential cladding. Very few producers are capable of producing tiles, slab, or shapes.
- Countertops are the largest use of granite, which now competes with synthetic and laminate tops. As the price of synthetics increases and that of granite decreases, granite use in kitchens will dramatically increase.

- The do-it-yourself market is significant.
- Local craftsmanship will rise as stone demand grows. The shortage of qualified stone professionals, a sore spot with consumers, is temporarily being filled mainly by workers from Mexico. Fabricators and installers must continually train workers to ensure quality installations that foster market growth.
- New domestic trade shows for hard surfaces are promoting flooring and countertops that include stone.
- Buyers want delivered-to-their-door prices from local companies rather than ex-factory imports with their price and timing uncertainties.
- Buyers will pay a premium for quicker service and delivery of stone, preferably in a designed package.

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Dimension Stone

L. Mead and G.S. Austin

Stone is considered by many to be the premium material in all kinds of construction. Its use dates to the dawn of civilization, and only buildings made of stone have survived from ancient times. Although the use of stone relative to other materials declined during the latter half of the 20th century and reached a low point in the 1970s, there was a strong resurgence in the use of stone in construction during the 1990s. This is most likely the result of new techniques for producing stone, a greater recognition of its beauty and durability, and greater affluence among consumers. The attraction of stone is confirmed by the many attempts to simulate it in synthetic materials. Today, natural stone is considered by many to be the ultimate in aesthetic appeal, durability, and ease of maintenance.

During the past decade, production and consumption of dimension stone has increased dramatically worldwide. Figure 1 shows a dimension stone quarry recently opened in the Dominican Republic, exemplifying the dramatic increase in global stone production. The U.S. Geological Survey (USGS) reports that U.S. production and consumption of domestic dimension stone in 2003 had a value of \$236 million. For the same period, the value of imported stone was \$1.46 billion. Similar figures for 1992 show the value of domestic dimension stone consumption was \$198 million, with an additional \$404 million worth of dimension stone imported from various worldwide sources.

Meaningful statistics on dimension stone are difficult to acquire. Although the finished piece of stone is a highly value-added product, stone can be sold as rough blocks, sawed slabs, or finished product. The same piece of stone can therefore be sold and reported three or more times. Furthermore, although the quantity of stone is most commonly reported in tons, stone cladding is more often sold by the surface area and at the same price for different thicknesses. By any measure, however, the production and consumption of dimension stone has increased dramatically during the past decade. A significant indication of the resurgence of stone has been the increased circulation of new trade publications and the increased membership in the stone trade organizations.

DEFINITIONS

In this chapter, the term *dimension stone* refers to stone that is finished to specific dimensions and shapes. Most commonly it is quarried in large rectangular blocks, which are then sawed into slabs for further finishing, and used in buildings, monuments, furniture, industrial applications, and other uses. Other stone, sold as field-



Courtesy of Geomapping/Technographics.

Figure 1. White marble quarry in the Dominican Republic

stone, flagging, rubble, and other similar names, is sold in either natural or broken sizes and shapes that are sorted into size ranges but not finished or dressed to specific dimensions. These types of stone can be used for building, paving, decorative, or other purposes.

The American Society for Testing and Materials (ASTM) and the USGS include both of these groups as dimension stone. Nonetheless, the distinction seems important. The dimension stone industry as defined here is highly sophisticated, using complex, often computerized equipment and large quantities of industrial diamonds and other abrasives. This portion of the business is capital intensive and becoming more so. The production of stone that is not cut or finished to specific dimensions remains a less sophisticated, more labor-intensive industry. The equipment used is simpler—drills, front-end loaders, and trucks—and the products are hand picked and sorted. Common to both, however, are sophisticated marketing techniques. Although family-owned operations serving local markets produce some nondimension building stones, others are marketed nationally and/or internationally.

Three of the most widely distributed trade magazines reflect the distinction. *Stone* (formerly *Dimensional Stone*, Collingswood, New Jersey, www.stone@ashlee.com) covers dimension stone as defined here, with articles on new machinery, production techniques, market trends, and similar information. An annual directory and buyer's guide is published every December. *Stone World* (Paramount, New Jersey, www.stoneworld.com) also is devoted to dimension stone, publishing similar articles, with a buyer's guide published every November. *Building Stone Magazine* (Building Stone Institute, Purdys, New York, <http://www.buildingstoneinstitute.org/publications.htm>) covers the full range of building stones including rubble, flagging, and fieldstone. Its emphasis is more on the end product (finished buildings, homes, etc.) than techniques. Much of the advertising in this magazine is for stone that is not quarried in blocks and dressed to specific size. All three magazines have extensive advertiser indices and offer reader services to their advertisers.

There is no simple way to logically organize dimension and building stone into a neat outline. Building stone includes both dressed and undressed stone, so dimension stone can be considered a subset of building stone. Dimension stone (as defined here) can be used for buildings, furniture, rolling mills, and other industrial uses, so building stone can be considered a subset of dimension stone. In this chapter, dimension and building stone are subdivided into two classes:

1. **Dimension:** Stone that is cut and finished to specified sizes and shapes, which can be used for buildings, monuments, paving, furniture, and decorative objects. Sometimes called cut stone, it is typically quarried in rectangular blocks, then sawed and finished to specification.
2. **Building:** Stone that is sold in natural or broken sizes and shapes, which can be used for building, paving, rough construction, landscaping, and erosion control. It can be collected from the surface, be broken out of a quarry, or be the by-product of a block quarry. It is typically hand sorted into ranges of sizes and shapes.

Both types of stone can be used in building. When so used, broken stone will produce an irregular, or natural, appearance. Horizontal lines will be wavy. Cut stone used in building will produce a regular or geometric appearance. Horizontal lines will be straight. Many consider cut stone to be the only true dimension stone.

Dimension and building stone are also classified lithologically, which can create great confusion among geologists and engineers. The dimension stone industry is one of the oldest in the world, and many of its terms predate the advent of modern geology. For example, the *Oxford English Dictionary* (2nd edition, s.v. "Marble") lists five columns of definitions for marble, many of which have no relationship to a modern geologic definition. In Italy, marble includes all hard stone that is capable of taking a polish, including granite and other rock types. The ASTM committee on dimension stone has gradually modified its definitions to bring them more into line with modern geology, but large disparities remain. Most commercial retailers dealing in stone are not well versed in modern scientific definitions, nor is there any compelling reason why they should be. It is important for the geologist or engineer who becomes involved with the commercial stone business to learn the trade language.

Stone Sold and Used in Natural or Broken Sizes

This category includes all stone that is gathered from the surface, broken out of the quarry, or is an undressed by-product from a block quarry. In building construction, it produces a natural look

and in today's market is especially popular in homes and small commercial buildings. Some of this stone is produced and sold locally by small operations, but much is distributed nationally.

Fieldstone

Gathered from the surface, fieldstone is used to make stone walls, fireplaces, and similar structures. Dating back to antiquity, it was an important building material in early America. Although rock vendors may sell fieldstone, there is no generally accepted commercial connotation as to size, shape, or rock type except that it can be set by hand.

Rough Construction and Jetty Stone

Large blocks of rough-hewn granite or other stone have long been used in such structures as retaining walls, seawalls, and bridge work. For use in these applications, the stone must resist weathering and erosion and break naturally into rectangular shapes that are easily set. Granite fits these requirements admirably and is the most widely used stone for this purpose. Other good sources are waste or rejected blocks from dimension stone quarries.

Rubble

Smaller sizes of broken stone are very popular as wall-facing material in building construction, both for homes and small commercial buildings. The primary purpose is aesthetic—rubble replaces brick or other veneer—but ease of setting, weather resistance, light weight, and the ability to bond well to mortar are also important. With a minimum of capital investment by small operators, the stone can be produced as a by-product from other stone operations or from small pits. The only requirements are that it is marketable and that it can be transported easily and cheaply to market.

Because of the ease of production, there are many small producers supplying local markets. In 2003, some 132 companies produced dimension stone in 176 quarries located in 34 U.S. states (T.P. Dolley, personal communication). Some of the sellers quarry their own stone, but some also contract for the exclusive right to sell stone produced by a small operator in return for supplying advertising and distribution services.

The rock types advertised by the Building Stone Institute include all the standard dimension stone types as well as obsidian (which is actually pumice) and specialty stones. Some of these have national distribution.

Rubble is set in random patterns and the sizes of pieces range from about 0.05 to 0.5 m² of exposed rock. A few years ago, slabs of thin-bedded natural flagstone were commonly used with the bed set parallel to the wall, but recently the three-dimensional effect has become more popular, and natural flagstones are more commonly set in courses with the bed perpendicular to the wall (see next section). Nonetheless, slab-shaped rocks have an advantage in that they cover more surface with less volume and weight. Low-density rocks such as pumice and other porous rock have several advantages. Shipping costs are lower, setting is easier for the stone mason, and fewer or no anchors are required to tie the stone veneer to the wall. The wall, however, can be weaker.

Flagstone

Flagstone consists of thin slabs of stone used as paving. Slate and fine-grained sandstone are the most popular rock types, but any naturally fissile stone can be used, provided it has sufficient abrasion resistance.

Flagstone slabs are generally 25 to 75 mm thick, but thinner slabs can be used where they are placed on an exceptionally firm base and subjected to only light traffic. Flagstone can be sawed into

rectangular shapes or can be produced in naturally irregular shapes. It can be sold in either cut or broken sizes. The largest production of cut flagstone is from bluestone and slate. Much slate flagstone is from quarry blocks that are not suitable for mill stock or other higher-priced products. Random-shaped flagging is done by small producers for local markets. A standard for abrasion resistance of stone subjected to foot traffic is given in ASTM C241 (Table 1).

Paving Blocks

Small rectangular blocks of granite were formerly used to pave roads, docks, freight yards, and other areas subjected to heavy traffic. This market has all but disappeared, owing in part to the substitution of rubber tires for steel rim wheels. A small amount of granite is used for ornamental paving, and, in a similar application, a large amount of granite is used to cover slopes near bridge abutments and other areas where slope stability and erosion is a problem.

Stone Cut to Size

This group includes all stone that is cut to specific dimensions on at least two sides. Most of it is quarried as large, rectangular blocks that are sawed into slabs and pieces of the desired dimension.

Dimension Stone

Dimension stone includes all building stone that is cut to specific dimensions on all sides. The surface can be textured, smoothed, or polished, but is always controlled and finished to specifications. Dimension stone can be quarried and finished by a single producer or it can be finished by manufacturers who purchase quarry blocks or sawed slabs from a quarrier.

Accurate data on production of cut dimension stone are difficult to obtain. The USGS publishes annual reports on the production and value of various lithologies, but these data are deceptive because they are reported in mass units, whereas most cut stone used in construction is sold by volume. The production and finishing of cut stone is essentially a value-added business where the actual cost of raw material is a small portion of total cost.

Specifications for dimension stone are stricter than for other categories of building stone. The most important physical tests as specified by ASTM are listed in Table 1. In addition to these tests, the coefficient of expansion and thermal conductivity are important in some applications.

Most dimension stone is used as non-load bearing curtain walls, or veneer. In modern architecture, the use of natural stone as structural members in buildings is almost nonexistent, but columns, lintels, and other structural members can be faced with natural stone. The stone is hung using one of many systems on the market.

Stone panels ranging in thickness from about 20 to 100 mm are set as a veneer with horizontal supports at each floor and appropriate anchors to the structural wall behind. The load-bearing requirements of the stone are therefore limited to self-support for a floor height despite the rather high requirements for compressive strength called for in the ASTM designations.

Thin panels offer two advantages: savings in the cost of the stone and savings in weight resulting in the use of less structural steel to support the stone. Because of the increased cost of structural steel, there is constant pressure to reduce the weight and hence the thickness of panels. When carried to excess, this can result in failure of the panels. The problem is especially acute when very large panels are used.

Slate generally is used in natural thicknesses, commonly ranging from 6 to 50 mm and with natural cleft or face showing. Honing the surface destroys the natural beauty of the stone and increases the chance of deleterious weathering. Slabs too thick for a particu-

Table 1. ASTM specifications for building stone*

Number	Specification
C406	Roofing slate
C503	Marble dimension stone (exterior)
C568	Limestone dimension stone
C615	Granite dimension stone
C616	Quartz-based dimension stone
C629	Slate dimension stone
Number	Test Method
C97	Absorption and bulk specific gravity of dimension stone
C99	Modulus of rupture of dimension stone
C120	Flexure testing of slate (modulus of rupture, modulus of elasticity)
C121	Water absorption of slate
C170	Compressive strength of dimension stone
C217	Weather resistance of slate
C241	Abrasion resistance of stone subjected to foot traffic
C880	Flexural strength of dimension stone
Number	Definition of Terms
C119	Dimension stone

* Available from <http://www.astm.org>.

lar application can be ground to specification on the reverse side. Most slate is used for roofing and flooring. Other uses are for billiard tables, electric panels, blackboards, mantels, window sills, and similar functions.

Natural stone used in conjunction with other structural materials is a significant development in the dimension stone industry. This approach developed naturally with the use of very thin slabs in the marble industry; now limestone, granite, and slate are being individually suspended on the face of buildings so as to allow movement at the interface. Elastic jointing compounds have made weathertight seals possible. Stone is commonly preassembled into units such as column covers and window frames using epoxy glue and metal supports. The units are furnished with brackets for easy attachment to hangers built into structural members of the building.

A trend in the application of all kinds of dimension stone is toward larger slabs. It is not uncommon for limestone and granite panels to be used in single floor-to-floor spans. Marble slabs are more limited in size (2 m²), but marble-faced panels backed with precast concrete can be produced in single units for floor-to-floor installation. Because many of the large slabs are supported at top and bottom only, producers and producer associations have adopted wind load and other design specifications relating the size of the panel to the thickness of the stone in order to give adequate strength. Furthermore, these requirements have put additional burdens on the quarrier because no physical flaws in the stone along which separation might occur can be tolerated. Whereas smaller-sized pieces could be cut between natural flaws in a block, the quarrier is now called on to produce large, virtually flaw-free blocks of stone.

Although color and pattern are inherent qualities of stone, they can be influenced by the finish. Polished finishes tend to darken color and show vivid contrasts. Rough-textured surfaces tend to lighten color and subdue patterns but tend to catch dirt. Polished marble is used extensively on interior walls where the natural color and veining of many exotic marbles are used to advantage. In exterior work where uniform color and subdued pattern are currently in favor, rough-textured finishes can be used except where airborne



Courtesy of Geomapping/Technographics.

Figure 2. A polished green serpentine marble slab in Amman, Jordan

soot is a problem. These surfaces are achieved by abrading the surface or, in the case of granite, flame treating.

Granite and serpentine marble, or verde antique (Figure 2), are favored stone for use in the base course and entrance features of large buildings. These are the only natural stones that will hold a polish in exterior use, and polished surfaces are easily maintained as well as attractive.

Although seldom actually specified, the long-term availability of a particular stone may be an important factor in its selection for some uses. This is because of the possibility of additions or repair work that must match the original structure. A related factor is that some architects may prefer established building stones with which they are familiar. These considerations give long-established quarries an advantage over new or untried stone despite any other considerations.

Tile

Tile is thin (1 cm) stone cut into square or rectangular shapes, almost always with a polished surface. In the United States, tile is still sold in 1-sq-ft pieces or sizes that are integrally divisible into 1 ft. The principal use is flooring, but it can also be used on walls and countertops. Consumption of tile in the United States has greatly expanded in recent years, mostly because of the advent of automated tile cutting and polishing machines. Most stone tile currently produced is marble because of the ease of cutting and polishing, but granite tile is increasingly produced and consumed. Blocks not suitable for making large panels can be used for tile, an advantage to the producer.

Monumental Stone

Monumental stone encompasses a variety of products ranging from simple grave markers to statues, mausoleums, and elaborate structures such as the Lincoln and Jefferson memorials in Washington,

D.C. In construction and fabrication, the larger memorials and mausoleums differ little from building construction except that they may contain more elaborate carving.

Granite and marble, particularly white marble, are the preferred stones for monumental use. According to USGS statistics, more than half the granite quarried is used for monumental purposes. Georgia and Vermont are the largest producers of monumental marble, but the producing companies provide more building than monumental stone.

Standard sizes for building stones do not apply to monumental stone unless the purchaser specifies. The principal requirements are for uniformity of texture and color, freedom from flaws, suitability for polishing and carving, and resistance to weathering. These qualities either are aesthetic, and hence not amenable to standard specifications, or are qualities best determined by experience. So far, no one has developed a satisfactory test to predetermine the resistance of a stone to weathering.

Ashlar

Ashlar consists of rectangular pieces of stone of nonuniform size that are set randomly in a wall. The exposed surface of each piece is generally less than 0.4 m^2 , and the surface can be squared (smooth face) or roughewn (rock face). Ashlar blocks are prepared to specified thicknesses, usually about 75 mm. Ashlar can be squared from quarry blocks that are not suitable for finishing to cut dimension stone or it can be made from rocks that break naturally into rectangular pieces. Although smooth-face ashlar was popular in the past, the roughewn look of rock face is more in demand today.

Split-faced Ashlar

Split-faced ashlar consists of brick-shaped blocks of stone that are laid in courses. Blocks of marble or limestone are sawed into modular thicknesses and then split with a power-driven wedge called a guillotine. The blocks are trimmed and laid in courses with the broken face showing. Natural flagstones (sandstone, slate, and limestone) are similarly broken into brick-shaped pieces, differing only in that the thickness is not precisely controlled. In the limestone and marble industry, split-faced ashlar consumes much stone that is considered waste in the production of dimension stone.

Roofing Slate

During the last decade, the volume of slate being used has substantially increased. Domestic U.S. sources are being augmented by imports from Canada, Brazil, Spain, India, and China. Used both in new construction as well as for repairs and restoration of older buildings, slate is considered by many to be the most permanent type of roof covering. Standard specifications for roofing slate are given in ASTM C406.

Mill Stock Slate

Smooth-finished slabs of slate are used for electric switchboard panels, billiard tables, blackboards, counter tops, and similar purposes. Electric slate must have high electrical resistance and be free of magnetite and other conducting minerals.

Slate Dimension Stone

Either cleaved or smooth-finished slate can be used as hearthstones, mantels, steps, sills, or other structural purposes. Standard specifications for structural slate are given in ASTM C629.

Curbing

Granite curbing is used in large quantities because of its superior resistance to abrasion and weathering. In areas of abundant

freeze–thaw cycling where deicing salts are used, granite has proved an especially resistant material. Granite curbing is broken out along the rift and grain of the stone, but it is also possible to break out curved pieces by close drilling. Mt. Airy Granite Co. of North Carolina specifies a sawed upper surface, but the face and back are smooth-quarry split.

Miscellaneous Uses

Other uses of dimension stone include laboratory furniture and sinks, for which soapstone is considered the premium material. Sandstone, quartzite, and granite are used to line tube mills for grinding ore or other material. Precision surface plates for mounting optical instruments and fine machine work are made from granite, while sandstone and soapstone have been used as refractory brick. In the past, large numbers of grindstones and millstones were made from sandstone or granite. Arkansas novaculite, a fine-grained quartzite, is fashioned into hones. Because of its resistance to chemical corrosion and its favorable physical properties, granite is used to make cylinders up to 9.1 m long and 1.5 m or more in diameter for grinding pulp in paper mills. It is also used as skid caps and tank liners in steel pickling mills (Richter 1988).

LITHOLOGIC CLASSIFICATION

Almost every variety of rock can or has been used as dimension stone. The suitability of a particular stone is governed primarily by physical properties and aesthetic appeal. Mineralogy and chemistry are, for the most part, important only indirectly as they bear on the physical properties. The exception to this statement is the resistance of a rock to weathering, which is profoundly affected by mineralogy and chemistry as well as by physical properties.

ASTM has adopted standard definitions for granite, limestone, marble, greenstone, sandstone, slate, and certain subdivisions and varieties of each (ASTM C119). Standard geologic nomenclature and classification of rocks is needlessly cumbersome for an industry that is dominated by sales-oriented people and architects. Commercial definitions, however, recognize and respect history and use within the industry while attempting to keep the commercial definitions compatible with scientific terminology. This sometimes creates confusion. The following sections discuss both scientific and commercial definitions.

Granite

Commercial Definition

Commercial granite includes all feldspathic rocks of visibly granular or gneissic texture, including granite family rocks as defined scientifically, plus syenite, gabbro, anorthosite, and other plutonic igneous rocks. In commercial usage, fine-grained igneous rocks such as diabase or basalt are sometimes called black granite. Commercial granites are commonly named for the quarry or location where they are found, with names modified by adjectives giving color, texture, or some exotic description.

Scientific Definition

To the petrologist, granite is a visibly crystalline rock with interlocking texture and composed essentially of alkali feldspar and quartz. A member of the granite family of rocks that includes all rocks with granitic texture, it is composed of essential quartz and feldspar. The granite family is subdivided into specific members, such as granite (proper) and granodiorite, on the basis of the kind and proportion of the three major feldspar varieties in the rock. All members of the family contain quartz, and most contain minor accessory minerals such as biotite, muscovite, hornblende, and pyroxene.

Granitoid rocks containing essential feldspar, but without quartz, are called syenite if alkali feldspar predominates; diorite if calcium feldspar predominates; or monzonite if the feldspar are about equal in abundance. These rocks typically contain considerable amounts of ferro-magnesian minerals such as biotite, hornblende, and pyroxene as accessories. Rocks with approximately equal proportions of calcium feldspar and pyroxene are classed as gabbro or norite and are included in the typical black granites of commercial usage. Rocks with mineral composition of the granite family, but with a texture that shows distinct planar or linear properties owing to the parallel alignment of mineral grains, are called gneiss.

Most of the rocks discussed in this section are classed as plutonic by geologists, meaning that they formed deep within the earth's crust and characteristically have a visibly granular texture. Exceptions are basalt family rocks, generally known as traprock and sold as black granite. All but gneiss are typically of igneous origin, meaning that they formed by consolidation from molten material (magma). Most gneisses and some granite family members, however, are thought to have been formed by metamorphism; that is, by transformation from preexisting sedimentary or other rocks.

Granite family rocks can occur as dikes, sills, or large subadjacent masses of irregular or globular shape. For practical economic purposes, they can be considered bottomless. The mode of emplacement can be by forceful injection where the magma shoulders aside the country rock, or it can be more passive, in the form of stoping where the rising magma engulfs fragments of the country rock (which either sink into or are resorbed by the magma). Most granites are thought to have been emplaced in the roots of mountains that form at convergent plate margins and are exposed only after profound erosion has removed the covering rocks. Granite emplacement can be contemporaneous with orogenic folding (synorogenic) or can follow the principal orogenic movements (postorogenic). Postorogenic granites, passively emplaced by block stoping, are more apt to be free of internal strain and usually make better dimension stone.

Sandstone

Commercial Definition

ASTM defines commercial sandstone as “sedimentary rock composed mostly of mineral and rock fragments within the sand size range (2–0.06 mm) and having a minimum of 60% free silica, cemented or bonded to a greater or lesser degree by various materials including silica, iron oxides, carbonates, or clay, and which fractures around (not through) the constituent grains” (ASTM C119). This definition unnecessarily excludes many arkoses that have less than 60% free silica, including some brownstones from the Connecticut Valley (see Pettijohn 1975).

ASTM defines quartzitic sandstone as having 90% free silica and quartzite as “highly indurated, typically metamorphosed sandstone containing at least 95% free silica, which fractures conchoidally through the grains” (ASTM C119). This definition would exclude many metamorphosed sandstones mapped as quartzites by geologists.

Common commercial varieties of sandstone quarried in the United States include bluestone, “a dense, hard, fine-grained, commonly feldspathic sandstone of medium to dark greenish-gray or bluish-gray color that may split readily along original bedding planes to form thin slabs;” and brownstone, “a dense medium-grained stone, locally grading to conglomerate, with a distinctive dark brown to red color” (ASTM C119). Typical brownstones are

arkosic sandstones quarried from Triassic basins in the eastern United States. Freestone is sandstone or limestone that splits with equal ease in any direction.

Scientific Definition

Sandstone is a clastic sedimentary rock composed of indurated sand grains, most of which fall within the size range $\frac{1}{16}$ in. to 2 mm. The interstices typically contain cementing material, but enough voids can remain to give the rock considerable porosity and permeability. Rocks composed of clastic fragments larger than sand-size are called conglomerate if the pieces are rounded, or breccia if angular. Rocks composed of clastic particles smaller than sand-size are siltstone or shale.

Sandstones are deposited by waning currents, mostly in water, rarely by wind. They are the end product of a weathering and erosion cycle that starts with the disintegration and decomposition of source rock, followed by erosion and transportation of the resulting material to a final resting place where the sediment is deposited in horizontal layers. Quartz is the only abundant sand-size material in the source rocks that strongly resists alteration or decomposition by weathering. Typically, feldspar and other labile materials are depleted during the cycle, leaving a concentrated residue of quartz. The amount of quartz concentration is a measure of the maturity of the sand. Quartz-rich sandstones, sometimes called orthoquartzites, tend to be well sorted and cemented with secondarily precipitated calcite or silica.

Immature sandstones containing abundant feldspar are called feldspathic sandstones (5% to 25% feldspar) or arkoses (more than 25% feldspar). Alternately, immature sandstone containing abundant rock fragments is referred to as lithic sandstone, subgraywacke, or graywacke. Immature sandstones tend to be poorly sorted with the interstices commonly filled with clay, iron oxide, and other detritus.

Perhaps the most conspicuous feature of sandstone is bedding or stratification, which was formed by successive influxes of sediment. Bedding planes commonly are parting planes, and the direction of bedding is called *rift* in the industry. Those bedding planes, along which the rock splits with greatest ease, are termed *reefs*. Some sandstones have a second direction of easy splitting that is nearly perpendicular to bedding. The second direction, called *run*, can be of great aid to the quarrier.

Sandstones with thin, even, and regular bedding along which the rock easily splits are natural flagstones. Sandstones that are sawed into cut dimension stone must have massive beds, as the saw cuts are generally made perpendicular to the bedding. Some sandstone layers have internal cross-bedding that is not parallel to the principal stratification. If the stone parts along the cross-bedding, it is unsuitable for dimension stone.

Limestone

Commercial Definition

Limestone is "a rock of sedimentary origin composed principally of calcium carbonate . . . or the double carbonate of calcium and magnesium . . . or some combination of these" (ASTM C119). In its most recent designation, ASTM (C 119) recognizes the following special varieties: calcarenite, coquina, dolomite, microcrystalline limestone, oolitic limestone, and recrystallized limestone. Of these terms, only calcarenite, coquina, and oolitic limestone are commonly used in commerce.

Limestones are commonly designated by location and texture (e.g., Indiana Oolitic Limestone). The color may be included in a name such as Cream Kasota Vein, or other descriptive or exotic terminology may be used as sales representation dictates.

The Building Stone Institute, following industry usage, has defined an oolitic limestone as a stone formed of shells and shell fragments that are of more or less uniform size and generally 2 mm or less in greatest dimension. The original fossil texture is well preserved. By the present ASTM definition, such a rock should be called calcarenite. Because many commercial oolitic limestones are composed in whole or part of oolites, which are tiny spheres of calcite or aragonite, they would also fit the scientific definition of calcarenite.

Shell limestones generally contain larger unbroken fossil shells enclosed in a fine-grained matrix. Coquinas are composed of loosely cemented shells and shell fragments.

Travertine and recrystallized limestone can be considered either limestone or marble, based on the ability to take a polish.

Scientific Definition

Limestone is a sedimentary rock composed of one or both of the two polymorphs of calcium carbonate—calcite and aragonite. Although aragonite is common in limestones of Recent age, because it is unstable and inverts to calcite, it is rare or absent in ancient limestones. Sedimentary rock composed of the mineral dolomite (calcium-magnesium carbonate) is called dolomite or dolostone. Dolomitic limestone contains calcite and dolomite; magnesian limestone contains magnesium carbonate but not necessarily as dolomite. Many limestones and dolostones contain abundant sand or clay, in which case they may be called sandy or argillaceous limestone (or dolostone).

The vast majority of limestones are composed of shells or shell fragments. When deposited in turbulent water, the fragments are broken, sorted, and reworked. Resulting features such as size sorting and bedding are the same as for sandstones, and the rocks have been called calcarenites, where the word "arenite" designates sand-sized particles. In quiet water, the sturdier shells can remain intact but other shells readily disintegrate into ultrafine particles that can wash out, leaving a residue of larger shells sorted as to size. In very quiet water, the ultrafine material plus the shells of one-celled microorganisms can form a matrix in which larger fossils may or may not be embedded. Rocks composed of finely commuted calcite are called calcilutites. Limestones composed predominantly or entirely of the shells of microorganisms are called chalk.

The only limestones known to form by direct chemical precipitation in open seas are in the form of oolites. Oolites are commonly formed with a concentric structure around a nucleus consisting of a tiny fossil or other fragment. Modern studies show that oolites form in shallow, turbulent, warm seas where loss of carbon dioxide to the atmosphere causes supersaturation of calcium carbonate. Oolitic limestones can be composed entirely of oolites or of a mixture of oolites and shell fragments.

Modern petrologic studies show that much of the finely commuted material in limestones is reworked by burrowing organisms and pelletized by filter feeders. Modern carbonate classifications are based on the texture of particles—be they fossil fragments, pellets, oolites, or other fragments—and the degree of sorting of the particles. For further information, the reader is referred to various texts on sedimentary petrology and the chapter on Limestone and Dolomite in this book.

The origin of dolostone is less clear. Some appear to form by in situ replacement of calcium by magnesium, and the resulting stone commonly retains the texture and structure of the original limestone. Other dolomites are thought to form by direct precipitation in hypersaline waters where the climate is hot and dry.

Marble

Commercial Definition

Commercial marble is any crystalline rock composed predominantly of calcite, dolomite, or serpentine that is capable of taking a polish (ASTM C119). Marble is probably the oldest term used for dimension stone. In ancient Rome, the root word for marble—*mar-mare*—was used for all hard stones that could be polished. The same practice is followed in Italy today where the term “marble” is used for all hard stone that will take a polish, including granite. The practice is not followed in the United States, where commercial marble encompasses true marble in the geologic sense as well as many crystalline limestones, travertines, and serpentine, but not other lithologies.

Travertine is a cellular limestone deposited from hot springs. Onyx marble is a dense, crystalline form of limestone, deposited from cold water solutions and commonly found in caves. Verde antique is massive serpentine, commonly crisscrossed by veinlets of calcite and capable of taking a high polish.

Commercial trade names commonly give the quarry location, color, and an adjective describing the pattern or texture of the stone. Where a pattern is referred to as veined, the stone is generally cut across the bedding or layering. Fleuri patterns are achieved by cutting parallel to layering.

Scientific Definition

Marble in geology usage is a metamorphosed limestone or dolostone that is so thoroughly recrystallized that much or all of the sedimentary and biologic textures are obliterated. The result is an interlocking, mosaic texture. Bedding can be partially preserved in the form of compositional layering or banding. Where deformation is intense, the layering can be folded, stretched, and pulled apart, producing a swirly marbleized appearance (which, in an interesting note, gives “marble cake” its name).

Impurities present in the original carbonate sediment form a characteristic suite of magnesium and lime silicate accessory minerals. Most limestones are slightly magnesian to dolomitic, and the chief mineral impurities are quartz and clay minerals. Common accessory minerals are talc, chlorite, amphibole, and pyroxene. Accessory minerals are colorless to golden-brown magnesian varieties if iron is absent, but green if iron is present. Organic material entrapped within the rock forms graphite that is commonly accompanied by finely disseminated pyrite. Pure calcite marble is white, but tiny amounts of impurities will color it significantly. Graphite and pyrite commonly color marble gray. Finely disseminated hematite will color marble pink.

Most true marbles are deformed rocks in which original bedding planes have been folded, crumpled, or otherwise distorted. The crumpling is generally most intense along the axes of folds. On the limbs, the layering may remain straight and planar. Such is the case in West Rutland, Vermont, where the character of the marble is consistent parallel to the layering, but changes markedly across the layering. On the limbs of folds, the layers may be stretched rather than crumpled. In some Alabama deposits, brittle interbeds of dolomite marble have broken and pulled apart during deformation, and more plastic calcite marble squeezed into the spaces around the broken pieces. At Tate, Georgia, a combination of intense crumpling and stretching has practically obliterated all sense of the original bedding and the entire deposit is a nearly homogeneous mass of swirly veined marble.

Crystalline limestones that take a polish are commercially classified as marble. Such limestones are not considered marble by petrologists, particularly if sedimentary and biologic textures are

well preserved. These dense, nonporous rocks may show recrystallization of the matrix and be thoroughly cemented with secondary calcite. Many of the more decorative marbles are of this class.

Serpentine, classified as marble commercially, is not so delineated by petrologists. Most serpentine results from metamorphism of peridotite and related rock. Originally composed of pyroxene and olivine, peridotites are recrystallized at relatively low metamorphic temperatures in the presence of water to form serpentine minerals (hydrated magnesian silicates) and amphibole. Iron released in the reaction commonly forms magnetite, and lime released from pyroxene, or introduced from outside, commonly forms calcite veinlets. Serpentine commonly forms in tabular or lens-shaped bodies associated with other metamorphic rocks.

Travertine is a dense, commonly banded and cellular limestone deposited by chemical precipitation from springs or rivers. It is a hard, dense form of tufa. Much of the cellular structure is thought to have formed from the weathering out of plants or other debris around which the travertine precipitated.

Slate

For both commercial and scientific purposes, commercial slate is defined as a microgranular metamorphic rock derived from argillaceous sediments. It is characterized by closely spaced parting planes called rock cleavage, which is entirely independent of original bedding. The cleavage permits the rock to split easily into thin slabs (ASTM C119). Slates are formed by dynamic metamorphism. Beds of differing composition that form color stripes on cleaved surfaces are called ribbons, which are considered deleterious in high-grade slate. The best slate, therefore, comes from rocks having thick, massive, original bedding.

Quartz is usually the dominant mineral, but extremely fine-grained mica and other platy minerals are always present. The platy minerals tend to be aligned with the slaty cleavage and impart a sheen to the surface. Most slates contain pyrite or iron oxide and many contain graphite. The color of slate is determined principally by the oxidation state of the iron and the amount of graphite or other coloring material present. Graphite and pyrite impart a dark gray or black color; ferric iron oxides color the slate red. Green slates owe their color to the presence of chlorite, other iron silicates, or ferrous iron oxides.

Other Stone

Other rock types sold as dimension stone include greenstone, soapstone, and traprock or basalt.

Greenstone

Greenstone is a metamorphic rock containing “one or more of the following minerals: chlorite, epidote, or actinolite” (ASTM C119). It is derived by metamorphism of basalt, diabase, or other mafic igneous rocks.

Soapstone

Soapstone is a metamorphic rock derived from peridotite or other ultrabasic rocks and composed principally of talc. It has great heat-retaining properties and chemical inertness. For this reason, it is used for laboratory furniture, stoves, and fireplaces.

Basalt

Basalt is a microcrystalline volcanic rock composed of pyroxene and calcic plagioclase. Traprock is a common term for dike rock of the same composition. The correct petrologic term for traprock is diabase or dolerite. Diabase can have columnar jointing but lacks



Courtesy of Geomapping/Technographics.

Figure 3. Tipping marble block prior to extraction from underground Vermont marble quarry



Courtesy of Geomapping/Technographics.

Figure 4. Marble block ready for a gang saw in an underground Vermont finishing plant

flow structures and commonly is coarser grained than basalt. When sold for dimension stone, it is commonly called black granite or traprock.

QUARRY METHODS

Quarry operations typically involve isolating a mass of stone by cutting it free from the parent mass on all sides but one (Figure 3). The isolated mass is then lifted or separated from the parent mass by breaking it free or by undercutting it with a wire or chain saw. The freed stone can be a block size suitable for sale or further processing—a mill block—or it can be much larger—a quarry block (Figure 4). Quarry blocks are subdivided by breaking into smaller blocks that can be removed from the quarry and sent to the mill. Typical mill blocks range in size from 12 t to 30 t, but they can reach weights as large as 65 t. Quarry operations thus involve cutting the stone, breaking the stone, and removing the stone from the quarry.

Quarry Plan

The quarry plan is determined by the geometry of the deposit, the amount of overburden, and the necessity of handling rectangular blocks weighing up to 65 t. Most quarries are the open-pit type (Figure 5). They have relatively small surface area and are worked downward in a pit below the general surface level. Open-pit quarries have several advantageous characteristics:

- They can be located on outcrops or where overburden is thin.
- They are within reach of fixed derricks with movable booms.
- Electric service, air compressors, loading docks, and other service facilities can be more or less permanently fixed near the working area.

Traditionally, the quarry size is limited by the reach of the derrick boom. Larger open-pit quarries generally require several derricks, both for lifting out blocks and for emplacing and moving quarry machinery. In recent years, many operators have used large tractors, forklifts, and other machinery to move equipment and quarry blocks across the quarry floor, thus extending the reach of the derrick boom. Some have eliminated derricks altogether and built ramps to give access to fork lifts and other mobile equipment for moving blocks and equipment.

Open-pit quarries are particularly well suited to massive deposits such as granite and some marble formations (Figure 6). Steeply dipping layered deposits are also quarried by this method, and the hanging wall is commonly undercut. Wall support is generally not required where a single derrick makes one opening. If successive quarries are opened along the strike, however, a web between quarries can be left for wall support.

The depth of open-pit quarries is limited by the thickness or depth of good stone, by spalling or so-called pressure breaks, or by excessive time loss in entering and leaving the quarry and in lifting out blocks. Open pits seldom reach depths of more than 75 m.

Flat-lying, layered deposits can be worked as open-shelf quarries in a hillside. In this case, the quarry floor is level with the ground on one side. If the deposit is thick, the quarry can be changed into an open pit as deeper layers are removed. The quarry can also be extended under the hill as an underground quarry if the overburden is too thick for removal on the high side (Figure 7).

Blocks are nearly always cut parallel to layering if the layering is pronounced and regular. Therefore, where layering is tilted, the quarry floors are not flat. This increases the difficulty of moving equipment and removing blocks. Movable equipment, such as tractors and forklifts, cannot be used, and enough derricks must be set to reach the entire working area of the quarry.

Underground quarries are room- and-pillar mines. Generally, no more than 25% and commonly as little as 15% of the stone is left for roof support. Underground derricks are set for loading blocks. These can be of the fixed-boom type, as blocks are generally skidded under them for loading onto trucks or other conveyances. In recent years, forklifts strong enough to lift quarry blocks have become available, eliminating the need for underground derricks in flat-floored quarries.

The initial opening of a tunnel quarry can be made by cutting out blocks in a manner similar to removing key blocks in an open quarry. The cost of removing these key or tunnel blocks is higher than for removing floor blocks. After the initial opening is made, quarry methods are generally the same as for open quarries except for block removal. Alternatively, some underground marble quarries in Vermont have been opened by removing an overlying layer of rock with conventional mining methods (i.e., blasting and mucking). More efficient quarry equipment has made underground mining unnecessary.



Courtesy of Geomapping/Technographics.

Figure 5. Mature slate quarry in Vermont



Courtesy of Geomapping/Technographics.

Figure 6. Mature granite quarry in Vermont

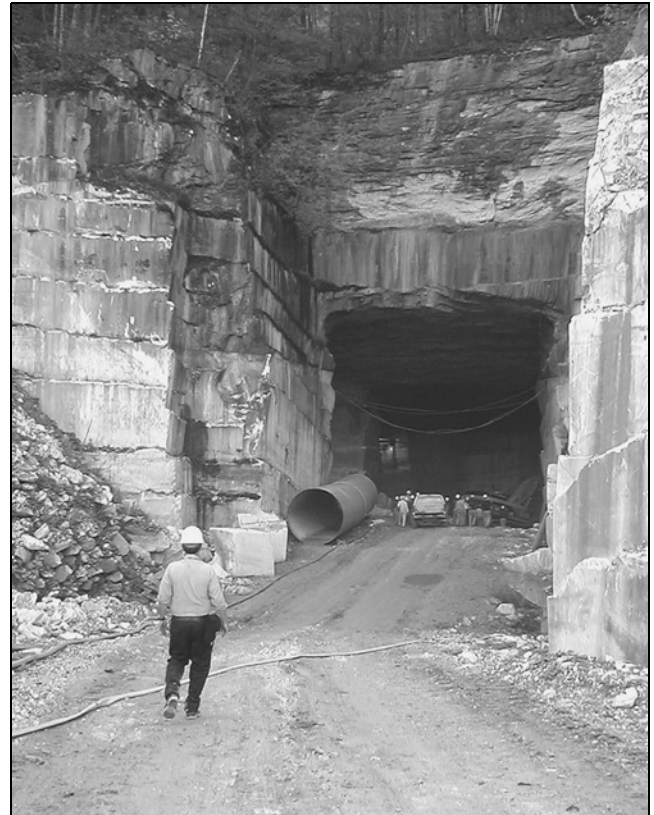
Cutting the Stone

Channeling Machines

One of the oldest methods for cutting stone is with channeling machines that cut with the chopping action of several chisel-edged steel bars clamped together. The machine travels back and forth on tracks, cutting a channel 50 to 64 mm wide. As the channel is deepened, longer bars are substituted in the machine. Because the method is slow and the channel bars require frequent sharpening, the quarry is practically obliged to have a blacksmith shop. Channeling has generally been replaced by other quarry methods.

Drilling and Broaching

Drilling and broaching is another long-established method for cutting stone. Drill and broaching tools are mounted on a quarry bar built into a rigid frame. The tools slide along the bar, which serves to align a series of closely spaced holes. The web between these is cut out by the chiseling and chopping action of the broaching tool. Although the method is suitable for all kinds of stone, drilling and broaching is slow, and, like channeling steel, the broaching steel requires frequent sharpening. In modern quarries, the method has largely been replaced by line drilling.



Courtesy of Geomapping/Technographics.

Figure 7. New tunnel opening in a Vermont marble quarry

Line Drilling

In line drilling, also called slot drilling, a line of overlapping holes is drilled. The drill is mounted on a quarry bar or frame, which serves to align the holes and hold the drill rigidly in position. A key to successful line drilling is a guide attached to the drill that is inserted into the last complete hole in the line and serves to ensure that successive holes overlap. The Tamrock Company has developed a machine (Slot Drill 600) that mechanically spaces 64-mm holes, then drills the web between them using a special guide. Tamrock claims a maximum depth of 6 m for the system. This machine illustrates a trend toward mechanization that cuts labor costs.

Jet Channeling

Jet channeling is the most common method of cutting granite. Also known as flame-cutting, this method consists of disintegrating the rock with intense heat from the combustion of fuel oil and oxygen. The thermal shock causes the rock to spall, and the fragments are blown from the channel. The torch, which is passed back and forth over the rock, is commonly attached to a frame in order to keep the cut true. In some granite quarries, large blocks are freed using this method and then are subdivided by using cheaper methods of breaking the rock. Although jet channeling works well in granite and other quartz-bearing igneous rocks that spall, it does not work in quartz-free rocks or carbonate rocks that calcine or fuse rather than spall.

Jet channeling has two significant disadvantages: (1) the noise level is high enough to constitute a serious health hazard, and (2) the kerf is wide and irregular, thus wasting stone. For these reasons, jet channeling is being replaced by other methods.



Courtesy of Geomapping/Technographics.

Figure 8. Wire and chain saw in Vermont

Wire Saws Using Abrasives

Wire saws using quartz sand or silicon carbide have been used for many years to cut marble and, more rarely, granite and limestone. The method, once dominant in some marble districts, has been and is being replaced by diamond wire saws (see following section).

The wire saw consists of a single, double, or triple strand of wire that runs over sheaves and is fed under tension into the stone. Sand, aluminum oxide, silicon carbide, or another abrasive is fed to the wire and wears a groove or channel in the stone. The sheaves are mounted on a tower or track so that they can be moved into the cut. In order to press the wire into the cut, there must be two free and parallel sides to the block of stone being cut, or else a large hole to admit the sheaves must be drilled. In some cases, the hole need only be large enough to admit the axle, hub, and supporting arm of the sheave. As it is pressed into the stone, the sheave is designed to cut its own groove. In some operations, other methods are used to cut parallel channels between which the stone can be wire-sawed.

The wire itself abrades and must last for the entire cut. If it breaks before the cut is finished, the kerf may be too small to insert a new wire and the cut is lost. Therefore, the wire is commonly several thousand meters long.

A single wire can be used to make many parallel or other cuts by guiding it with appropriate sheaves. In order to keep tension on the wire, at least one movable sheave must be set up with appropriate counterweights. Wire-sawing produces a smooth cut that minimizes subsequent finishing in the shop and saves stone in the mill.

Diamond Wire Saws

During the 1970s, diamond wire saws were introduced into the stone industry, first in mills and shops, then into the quarries. Since then, they have continued to replace the older wire-saw techniques. Detailed descriptions of the diamond wire are given in Hawkins et al. (1990) and Cia and Mancini (1989). The wire is a steel cable on which small, diamond-impregnated or diamond-bonded, cylindrical beads are mounted. The beads are separated by either wire springs for soft, nonabrasive rock or plastic for hard, abrasive rock. The wire is looped through drill holes and run by a motor-driven drive wheel mounted on tracks. Tension is provided by pulling the drive wheel assembly away from the cut on the tracks. Cuts can be either vertical or horizontal.

Because most cuts require the drilling of two intersecting holes, the wire must make a sharp angle when the cut is started, which becomes rounded as cutting proceeds. This requires care in providing correct tension during various phases of the cut. Cooling and lubrication is provided by water.

The technique requires precise drilling of the intersecting holes. In order to loop the wire, a nylon line is attached to a ball or wad of paper or other material that is forced through the holes hydraulically or with compressed air. The diamond wire can then be pulled through the intersecting holes with the nylon line. Further details can be provided by the Diamond Bort Company of Columbia, South Carolina.

Chain and Belt Saws

Chain saws using carbide teeth were used more than 30 years ago to cut soapstone in Virginia. More sophisticated saws made in Europe and also using carbide teeth were used to cut limestone and soft marble but were unsuccessful for cutting harder stone. Finally, with the incorporation of diamond-set teeth, chain saws became practical for use in marble and slate. The most recent development is a belt saw in which a neoprene belt carrying diamonds embedded in metal segments replaces the chain (Figure 8). Cooling and lubricating water flows through the blade, which is hollow. Blades up to 5 m long are used in softer limestone; shorter blades are used in harder stone such as marble. Belt saws are also used in sandstone and slate but apparently not yet in granite. Ultimately, belt or chain saws will probably be used successfully in granite and other hard stone.

Water Jet

A promising new development in cutting granite is the water jet. A pulsating jet of water at pressures ranging from 96.5 to 275.8 MPa is directed at the granite and causes it to disintegrate. It is less noisy, produces less dust, and promises to be more economical than jet piercing. Rocky Mountain Rose Re d, Inc., of Lyons, Colorado, is currently using a water jet system (Anon. 1991; Zielinski 1992). The Elberton Granite Association in Georgia has tested two experimental machines, but they have apparently been less successful than diamond wire saws.

Breaking and Lifting the Stone

In open-pit quarries, vertical cuts are made by dividing the floor of the quarry into appropriately sized blocks. After an initial key block is broken free by drilling a hole in the center to the depth of the vertical cuts, an explosive charge in this hole frees the block with or without damage to the block. Alternatively, the block can be wedged free or forced free with an air bladder. In underground quarries, essentially the same technique is used except the initial cuts are horizontal and the key block is taken out of the tunnel face.

Once the key block is removed, a series of closely spaced holes is drilled underneath or behind the remaining blocks, and they are broken free with the use of feathers and wedges, with explosives, or, in some cases, wire saws. Feathers are pieces of half-round steel that are inserted into the hole. To produce the break, steel wedges are driven between the feathers.

Dimension stone quarriers have traditionally shied away from use of explosives, but recent experience indicates that, if used properly, explosives can be successfully and economically employed without damaging the stone. Most modern quarriers use explosives to break the block free. Primacord or light plastic-enclosed charges inserted into the holes generally provide enough force and do not damage the stone. When a block of stone is broken free, it can be further subdivided by the same technique.



Courtesy of Geomapping/Technographics.

Figure 9. Prospect opening in granite with heavy equipment in Vermont

Granite typically has two directions of easy breakage, called rift and grain, or rift and run. In some quarries, large blocks containing many thousand cubic meters of stone are cut free by jet channeling or other means. These blocks are then broken into mill-size blocks along the rift and run directions. Some granite ledge quarries rely entirely on breakage to produce dimension blocks. Holes drilled for feathers and wedges in granite commonly need penetrate only a few centimeters of stone. If the rift is strong, the break produced runs true for the entire length of the block. If the rift is not strong, however, drill holes can penetrate the entire width of the block as in the so-called Finnish method (described in the next paragraph). Often, odd-shaped blocks are trimmed and squared by line drilling and breaking.

In the Finnish method, marble and limestone are often cut into pieces of appropriate height and width for mill blocks, but of much greater length than granite. These are then lifted (broken free from the quarry floor), using feathers and wedges. Using the same technique as for granite, the y are also broken into appropriate lengths. Drill holes for the feathers and wedges generally penetrate the entire width of the block.

The stone can also be broken free with air pressure. After a quarry block is cut free on all sides but the bottom, the bottom is drilled as though for using feathers and wedges. A large reinforced bladder is inserted in the vertical kerf that separates the block from the quarry. Air pressure applied to the bladder breaks the block free and sets it out from the quarry face. Usually 23 kg of pressure or less is sufficient. In some cases, the air bladder can also be used to break loose key blocks.

A serious problem in some quarries is the failure of stone to break along predetermined directions. This may happen in stone that does not have a natural grain or in which the quarry direction does not parallel the natural grain. In some deep marble quarries in Georgia, stone that is cut free on the sides has a tendency to break loose from the floor along arch-shaped fractures rather than parallel to the quarry floor. This not only ruins a mill block but presents a costly cleanup problem in order to keep the quarry floor flat. These breaks, called rainbow breaks by the quarriers, are most common in large, deep quarries and where a long period of time has elapsed between cutting the block free on the sides and lifting it from the quarry floor. Some deep quarries have been abandoned because of rainbow breaks, even though the stone was good otherwise.

Some quarriers use a wire saw to cut quarry blocks with a very large surface area. These slabs are broken free, turned on their sides, and broken into appropriately sized mill blocks. This procedure not only eliminates much expensive cutting but allows the quarrier more flexibility in choosing the size and position of the mill blocks to be cut from the slab. The slab can often be subdivided in such a manner that a minimum number of blocks contain natural flaws, whereas the quarrier has less control with a set floor pattern.

Removing Blocks from the Quarry

Mill blocks are traditionally removed from the quarry with fixed derricks. The procedure is slow, and all other operations under the derrick boom must be halted while blocks are removed. The length of the boom also limits the size of some quarries. Blocks can be skidded from greater distance with tractors and crawler-type derricks, which can also add flexibility. A more efficient method is the use of forklifts that are now available in sizes large enough to handle mill blocks. Because forklifts require a flat or nearly flat floor and access ramps, they are not appropriate for all quarries. For large quarries, however, an investment in ramps is probably justified (Figure 9).

Mill Operations

Most stone is sold as blocks, slabs, or finished product. Mill operations involve cutting blocks into slabs and then cutting the slabs into appropriate sizes and shapes for the final product. Finally, the stone surface is given a final finish.

Sawing Slabs

Primary saw cuts can be made with a gang saw, wire saw, or circular saw.

Gang saws consist of a group of flat steel blades set in a frame that moves with a reciprocating motion. The frame is automatically fed into the block at a rate that depends on the type of stone and the abrasive or cutting edge used. A sand-water mixture may be fed into the saw for cutting soft stone. For harder stone such as granite or quartzite, heavier notched blades have been used, and the cutting medium is steel shot. For faster cutting, the blade can be fed with aluminum oxide or another abrasive. Nearly all modern mills use set teeth of diamond or carbide (mounted in wheels that grind the stone to a reciprocal shape just as a wood-router bit shapes a board).

Although carbide can be used for softer limestones, harder rocks, such as marble and granite, require diamonds, which are set in segments that are brazed to the gang saw blade. Set teeth generally cut faster and smoother than loose abrasives. As many as 40 blades can be set in a single gang saw when thin stock is being cut.

In most gang saws, the blade is horizontal and the frame is pressed downward through the block. The size of the block that can be sawed is thus limited by the size of the frame and blades. A newer development is vertically set gangs through which the block moves horizontally, producing longer slabs.

One of the problems in gang saws is keeping equal tension on the blades. If a blade loosens, it can wander or buckle and jam the saw or ruin the cut. The traditional method of holding a blade in position is with wedges driven through a hole in the blade outside the frame. Considerable skill is required to maintain a large number of blades under equal tension in a single frame. A more modern method involves the use of hydraulic tensioners.

Wire saws are commonly used to make primary cuts in granite blocks. These can be grouped into multiple or ganged wire saws. The wire saws can be either twisted wire using abrasive or diamond wire saws.

Wire saws are also used to make irregular or curved cuts. The saw is set vertically and the stone is fed into it as wood is fed into a band saw. Wire saws have also been used to turn large columns, in which case the saw is usually set horizontal and the stone is slowly turned into it.

A recent development in the granite industry is the use of large-diameter circular saws to make primary cuts. The saw makes repeated passes across the block, cutting 5 to 10 mm at each pass. The resulting cut is remarkably smooth so that increased sawing costs are more than compensated for. The largest circular saw in operation is reported to be 4.2 m in diameter and capable of 1.6 m total depth of cut. Another recent development is the use of the W.F. Meyers' narrow-belt block saw for primary cuts in quarries and mills in the Indiana Limestone District.

Secondary Cuts

Sometimes called bridge saws, secondary cuts are set in a frame that guides the saw and, in most modern versions, are automatically controlled, often by computer.

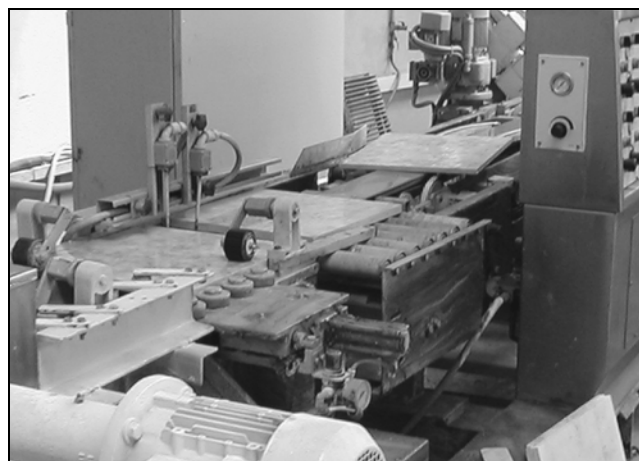
Shaping, Grinding, and Polishing

A wide variety of methods is used for finishing the stone. Shaping can be done using hand-operated pneumatic tools, wire saws that cut as a band saw cuts wood, or silicon carbide. For softer stones, large milling machines employing carbide teeth can be used to gouge shapes into the stone. In modern mills, diamonds have almost universally replaced other abrasives, and automated machines are common.

Cylindrical shapes are made on a lathe that turns the stone into a carbide or diamond bit or into a wire saw. Boring machines can be set with diamonds or with carbide.

In older mills, flat surfaces can be ground on a large horizontal cast-iron wheel called a rubbing bed. A water-sand mixture is used as abrasive. More modern plants have replaced rubbing beds with automatic surfacing machines using impregnated diamonds. The stone is belt-fed under a series of successively finer horizontal wheels. Some machines fine-grind the edge of the stone as well as the surface. Much polishing is still done by a conventional grinding-polishing machine that moves a spindle over the stone surface. Wheels using successively finer abrasives are set on the spindle.

A significant development in the last several years is the introduction of automated tile-making machines that trim and polish the



Courtesy of Geomapping/Technographics.

Figure 10. Automated tile line in Amman, Jordan

tile at lower cost and with more accuracy than previously possible (Figure 10). These machines are largely responsible for the much greater production and consumption of stone tile.

Another significant development is an automated shaping machine that can duplicate intricate, carved pieces. Traditionally, much finishing was hand work by skilled stone workers. As these skills are being lost, much effort has gone into automation of the finishing process.

DISTRIBUTION OF DEPOSITS AND RESERVES

The ultimate reserves of dimension stone must be considered inexhaustible. There can only be shortages of particular types or colors that can be discovered and produced at a competitive price. Although the distribution of various lithologies is a result of geologic factors, the location of producing quarries is governed by economics. Because dimension stone, particularly marble and granite, is traded internationally in blocks, slabs, and finished products, every continent and nearly every country is a producer or potential producer of dimension stone.

Following is a brief summary of the major producing areas, described by lithologies, first in North America, then in the rest of the world.

The United States and Canada

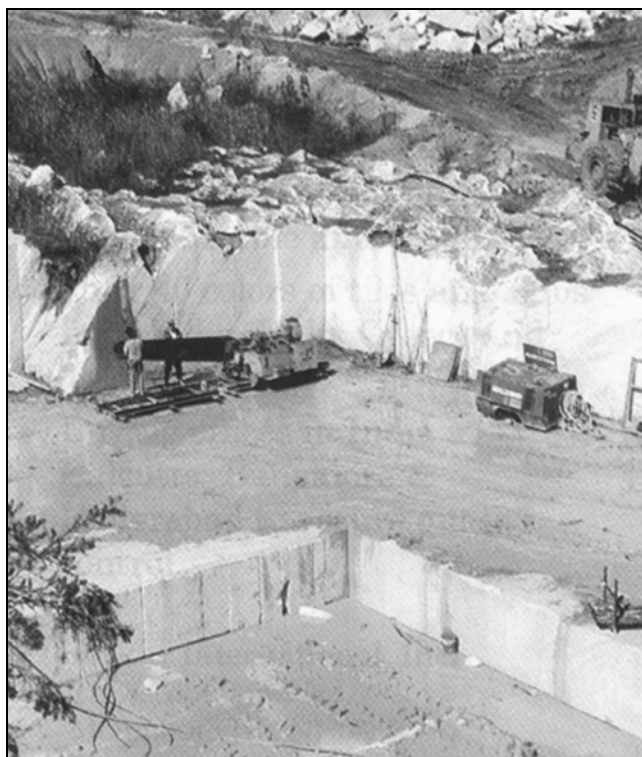
Currier (1960) divided the United States into five geologic provinces for the purpose of describing the distribution of the major lithologies. All but one extend into Canada.

Atlantic and Gulf Coastal Plain Province

The Atlantic and Gulf Coastal Plain lies east and south of the Appalachian Mountains, extending from New York to Alabama, and south of the Interior Sedimentary Province from Alabama through Texas. It is underlain by poorly consolidated sedimentary rocks of Cretaceous and younger age that lie in nearly horizontal strata. Although little dimension stone is produced in the province, soft coquina that hardens on exposure to air has been used as building stone in Florida since the 17th century, and Cretaceous limestone is quarried near Liberty Hill, Texas.

Appalachian Crystalline Province

This province extends from Alabama to Maine and north through eastern Canada to Newfoundland. Because it is the exposed root



Courtesy of Geomapping/Technographics.

Figure 11. White marble quarry in Alabama

zone of an ancient mountain chain that formed during mid-Paleozoic time, it is sometimes called the “older Appalachians.” Granite, gneiss, marble, serpentine, slate, and other crystalline rocks are produced from this region (Figure 11).

Granite. The principal granite-producing areas in this province are in Georgia and New England. North Carolina is also a significant producer.

Georgia produces more granite than any other state or province in North America. The industry is centered in the town of Elberton in northeast Georgia. Unlike many districts, Elberton is not dominated by one company but rather has many producers. Some producers specialize in quarrying blocks, some in sawing slabs, and some in making finished products. Still other companies are vertically integrated, performing all operations from quarry to finished product. The production in Elberton is principally aimed at the memorial market, but structural stone such as building facing and floor tiles is a growing market. In 2003, more than 45 granite quarries were operating in the batholith within a 25-mile radius of Elberton. Elberton firms also operate quarries or buy stone in several other states or countries.

The prevailing method of cutting stone in Elberton is jet channeling, but some operators are switching to high-speed drilling using Tamrock’s slot drill or to diamond wire saws. Because jet channeling is noisy, wasteful, and less efficient than the other methods, this trend will probably continue. A summary of quarry techniques is given in the Elberton *Graniteer* (Anon. 1990a).

The three New England states of Vermont, New Hampshire, and Massachusetts are the primary sources of granite in the Appalachian Crystalline Province. The largest single granite-producing district in this region is in Barre, Vermont, where the Rock of Ages Co. is the sole producer.

Descriptions of the Barre District are given by Richter (1987) and Ratté and Ogden (1989). Since the mid-19th century, granite has been quarried from a mid-Paleozoic pluton, mostly for monuments but also for building facing panels, surface plates, and paper rollers up to 10 m long and 2 m in diameter. Quarriers use natural rift and grain to remove blocks averaging 5 to 6 m³ (Richter 1987).

North Carolina is also a major producer of granite, principally from the Mt. Airy District. Connecticut, Maine, Pennsylvania, and South Carolina are minor producers.

Sandstone. For more than 100 years, arkosic sandstone has been produced from down-faulted basins of Triassic age, which form a subprovince within the Appalachian Crystalline Province (Currier 1960). Known as brownstone, the stone was formerly used extensively for buildings and residences in New England and the mid-Atlantic states but production is much reduced today.

Marble. True marble (i.e., marble formed by metamorphism of limestone or dolostone) occurs throughout the province, and most states within the province have produced marble at one time or another. Today, however, nearly all production comes from Georgia and Vermont with some minor production from Alabama.

The Polycor Group purchased all of what had been the Georgia Marble Company and now extracts marble from several large dimension-stone quarries in Pickens County, Georgia. The stone is medium- to coarse-grained white or light gray and most commonly veined with darker material. The stone is cut with diamond belt saws and quarry bars; quarry blocks are broken free and subdivided using mild explosives in spaced drill holes; and small blocks are removed with large forklifts. Stone from this large-volume, low-recovery operation is used for monuments and buildings.

The Vermont Quarries Company has leased the Danby Imperial Quarry from what had been the Vermont Marble Company. Recent underground expansion has secured reserves of this source of white marble in the town of Danby, Vermont, where a 10- to 20-m-thick layer of Ordovician marble lies in a broad, shallow syncline. Tunnel cuts are made horizontally with a diamond-toothed chain saw, and the sides are cut with a diamond wire saw. Vertical floor cuts are then made with a diamond chain or belt saw and bottom cuts with a diamond wire saw. Average block size is about 20 t (Ratté and Ogden 1989). A complete block-sawing and slab-manufacturing facility has been incorporated in the portion of the underground workings that had been previously quarried.

The black marble quarry at Isle la Motte, Vermont (which was previously owned and operated by the Vermont Marble Company) has been sold, along with the red marble quarry property in Swanton, Vermont. The new owners, a group of Vermont quarriers, have resurrected the operations under the name of Barney Marble—the historical company in Swanton, Vermont, that produced stone from these quarries and supplied many buildings in Washington D.C. in the late 19th century. Similarly, the Rochester Verde Antique quarry at Rochester, Vermont, was sold by the Vermont Marble Company and is supplying stone to the world market under the company name of Vermont Verde Antique International.

Alabama was once a major producer of white marble from the Sylacauga marble belt, but the principal producers have switched to industrial fillers. A small quarry producing block marble for export southwest of Sylacauga has been a small but consistent producer. Marble also has been produced from the Murphy marble belt in western North Carolina. White marble from the Cockeysville Formation in Maryland was used in the Washington Monument, and white marble from Lee, Massachusetts, helped construct the U.S. Capitol building in the last century. During the 1990s, a Canadian firm ceased block production in Lee and none of these districts have significant production today.

Slate. Vermont and Pennsylvania account for 70% of U.S. production of slate. In Vermont, lower Ordovician- and upper Cambrian-aged slates are quarried into blocks by drilling and blasting, followed by manual splitting. The high angle of dip of the slaty cleavage makes conventional quarry techniques difficult. Blocks are taken to the mill where they are cut by diamond saws and trimmed to size for manual splitting into roofing slates. Floor tile and flagging are gauged by planers to specified thicknesses. Structural slate (mantels, electric panels, and similar products) are finished in the mill using standard cutting, honing, and polishing equipment (Ratté and Ogden 1989).

Pennsylvania slates of upper Ordovician age in the Lehigh-Northampton District have a nearly horizontal axial plane cleavage. The slate is quarried in benches 4-m thick using wire saws with silica sand abrasive to isolate quarry blocks. These are then lifted by drilling and wedging. Quarry blocks are reduced to manageable size (mill blocks) by splitting along “watersplits” and a natural grain, or sculp, which is perpendicular to the slaty cleavage. In the mill, diamond saws, splitters, and various other tools turn blocks into finished products (Berkheiser 1984; Colley 1990).

Slate is also produced in Virginia (Sweet 1990), in New York, and intermittently in Nova Scotia and Newfoundland (Vagt and Bergeron 1990) as well as Quebec.

Soapstone. Soapstone is produced in Nelson County, Virginia. Blocks are cut out by a large German-made chain saw and finished into fireplaces, cook stoves, and other products benefiting from the heat-retaining properties of the stone (Sweet 1990). This district was formerly a major producer of laboratory furniture. The greatly increased demand for soapstone is being supplied by Brazilian producers from quarries in the Minas Gerais District of Brazil.

Interior Sedimentary Province

This province extends from the Appalachian Mountains to the Rockies and from Mexico north into the prairie provinces of Canada. It is underlain by nearly flat-lying, mostly marine sedimentary rocks ranging in age from Cambrian to Cretaceous. These sedimentary rocks cover an older, Precambrian basement, which is an extension of the Canadian Shield and is exposed in several isolated uplifts. Limestone, sandstone, and marble (crystalline limestone) are produced from the sedimentary rocks, and granite from basement rocks exposed in the isolated uplifts.

Limestone. The amount of dimension limestone produced in Indiana exceeds the amount of all dimension stone produced in any other state. Indiana limestone has probably been the dominant building stone in the United States for more than a century. The industry is centered around the towns of Bloomington and Bedford in south-central Indiana where quarries have been operated since 1827. The district and its history have been described by Patton and Carr (1982).

The stone has been called Bedford Rock, Bedford Oolitic Limestone, Indiana Oolitic Limestone, and Indiana Limestone. Today Indiana Limestone is a generic term for building stone quarried from the Salem Limestone of Mississippian age in the Bedford-Bloomington District (Patton and Carr 1982). The stone is a light gray to bluish-gray, massive, even-grained, granular, porous, and cross-bedded calcarenite (Patton and Carr 1982). The industry markets buff, gray, and variegated, a combination of the two stone colors.

Because of the district's long history, many kinds of quarry methods have been used to extract stone. Today, many quarries in the district combine W.F. Meyers' diamond-belt quarry saws with diamond wire saws.

In northwestern Alabama, similar stone of the same age is quarried in an underground mine. Here, tunnel cuts are made with three quarry bars mounted on a massive frame and aligned so that the top block tapers to the rear, making extraction easier.

Limestone is also produced from the Oneota Formation of Ordovician age in the upper midwestern United States. In central Texas, limestone is produced from lower Paleozoic rocks.

Marble. Some crystalline limestones within the Interior Province take a polish and, therefore, are classed as marble. The most notable is the Holston Formation in east Tennessee from which vast quantities of Tennessee Marble have been produced. The district lies within the Valley and Ridge Province of the Appalachian Mountains where the rocks are steeply folded and faulted. Blocks must be quarried parallel to bedding, and, because of the steep dip, it is difficult to use forklift trucks and belt or chain saws. Most of the best deposits have been worked as far as possible without underground tunneling. Tennessee Marble remains one of the most attractive and durable dimension stones. One quarry near Friendsville remains in operation with a modern finishing facility that satisfies the current market. In addition, the Imperial Black Marble quarry in Grainer County has been a source of black marble in this area of Tennessee.

Sandstone. Most sandstone production in the United States comes from the Interior Province. Because most sandstone is sold in broken and irregular sizes, however, it does not qualify as dimension stone in this chapter. Bluestone from New York and Pennsylvania is sawed and dressed and a small amount of sandstone from Tennessee is cut and polished for furniture.

Granite. The sedimentary rocks of the Interior Province are underlain by crystalline rocks that are an extension of the Canadian Shield. These basement rocks are exposed in localized uplifts in southeastern Missouri, central Texas, the Arbuckle and Wichita mountains of Oklahoma, and the Black Hills in South Dakota. All of these areas have produced or are producing dimension granite.

Lake Superior Crystalline Province

The Canadian Shield includes the Lake Superior crystalline province of Currier (1960) and underlies most of Canada west of the Maritime Provinces and east of the Rocky Mountains. Although it is underlain by Precambrian rocks—mostly granite and gneiss—extensive marble occurs in the Grenville subprovince of southern Ontario and Quebec.

Granite. In the United States, the principal producer from this province is the Cold Spring Granite Company of Cold Spring, Minnesota, which operates a number of quarries in Minnesota and elsewhere, including Texas and Manitoba.

In Canada, granite is produced in Manitoba, Ontario, and Quebec (Anon. 1990b). Quebec is the largest producer with about 25 active quarries (Nantel 1983; Anon. 1990b).

Although there are few active quarries in the other provinces, the potential is very large. Several provinces are working to find and promote dimension stone deposits. Two provinces, Ontario and Saskatchewan, publish catalogs depicting potential sources.

Other Stone. Only small amounts of other dimension stone, including marble and quartzite, are produced from the Canadian Shield.

Western Province

The Western Province includes a wide variety of subprovinces that encompass nearly every conceivable geologic environment. Nearly every type of rock can be found and at one time or another has been quarried. It is the only province in which recent volcanic rocks are

found and is the only region in North America from which travertine is produced.

Travertine. Travertine deposits are typically associated with recent geologic activity such as volcanism and faulting. For this reason, the Western Province is the only province in the United States and Canada from which travertine is produced. Currently, the only production is from Idaho, Montana, and New Mexico, but potential deposits are known to occur in Oregon and possibly other states.

Two travertine deposits in southeast Idaho are operated by Idaho Travertine, Inc., of Idaho Falls, Idaho. Production since 1968 is said to have averaged 2,000 m³ per year (Neumann 1991). The principal deposit, just west of Swann Valley, Idaho, is a boulder deposit, meaning that it consists of large masses or boulders of travertine embedded in a highly fractured matrix. The boulders are excavated by dozers and loaders. A D-9 dozer fitted with a ripping bar on the front end is used to pry loose the boulders. Those that are too large to transport to the mill are trimmed by line drilling at 15- to 20-cm spacing and blasting with primachord. Recovery is said to range from 5% to 10% of volume removed.

The Montana deposit, near Gardiner, north of Yellowstone Park, is also a boulder deposit, and quarrying methods are similar to that of Idaho Travertine. Five- to ten-ton blocks are removed, and slabs, tile, and ashlar are produced at a shop in Livingston.

About 50 discrete deposits of travertine have been identified in New Mexico (Barker 1986). New Mexico Travertine Co. quarries one of these from a deposit approximately 40 km west of Belen, producing five color-varieties of travertine and one limestone (Austin and Barker 1990). The stone is quarried using a concrete saw to remove cap rock and diamond belt and wire saws to cut the travertine. A mill just west of Belen finishes the stone to polished slabs and split-faced ashlar.

Other Stone. Most of the quarries in the Western Province were worked in the early part of the 20th century and were abandoned long ago. No permanent centers of dimension stone production have developed similar to those in Georgia, Indiana, and Vermont. Information on quarry sites and past activity can be obtained from most state or provincial surveys.

Since the early 1990s, the Colorado Yule marble quarry, Gunnison County, Colorado, which supplied white marble for the Lincoln Memorial and the Tomb of the Unknown Soldier, has been quarrying and selling quarry blocks to domestic finishing shops as well as exporting to off-shore fabricators.

Outside the United States and Canada

International trade in dimension stone is in the form of finished stone ready for installation, in dressed slabs, and in rough blocks or slabs. Granite and marble (including travertine) are the principal rock types, with limestone and slate becoming increasingly important in the marketplace.

As the leading importer of rough blocks and the leading exporter of finished material, Italy dominates international trade, and is also a leading manufacturer of stone-working machinery. It is through the establishment of turnkey finishing facilities around the world that the Italian stone industry has become a principal exporter of equipment and technology, as well as a principal importer of raw blocks. The United States continues to be the principal importer of both finished products and unfinished slabs.

Marble

Most of the world's commercial marble formed from carbonate rocks that were deposited in the great Tethyan seaway that stretched from the Iberian Peninsula to the Himalayas. These rocks were

metamorphosed into marble during the Alpine orogenies and have been quarried since classic times.

The Carrara District in northern Italy produces what is probably the world's most famous marble. Travertine has been produced from Tivoli and marble in many patterns and colors has been quarried in the area since Roman times; the classic names for these have become generic in much of the rest of the world.

In Greece, marble has been quarried from at least the sixth century BC. Recently, the Greek marble industry has undergone a significant revival, and Greece, along with Turkey, has become a major source of marble. China, Israel, Spain, and Mexico have dramatically increased their exports of marble and limestone into the U.S. market (Reis 2004).

Granite

Granite is the most abundant rock on earth and is found on all continents and in most countries. Italy, the major exporter to the United States, gets its stone from Scandinavia or by importing blocks from Scandinavia and shipping finished stone. Other countries that export significant granite to the United States are Brazil, Canada, China, and India. Notably missing from the list are the Scandinavian countries of Finland, Sweden, and Norway, which produce large quantities of granite for the European market. Most of the Scandinavian stone is first shipped to Italy for fabrication before entering the European and North American markets.

Limestone

France, Israel, Jordan, Spain, and Turkey have been major suppliers of limestone to the world market for use as exterior building applications. The ease of working the stone and the natural warm colors make it an attractive stone, both in commercial as well as residential applications.

Soapstone

Brazil has dominated the world market as a source of supply for soapstone. Traditionally, soapstone was used as acid-resistant laboratory counter tops, but composite materials have replaced this outlet. Today, soapstone has gained acceptance for use in residential kitchen and bathroom installations.

Slate

Slate from Brazil, China, India, and Spain has been imported in increasing quantities into the North American marketplace. Although North American brokers are the usual suppliers for the commercial markets, wholesale outlets are the sources for the residential market. Large-scale commercial installations of slate that need a consistent material and reliable supply source are generally serviced by domestic producers.

EVALUATION OF DEPOSITS

In order to properly evaluate a potential dimension stone deposit, one must determine the marketability of the stone; its soundness; its size and shape; the overburden; the distance to market; the kinds of transportation available; the availability of labor; the accessibility of power and other utilities; and similar concerns. Most of these determinations are the same for the evaluation of any mineral deposit, but several are unique to dimension stone deposits.

Marketability

The marketability of a stone is governed largely by aesthetic factors not subject to quantitative measurement, including color, pattern, and texture. Unless the deposit is an extension of a proven quarry or an exact duplicate of a popular stone, the judgment about

marketability should be left to an experienced architect or marketing person.

It is important that a reliable sample be obtained. The best sample is a block from which slabs 0.3 m² or larger can be sawed and used to evaluate color and pattern and also for making required physical tests. The more varied the color and pattern, the larger the sample should be. Drill cores are commonly deceptive but can be suitable for fine-grained uniform-textured stone or for extensions of known deposits.

It is the responsibility of the examining geologist or engineer to determine the size, extent, and uniformity of the deposit and to obtain samples that are truly representative. In the case of layered deposits, samples from each separate stratum should be obtained and compared for uniformity.

Purchasers of stone for large buildings generally make their choice on the basis of the history and reputation of the quarry, samples submitted by the quarrier, or, more commonly, both. Swenson (1991) observed that the buyer is often disappointed because the color and texture of the final product does not meet the buyer's expectations. He pointed out that "stone continually changes during the life of the quarry" (Swenson 1991, p. 46) and samples do not always represent what the quarry is currently producing. The fault may lie with an overly optimistic salesperson, lack of sufficient quarry development, or insufficient knowledge of the deposit. Swenson offered a number of suggestions to architects but warned, "Geologic studies are ineffective in determining the long-term resource . . . but may indicate nothing about the short-term design needs of a project" (Swenson 1991, p. 46). This, it seems, indicates a lack of communication or quarriers' understanding of the limits of geological investigations. Few quarriers have geologists on their staff or even hire consulting geologists. Fewer still map their quarries. Some, like Vermont Marble Co., which remained under the same management for years and had competent geological staffs, knew their deposits intimately and could predict quality and grade with great accuracy. Good, detailed geologic mapping, sometimes supplemented with core drilling, should allow a quarrier to predict changes in the nature of the stone.

One of the problems is that few in the quarry business are knowledgeable enough about modern geology to recognize that a consultant must be either well versed in dimension stone problems, or be a specialist in the lithologic type under consideration, or both. A limestone or crystalline limestone requires a carbonate petrologist; granite requires an igneous petrologist—structural geologist. Whether it is cost-effective to hire a specialist is for the quarriers and architects to decide, but even geologic specialists are generally less expensive than lawyers.

Soundness

Soundness, or freedom from flaws, is one of the most critical factors in evaluating a dimension stone deposit and one of the most difficult to determine. Every joint and fracture should be mapped. This should be supplemented by core drilling parallel to the direction in which the stone is to be sawed. If at all possible, the deposit should be drilled in two intersecting directions in order to find all possible weakness directions that may limit the size of blocks and slabs. If mapping shows a pronounced joint direction, the drilling should be perpendicular to it. The drilling must be done with extreme care, and nothing smaller than NX size should be used. If the core breaks on anything but a natural weakness, the drilling will have failed in its purpose of proving sound stone.

Any directions of natural splitting that would aid in quarrying should be determined. Rift, run, and grain can be beneficial, whereas close-spaced open fractures are deleterious. The investiga-

tor should remember that the ultimate objective is to free large blocks that are without internal fractures.

Some rocks that have been subjected to great stress are still strained. In many cases, such stone will develop new fractures and split after blocks are quarried. Some hidden fractures show up only after the block has been sawed, which proves costly because the flaw appears only after a large investment has been made in the stone. This type of fracture is probably less common in horizontally layered sedimentary rocks and in postorogenic granites that have intruded passively than in rocks that have been subjected to tectonic stress.

Other Factors

The investigator should remember that quarrying blocks for cut and sized dimension stone is still a high labor-input industry. He or she should also keep in mind that each salable unit—a mill block—will weigh 9 t or more and will require special handling methods to extract and transport to market. Compared to other industrial minerals and rocks, the total output of a dimension stone quarry is small. Only a large operation would extract more than a few blocks a day, and few, if any, deposits would justify building new roads, railroads, or expensive utility lines just to service a quarry.

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Strontium Minerals

Joyce A. Ober

INTRODUCTION

Strontium occurs commonly in nature, averaging 0.034% of all igneous rock, and is the 15th most abundant element in the earth's crust. Only two minerals, however—celestite, or celestine (strontium sulfate, SrSO_4), and strontianite (strontium carbonate, SrCO_3)—contain strontium in sufficient quantities to make recovery practical, and these minerals are found predominantly in sedimentary rocks. Of the two, celestite is more common in economic deposits. It is similar in structure to barite, the barium sulfate mineral. Strontianite is more desirable of the two common minerals because strontium is used most commonly in the carbonate form and contains more strontium, but few deposits have been discovered that are suitable for economic development. Table 1 lists the properties of celestite and strontianite.

In 2003, celestite production was reported in Argentina, Iran, Mexico, Morocco, Pakistan, Spain, and Turkey (Ober 2004). Although large deposits have been identified in these and other countries, detailed descriptions of the deposits and locations are not available.

Nearly all celestite is converted to strontium carbonate, which may be used as-is or converted into other strontium compounds,

including strontium chloride, chromate, nitrate, oxalate, oxide, and peroxide. The largest end use for strontium is in faceplate glass for cathode-ray tubes (CRTs) such as is used in televisions and computer monitors. Probably the oldest use for strontium is in pyrotechnics such as fireworks, signal flares, and tracer ammunition, because strontium compounds burn with a brilliant crimson flame; strontium nitrate and peroxide are the most common strontium compounds used in pyrotechnics. These and other strontium compounds are used in lesser quantities in ceramics and glass, permanent ferrite magnets, paint, and toothpaste for temperature-sensitive teeth.

MAJOR DEPOSITS AND PRODUCTION

Although the average strontium content of sedimentary rocks is less than in igneous rocks, nearly all commercial operations are in sedimentary deposits. These sedimentary deposits (primarily as celestite) formed in lakes and lagoons by replacement of preexisting clastic sediments and frequently occur as beds or lenses associated with gypsum, anhydrite, or halite. This type of deposit occurs in Iran, Mexico, Spain, the United Kingdom, and the United States. Hydrothermal strontium mineral deposits have been found in Russia and the United States. Infiltration deposits that can be predominantly

Table 1. Physical properties of strontium minerals

Property	Celestite	Strontianite
Chemical formula	SrSO_4	SrCO_3
Crystal structure	Dipyramidal orthorhombic, tabular. Sometimes fibrous and granular.	Dipyramidal orthorhombic. Radiating, columnar, fibrous, or granular.
Cleavage	Perfect basal and prismatic	Imperfect prismatic
Color	Primarily white to grayish blue. Sometimes shades of yellow and red.	Primarily white or grayish white. Sometimes pale green or yellowish.
Flame color	Crimson	Crimson
Fracture	Uneven	Conchoidal
Hardness	3.0–3.5	3.5–4.0
Index of refraction	1.622–1.631	1.520–1.667
Luster	Vitreous, pearly on cleavage	Vitreous
Solubility	Insoluble	Effervescent in hydrochloric acid
Specific gravity	3.9–4.0	3.6–3.8
Streak	White	White
Theoretical strontium content	47.6%	59.3%
Transparency	Translucent to opaque. Rarely, nearly transparent.	Translucent to transparent.

celestite or strontianite appear as geodes in calcite, celestite veins in clays and carbonate rocks, and metasomatic bodies in carbonate rocks. One deposit of this type is identified near Münster, Germany. Volcanic–sedimentary deposits are associated with rhyolites, andesites, basalts, and their tuffs and tuffites. Strontianite is believed to be a secondary mineral formed through the weathering of celestite (Harben and Kužvart 1996).

United States

Although celestite deposits have been identified nationwide, domestic production has been very limited. During World War II, celestite was mined in California and Texas. Since 1959, all demand has been met from foreign sources. Only one U.S. company, Chemical Products Corporation (CPC), produces strontium carbonate—by far, the most important strontium compound. CPC uses the black ash method to convert imported Mexican celestite to strontium carbonate production at its 22-ktpy plant in Cartersville, Georgia. The company also produces strontium nitrate.

A few companies produce other minor strontium compounds from strontium carbonate. Mallinkrodt Inc. of St. Louis, Missouri, produces strontium chloride, and La porte Pigments Corp. of Beltsville, Maryland, produces strontium chromate. Other companies produce smaller quantities of other downstream strontium compounds.

In 1944, domestic strontium deposits were operated at the following sites: near Blanket in Brown County, Texas; in Nolan County, Texas; in the Fish Mountains in Imperial County, California; and near Ludlow, California (Gwinn 1944). At that time, the major use for strontium chemicals was for pyrotechnic applications such as signal flares and tracer bullets required for military applications. Immediately following World War II, this demand dramatically decreased, resulting in reduced domestic production of celestite.

Resources in the United States have been estimated at 3.2 Mt with an identified reserve base of 1.4 Mt. The reserve base figure includes material containing no more than 60% strontium sulfate, a much lower grade than specified by modern consumers. In addition to deposits mined in the early 1940s, celestite has been discovered in Arizona, Arkansas, Kentucky, Michigan, Missouri, New York, Ohio, Pennsylvania, Tennessee, Utah, and Washington (Schreck and Arundale 1959).

Other Countries

Huge deposits of high-grade celestite have been discovered throughout the world. In almost all instances, celestite deposits occur far from population centers in remote, undeveloped locations where inexpensive labor is a valuable for mining. World celestite production is listed in Table 2.

Detailed information on most world resources is not readily available. Many of the large deposits are in remote, sparsely inhabited areas, where very little exploration has occurred. Other known deposits are in countries where specific mineral information is not easily obtained.

Two types of strontium capacity exist. The first is ore production capacity in which celestite is mined and beneficiated for use or additional processing. The second, strontium compound production capacity, represents the size of the operations that convert strontium minerals (almost always celestite) through chemical reactions to other forms of strontium, including strontium carbonate and strontium metal. Strontium compound capacity is deemed the more important for several reasons. Essentially, all strontium is consumed in compound form, primarily as the carbonate and to a lesser extent as the nitrate. Strontium carbonate is also the intermediate product in production of downstream compounds. At least nine countries mined celestite in 2003, as shown in Table 2.

Table 2. Celestite: World production by country, * t

Country†	1999	2000	2001	2002	2003‡
Argentina	2,141	4,656	2,440	3,106	3,323§
Iran‡ **	1,650††	2,000	2,000	2,000	2,000
Mexico	164,682	157,420	145,789	94,015	126,747§
Morocco	0	7,539	1,879	3,780	2,700
Pakistan	634	1,918	2,000‡	2,000‡	2,000
Spain	128,457	148,352	129,794	160,519	160,000
Turkey	60,540	24,150	63,635	70,000‡	70,000
Total	358,000	346,000	348,000	335,000	367,000

Adapted from Ober 2004.

* World totals and estimated data are rounded to no more than three significant digits and may not add to totals shown.

† In addition to the countries listed, China and the Commonwealth of Independent States (CIS) produce strontium materials, but output is not reported quantitatively and available information is inadequate to make reliable estimates of output levels.

‡ Estimated.

§ Preliminary.

** Data are for year beginning March 21 of that stated.

†† Reported figure.

Virtually all of the celestite mined annually is consumed in the production of strontium carbonate and other strontium compounds. Very little strontium was consumed directly in the mineral form. Because most ore is produced for market by means of very simple sorting and beneficiation techniques, capacity can easily be raised to meet increased demand. Strontium carbonate production capacity is the limiting factor in strontium production, requiring more complicated and sophisticated processing facilities. Estimated strontium carbonate production capacity listed in Table 3 was compiled from reports cited in the following specific country sections.

Algeria

Celestite was mined in Algeria from the Beni Mançour surface deposit near Boira, although no production has been reported since at least 1996. The deposit was mined by Entreprise Nationale des Produits Non Ferreux et des Substances Utiles (ENOF) and was controlled by L'Entreprise Nationale de Développement Minières (SON AREM). In the past, as much as 3.6 ktpy was exported to nations in Eastern Europe and the former Federal Republic of Germany. Although the celestite was relatively low grade—only about 70% strontium sulfate—it contained low concentrations of barite, silica, gypsum, and iron, making it possible to concentrate the ore to acceptable levels using only gravity separation (Anon. 1988a). Reported reserves at Beni Mançour were more than 6 Mt of 70% strontium sulfate. ENOF was considering new production from the deposit to supply a possible domestic strontium carbonate plant whose output would be exported (Senouci, Nadir, and Houssa 2000).

Argentina

Although not a major producer of celestite, some is mined in Argentina. Little information about the Argentine strontium industry, other than production data, has been published for several years (Torres 2003). When detailed information was last reported in 1988, celestite mining was controlled by the Argentine Mining Union at the San Juan mine in the province of Mendoza. Celestite was identified at a few additional small mines, the Maria Del Carmen and Don Luis mines, also in Mendoza Province, and the Rayoso, Julio, Cerro Partido, and Llao mines in the province of

Table 3. Estimated world strontium carbonate annual production capacity, t

Country	Rated Capacity*
North America	
Mexico	127,000
United States†	22,000
Total	149,000
Europe	
Germany‡	70,000
Spain	20,000
Russia and CIS	‡
Total	90,000
Asia	
China	200,000
Japan†	20,000
Korea, Republic of	40,000
Total	260,000
World total	499,000

* May include capacity at operating plants as well as plants on a standby basis.

† Production was entirely from imported celestite.

‡ Strontium carbonate production capacity existed in these countries, but specific data are not available.

Neuquen. It is unlikely that production has occurred on a regular basis at these mines. Most Argentine production was exported to Brazil (Anon. 1988b).

Canada

Canada has produced celestite ore in the past from the McRae deposit, also known as the old Kaiser Celestite Mining Ltd. mine, at Enon, Cape Breton County, Nova Scotia. Timminco Ltd. of Toronto holds the mineral rights for this deposit. Exploration identified reserves of more than 1 Mt of celestite, with grades ranging from 60% to 65% strontium sulfate. Reopening the mine has been considered, but the low grade of the ore makes economic feasibility questionable. Other strontium deposits have been identified in British Columbia, Newfoundland, and Ontario, but none are as significant as the deposit in Nova Scotia (Dawson 1985). Celestite has not been produced in Canada for many years.

Timminco, the world's leading producer of strontium metal, produces strontium metal in Ontario from imported strontium carbonate. The company also produces strontium-aluminum master alloys, which Timminco advertises as the highest quality in the world, referring to their purity, low gas content, fast dissolution rate, low porosity, and precise weight. Timminco sells strontium as crowns, sections, and turnings, and in master alloys containing 90% strontium and 10% aluminum (Timminco 2000).

China

A long-time producer of celestite and strontium carbonate, China has dramatically expanded its carbonate capacity to reach more than 200 ktpy in 2003 from about 50 ktpy in 1995. Celestite production has not kept pace, and so China has become a major importer of celestite to supply its strontium carbonate plants. Strontium carbonate is used for televisions and magnets in China, but the majority of it is exported. Exports grew to 97 kt in 2002 from 42 kt in 1995.

Although China may have sufficient reserves to supply its domestic strontium carbonate plants, celestite concentrates vary from 80% to 85% strontium sulfate, much lower quality than prod-

ucts from deposits in Mexico, Spain, and Turkey. Celestite is produced from the Hechuan deposit in Sichuan Province and from the Lishui deposit in Jiangsu Province. Coope reported reserves to be nearly 30 Mt. Celestite is also produced in Henan Province (Harben and Kužvart 1996; Coope 2003). A strontium carbonate plant in Sichuan Province was the only one in the world based on strontianite. Technical problems hampered the success of the process, and the current status is unknown (Hong 1993).

Cyprus

Celestite was mined briefly in Cyprus starting in 1985 from a deposit near the village of Maroni near the southern coast of the island. Hellenic Mining Co. Ltd. operated the mine (Malinotis and Ilich 1986). The ore averaged about 54% strontium sulfate and, therefore, required beneficiation to make it marketable. The ore was beneficiated through a flotation process to reach 94% strontium sulfate. The reserves were reported to be 200 kt of celestite (Griffiths 1984). No production has been reported, however, since 1987.

Germany

Strontianite was produced sporadically from deposits in Westphalia. Celestite deposits have also been identified, but no strontium concentrates have been produced in Germany for nearly 50 years.

Solvay Barium Strontium GmbH (a subsidiary of Belgium's Solvay S.A.) operates a 150-ktpy barium and strontium carbonate plant at Bad Hönningen; the effective strontium carbonate capacity is about 70 ktpy. Solvay uses imported Spanish celestite as the raw material for its black ash strontium carbonate plant. Including its strontium carbonate plants in Italy, the Republic of Korea, and Mexico, Solvay is the world's largest strontium carbonate supplier (Houssa 1999).

Iran

Iran has a very large celestite deposit about 200 km southeast of Tehran in the northwestern part of the Dasht-e-Kavir salt desert. Average strontium sulfate values for the deposit have been reported at more than 91%, but the levels of barium sulfate and calcium sulfate are unfavorably high (Shiebel 1978). Iran Strontium Co. produces celestite concentrate from the Nakhjir deposit. Celestite reserves in Iran were reported to be about 3 Mt (Harben and Kužvart 1996; Regueiro 1998).

Italy

In the past, Mineral Chimica Farnesiana SpA in Tarquinia mined celestite near Rome. The product was 75% strontium sulfate and 5% barium sulfate, most of which was sold domestically. Annual production capacity at the mine was 7.3 ktpy (Anon. 1992). Production ceased in 1988. Celestite deposits have been identified on Sicily, but, because costs were high, production probably was restricted to material that was exported to Germany during World War II.

Solvay owns a plant in Massa that can produce barium or strontium carbonate. Its capacity is not known (Anon. 1999b).

Japan

Once a large producer of strontium carbonate from imported celestite, Japan's importance as a strontium compound producer has declined as production in the Republic of Korea and Mexico has increased. Four companies produced strontium carbonate from imported celestite, although up-to-date information on plant capacities and status are difficult to confirm. Capacity is believed to be about 20 ktpy. All celestite is imported. Honjo Chemical Corp. and Sakai Chemical Industries Co. operated strontium carbonate

production facilities and still offer strontium carbonate for sale. No current information is available for the other two companies.

Korea, Republic of

Celestite deposits have not been identified in the Republic of Korea, but its television industry consumes large quantities of strontium carbonate. Daehan Specialty Chemicals Co., Ltd., a joint venture between Solvay and Samsung Display Services, has produced strontium carbonate and barium carbonate since 1990 at its 40-ktpy plant in Onsan. The black ash process is used (Anon. 1999a).

Malawi

In 2002, Rift Valley Resource Development Ltd. conducted a feasibility study on the development of the Kangankunde strontianite/rare-earths deposit. The Malawian Geological Survey reported that the deposit contains 11 Mt of strontianite and monazite (a rare-earth mineral). Phase 1 of development would produce strontium carbonate for export and monazite concentrates that would be stockpiled for later phases of the project. Glass-grade strontium carbonate production was expected to be about 20 ktpy (Tassell 2002). The European Investment Bank and the Development Bank of South Africa funded the feasibility study (Saner 2002).

Mexico

Mexico is the world's largest celestite producer, and virtually all U.S. imports of celestite since 1991 have been from Mexico. Although mining methods are very simple, mining efficiency has increased, and improved mining methods have expanded productivity at several small operations. The largest Mexican celestite producer is Minas de Celestita SA de CV, a company that controls celestite reserves in Coahuila State of between 6 Mt and 6.5 Mt of proven and inferred ore. Cia. Minera La Valenciana SA de CV (CMV) operates the San Agustín mine, the single largest mine in Mexico. As much as 1 Mt of celestite has been mined from this deposit that may be nearing depletion. Minera La Roja, SA de CV is the third major celestite producer in Mexico.

Minas de Celestita operates mines that supply CPC's operation in Mexico and the United States exclusively. In addition to its Georgia plant, CPC operates a 50-ktpy-strontium carbonate plant in Reynosa, Tamaulipas State. CMV's mine provides the celestite to operate its own 50-ktpy-strontium carbonate plant in Torreón. Solvay Química y Minera, SA de CV (a subsidiary of Solvay), uses celestite produced by Minera La Roja at its 27-ktpy strontium carbonate plant in Monterrey (Moore 2002). Mexico is the largest strontium carbonate producer in the world, and the vast majority of all U.S. strontium imports, including minerals and compounds, come from Mexico.

Pakistan

Recent reports describing the strontium industry in Pakistan are unavailable, although production data are reported annually. Older publications reported celestite production from two mines, one near Dawood Khail and one near Karachi (Anon. 1988c). Tawakkal Mineral Exports Corp. recovered celestite from these mines in the Dadu District of Sind Province. No beneficiation was necessary to produce 95% strontium sulfate. Reserves of celestite have not been reported at this location (Griffiths 1987). Other deposits, with 500 kt of reported reserves, have been identified in the Punjab Province (Anon. 1992).

Russia and the Commonwealth of Independent States

Very little is known about production of strontium minerals in this part of the world. Deposits are known in the following regions: the

Karakum Desert, Zaunguz Plateau; near Bashkir; in the Pinega Area, Archangel Province; near Yakutsk, eastern Siberia; and in Turkestan from eastern Fergana to the shores of the Caspian Sea and from southeastern Bucharra to the shores of the Sea of Aral. Celestite also has been found in the cap rocks of the Romy and Isachkov salt domes. Reserves are believed to be very large, but the ore grade is probably not high (Kishimoto 1982). Few details are available concerning the production of celestite or strontium carbonate since the breakup of the Soviet Union. Celestite was reportedly produced from two deposits in Turkmenistan (Regueiro 1998).

Spain

As the world's second largest celestite producer, Spain mines celestite at two locations. The Montevive deposit, which is operated by Canteras Industriales SL, has been in production since about 1940, and the Escúzar deposit, which is mined by Solvay Minerales SA (a subsidiary of Solvay), has been in production since 1989 (Griffiths 1992; Coope 1997). The Montevive deposit contains an estimated 8 Mt of reserves grading 80% strontium sulfate. Selective mining, hand sorting, crushing, and granulometric sorting results in a product containing 95% strontium sulfate. A mobile secondary screen separates a second 90% strontium sulfate product; additional concentration facilities are planned. Much of the Montevive production is exported to China. The Escúzar deposit has reserves estimated at about 4 Mt of 54% strontium sulfate. More complicated beneficiation techniques than those used at Montevive produce a 94% strontium sulfate concentrate. Most of this material is exported to Solvay in Germany or Daehan in the Republic of Korea (Regueiro 1998).

Promotora de Industria del Sur (Prominsur SA) produced strontium carbonate and strontium nitrate at a combined facility near Granada until 1991 when market conditions forced its closure. The plant had a theoretical design capacity of 8 ktpy of carbonate but never reached that level of production. Strontium carbonate was produced by the soda ash method. The plant also had an unattained production capacity of about 3 ktpy of nitrate (Griffiths 1992). Químico Estroncio (a joint venture of Minas de Almadén y Arrayanes SA, Fertiberia SA, and Erkimia SA) built a 20-ktpy strontium carbonate plant in Cartagena that opened in 2000. The plant was to use an unusual technology for strontium carbonate production, and it seems to have experienced some technical problems scaling up to commercial production. Significant production has not been achieved, although Fertiberia, the new owner of the plant, continues to work toward successful operation (Coope 2003).

Turkey

A long-time celestite producer for the export market, Barit Maden Turk AS sold most of its production to the Republic of Korea and China. Barit Maden produces celestite from a mine near Akkaya in Sivas Province. Run-of-mine ore is gravity-separated to produce a concentrate with a minimum of 95% strontium sulfate. Because of the harsh winters in the region, the mine can be operated only seasonally, from May to October. Identified reserves have been placed at 550 kt, and further reserve potential was estimated to be greater than 2 Mt (Karayazici 1987).

As of 1999, the company was building its own strontium carbonate plant; progress on this project is unknown. In preparation for its expansion into carbonate production, Barit Maden built a carbon dioxide plant that was profitable even before the strontium carbonate facilities were completed. Its high-quality celestite resources and the in-house carbon dioxide supply contributed to Barit Maden's confidence that its strontium carbonate would be high quality and cost-competitive with other producers (Houssa 1999).

United Kingdom

The world's largest supplier of celestite from around the time of World War I until about 1968, Bristol Minerals Co. Ltd. mined deposits in the Bristol area. The ore was crushed, washed, and graded to achieve a product with 95% strontium sulfate. One of the few sites in the world where celestite deposits were in populated areas, the British deposits were encroached on by large-scale housing developments, which limited exploitation of the minerals (Griffiths 1984). Mining ceased in 1991 when the accessible reserves were exhausted. For a short time following the closure of the mine, Bristol Minerals continued to reprocess mine tailings that were sold to Solvay in Germany (Griffiths 1992).

Other Countries

Strontium minerals have been identified in other countries, but the deposits were not commercially developed on a large scale. Celestite occurs in Australia, France, India, Morocco, Poland, and Tunisia (Schreck and Arundale 1959; Harben and Kužvart 1996).

PROCESSING

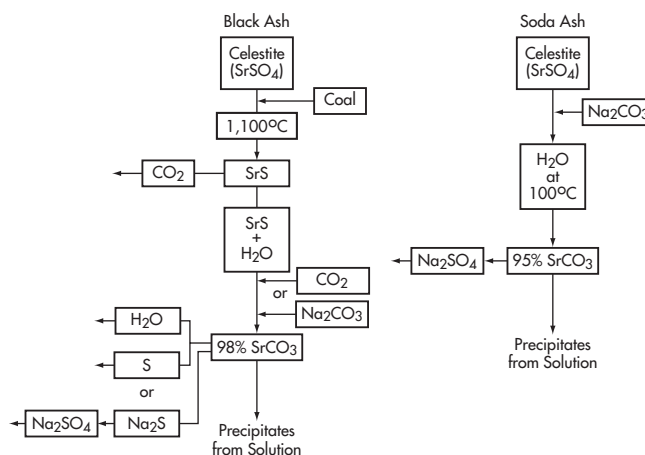
Strontium commonly occurs with barium and calcium, two elements with properties very similar to strontium, making separation difficult. Because removing many impurities from celestite is difficult and energy intensive, strontium chemical producers require that material contain at least 90% strontium sulfate. Most of the operating celestite facilities in 2003 produced sufficient supplies with only minimal processing necessary to achieve acceptable specifications. Hand sorting and some washing are adequate at many strontium mines to produce celestite that meets customer specifications. A few operations use froth flotation or gravity separation to beneficiate their ore.

Strontium carbonate is the most important strontium compound, and two methods are used to produce it. The black ash and soda ash methods are the two most common recovery techniques.

The black ash method, known alternatively as the calcining method, produces chemical-grade strontium carbonate, which contains at least 98% strontium carbonate. This method received its name because, in the first step in the procedure, the crushed and screened celestite is mixed with powdered coal, making a black mixture. The mixture is then heated to about 1,100°C, expelling oxygen in the form of carbon dioxide from the insoluble strontium sulfate to form water-soluble strontium sulfide. Strontium sulfide is dissolved in water, and the resulting solution filtered. Carbon dioxide then is passed through the solution or soda ash is added. Either compound provides the necessary carbon and oxygen for strontium carbonate to form and precipitate from the solution. The precipitated strontium carbonate is then removed from the solution by filtering and is dried, ground, and packaged. The sulfur released in the process is either recovered as elemental sulfur or in other by-product sulfur compounds. A simplified flow chart illustrates both processes in Figure 1.

In the soda ash method, ground celestite is washed and most of the water removed. The thickened mixture is then mixed with soda ash and treated with steam for 1 to 3 hours. During this time, celestite and soda ash react to form strontium carbonate and sodium sulfate. Sodium sulfate is water soluble, making it possible to separate the insoluble strontium carbonate by centrifuging. Although the soda ash method is a simpler process than the black ash process, the lower grade of the product makes it the less preferred method of recovery. The black ash method is more common for strontium carbonate production.

Other strontium chemicals are produced from strontium carbonate. Strontium nitrate is produced through the reaction of



Adapted from Ober 1989.

Figure 1. Simplified flow chart of the two methods for strontium carbonate production

strontium carbonate with nitric acid. Other strontium chemicals are produced through similar procedures of reacting strontium carbonate with the acid appropriate for the desired result. Some of the acids used are bromic, hydrochloric, oxalic, stearic, and tartaric (Schreck and Arundale 1959).

Strontium ferrite magnets are prepared by mixing strontium carbonate with iron oxide and crystal growth inhibitors and presintering at between 1,000° and 1,300°C (Reynolds 1980). Strontium titanate is formed by reacting a mixture of high-purity strontium carbonate and titanium dioxide (Griffiths 1985).

Strontium metal can be produced in two ways. The more common method is through the thermal reduction of strontium oxide and aluminum metal, subsequent distillation under high vacuum, and condensation of metallic strontium on a cooled plate. The other method is electrolysis of a fused bath of strontium chloride and ammonium chloride or potassium chloride (Schreck and Arundale 1959).

ECONOMIC FACTORS

Uses

Approximately 80% of all strontium is consumed in ceramics and glass manufacture, primarily in television faceplate glass and ceramic ferrite magnets (Table 4), and smaller amounts in other ceramic and glass applications. In the past 20 years, color television production has become the major consumer of strontium. Because of the unique properties that strontium compounds possess, including the ability to block x-rays, magnetic characteristics, and the brilliant red flame when burned, technologies have been developed that take advantage of those properties for specific applications. All color televisions and other devices containing color CRTs sold in the United States are required by law to contain strontium in the faceplate glass of the picture tube. Strontium blocks x-rays better than barium, which was previously used, and, although lead is a better x-ray barrier than strontium, it causes a brownning of the glass. Major manufacturers of television picture-tube glass incorporate about 8% strontium oxide, by weight, in their glass faceplate material. The strontium is added to the glass melt in the form of strontium carbonate, and during processing it is converted to strontium oxide. In addition to blocking x-rays, the strontium improves the appearance of the glass, increasing the brilliance and improving the quality of the picture (Wagner 1986).

Table 4. U.S. estimated percentage distribution of primary strontium compounds, by end use

End Use	1999	2000	2001	2002	2003
Electrolytic reduction of zinc	2	2	2	2	2
Ferrite ceramic magnets	10	8	9	9	10
Pigments and fillers	3	2	3	2	2
Pyrotechnics and ignals	6	9	9	9	10
Television picture tubes	75	77	75	75	73
Other	4	2	2	3	3
Total	100	100	100	100	100

Source: Ober 2004.

Trends in CRT production show a shift to larger, flatter tubes that require thicker glass and therefore more strontium. Although the U.S. television industry is considered mature, the demand for replacement TVs as well as for additional sets in large numbers of households continues. The rising sales of personal computers and sophisticated, computerized instrumentation increased the demand for strontium in color monitors for these devices. The increasing popularity of flat-screen devices for television and computer monitors is, however, starting to adversely affect the consumption of strontium in CRT applications. Flat-screen technology, such as liquid crystal displays (LCDs) and plasma devices, do not require strontium. These devices are becoming more affordable, causing decreased demand for more traditional CRTs and thus lower demand for strontium carbonate.

The presence of strontium in other glass applications improves the brilliance of the glass and the quality of certain ceramic glazes as well as eliminates the toxicity that may be present in glazes containing lead or barium. One high-tech strontium ceramic is strontium titanate, which is sometimes used as a substrate material for semiconductors and also in some optical and piezoelectric applications.

Permanent ceramic magnets are another large end use for strontium compounds, in the form of strontium ferrite. When these magnets were first developed, they were used primarily as magnetic closures for refrigerator doors. Applications have expanded to include extensive use in small direct current (DC) motors, especially for automotive applications such as windshield wiper motors, as well as loudspeakers, other electronic equipment, toys, and magnetically attached decorative items.

Strontium ferrites are used in permanent ceramic magnets because they have high coercive force, high thermal and electrical resistivity, and are chemically inert. They retain their magnetism well, are not adversely affected by electrical currents or high temperatures, and do not react with most chemical solvents. Other properties that make the strontium magnets more attractive for specific applications are their resistance to demagnetization and lower density, making them more desirable in applications where weight is a factor (Haberberger 1971). Barium or lead can replace the strontium in ferrite magnets, but strontium ferrites have been found to possess the best combination of properties necessary for superior magnets.

One of the most consistent and continuing applications for strontium has been in pyrotechnic devices. Strontium burns with a brilliant red flame, and no other material has been found to be better in this application. The strontium compound used most frequently in pyrotechnic devices is strontium nitrate. Some strontium compounds are slightly hygroscopic, but strontium nitrate takes on very little water and imparts the desired brilliant red. Strontium carbonate, strontium oxalate, strontium sulfate, and strontium chlorate are used in pyrotechnic applications, but strontium nitrate is used in significantly larger quantities than any of them. Pyrotechnic devices

are used in military and non-military applications. Military pyrotechnic applications that contain strontium include tracer ammunition, military flares, and marine distress signals. Nonmilitary applications include warning devices and fireworks (Conkling 1981). The strontium content in military flares can be up to 40% by weight and about 20% for Roman candle fireworks (Harben and Kužvart 1996).

Strontium is used to remove lead impurities during the electrolytic production of zinc. Zinc used in die-casting alloys is required to contain less than 0.003% lead. The addition of strontium carbonate in sulfuric acid to the electrolyte reduces the lead content of the electrolyte and of the zinc that is deposited on the cathode (Bratt and Smith 1963).

Adding strontium chromate to paint creates a coating that is resistant to corrosion and effective for aluminum, most notably on aircraft fuselages and ships. These paints are used to some degree on aluminum packaging to prevent package corrosion. The nitrate and chloride contents of strontium chromate paint pigment are very strictly controlled to prevent corrosion (Anon. 1992).

Metallic strontium is a small part of total strontium consumption. Small amounts of strontium are added to molten aluminum to improve the castability of the metal, making it much more suitable for casting items that have been traditionally made from steel. The addition of strontium to the melt improves the machinability of the casting. Although aluminum parts were impractical before modification techniques were developed, the use of cast aluminum, rather than steel parts, has become common in the automotive industry. The resulting reduction in the weight of the automobile helps to improve the energy efficiency of the cars incorporating these parts (Lidman 1984).

At the present time, other strontium end uses consume only small amounts of strontium and strontium compounds. Strontium chloride is used in toothpaste for sensitive teeth. For this application, the content of impurities must be strictly controlled, with limits for some of them in the parts-per-million range. Strontium phosphate is used in the manufacture of fluorescent lights, and the entire range of strontium chemicals is used in analytical chemistry laboratories.

Prices

Published prices for celestite and strontium compounds are not available. Tracking the customs values of various imported material is the best available way to evaluate trends in strontium pricing. Although the customs values may not represent the exact price any specific consumer pays for celestite or another strontium product, they are a good basis for estimating and evaluating trends in pricing. The average customs value for celestite imported from Mexico, the sole source of U.S. celestite imports in 2003, was about \$57/t, a decrease of nearly 29% since 1990 when the customs value was \$80/t. In 2003, the average unit customs value of imported strontium carbonate was \$0.48/kg and the corresponding value for strontium nitrate was \$2.95/kg. Strontium carbonate values have been relatively steady or lower in recent years, and strontium nitrate prices have been increasing. Table 5 lists the average value of imported celestite, along with other important strontium statistics.

Foreign Trade

The United States has never been a major exporter of strontium compounds. The U.S. Bureau of Mines published estimated export statistics for the first time in 1985 at a total of about 21 t of strontium exports. The U.S. Census Bureau reported strontium exports for the first time in 1990 including the two categories of strontium carbonate and strontium oxide, hydroxide, and peroxide that totaled 2.88 kt. Exports peaked in 2000 at 7.18 Mt (Table 6). Since that time, exports

Table 5. Salient strontium statistics, t^{\dagger}

	1999	2000	2001	2002	2003
United States					
Production, strontium minerals	0	0	0	0	0
Imports [‡] for consumption					
Strontium minerals	13,700	7,460	5,640	1,150	1,120
Strontium compounds	26,800	29,900	26,500	25,400	23,300
Exports [‡] (compounds)	2,890	4,520	929	340	693
Shipments from government stockpile excesses	0	0	0	0	0
Apparent consumption [§]	37,600	32,800	31,200	26,500	23,600
Price, average value of mineral imports at port of exportation, dollars per ton	73	62	63	60	58
World production** (celestite)	358,000	346,000	348,000	335,000	367,000 ^{††}

Source: Ober 2004.

* Data are rounded to no more than three significant digits.

† The strontium content of celestite is 43.88%, which was used to convert units to celestite.

‡ Data from the U.S. Census Bureau.

§ Production plus imports minus exports.

** Excludes China and CIS.

†† Estimated.

Table 6. U.S. exports of strontium compounds, by country*

Compound and Country	1999, kg	2000, kg	2001, kg	2002, kg	2003	
					kg	Value, US\$ [†]
Strontium carbonate, precipitated						
Australia	0	67,800	0	0	0	0
Brazil	0	0	5,460	0	0	0
Canada	254,000	138,000	289,000	76,500	42,600	39,600
Germany	10,800	4,610	21,500	15,000	32,000	130,000
Hong Kong	0	0	17,400	16,400	35,100	50,600
Japan	2,480,000	5,170,000	108,000	3,840	12,300	12,600
Korea, Republic of	0	82,000	0	0	171,000	62,800
Mexico	51,200	417,000	204	0	60,500	57,500
Singapore	577,000	307,000	0	0	0	0
South Africa	38,800	0	0	0	0	0
Taiwan	228,000	119,000	0	0	0	0
Thailand	213,000	0	0	0	0	0
Tokelau	0	0	0	0	2,580	3,040
United Kingdom	907	1,620	4,280	3,370	18,600	96,300
Venezuela	0	10,000	0	0	0	0
Total	3,860,000	6,320,000	446,000	115,000	375,000	452,000
Strontium oxide, hydroxide, peroxide						
Australia	0	14,900	8,810	11,600	0	0
Brazil	124,000	26,700	0	0	6,910	20,000
Canada	272,000	432,000	263,000	20,400	50,500	26,200
Colombia	0	0	548	0	0	0
Germany	19,600	99,200	14,400	0	35,400	19,500
India	0	0	34,100	0	0	0
Italy	0	0	18,900	0	0	0
Japan	176,000	74,000	9,010	0	0	0
Korea, Republic of	82,800	161,000	548,000	63,900	0	0
Malaysia	21,600	0	0	0	0	0
Mexico	127,000	0	3,210	189,000	523,000	287,000
Netherlands	0	0	0	0	29,200	16,100
Norway	20,100	44,200	0	34,400	0	0
Portugal	0	10,200	6,780	0	0	0
Sweden	0	0	0	57,200	0	0
Switzerland	0	0	7,090	0	0	0
Thailand	0	0	0	0	8,410	4,630
United Kingdom	10,600	0	9,440	0	0	0
Total	854,000	862,000	923,000	377,000	653,000	374,000

Courtesy of the U.S. Census Bureau.

* Data are rounded to no more than three significant digits and may not add to totals shown.

† Customs value.

have fallen sharply with total exports of 1.03 Mt in 2003, an 86% decrease in 3 years (Table 6). This is a result of increased production worldwide, which created additional competition for U.S. exports.

Much larger quantities of strontium products are imported into the United States than are exported, as shown in Table 7. Imports of celestite have decreased significantly to 2.32 kt in 2002

from 31.3 kt in 1999. Strontium carbonate is the most important strontium compound that is imported, consistently representing at least 97% of total imports of strontium compounds. Mexico is the source of 94% of strontium carbonate imports. Strontium compound imports were more than 22% lower in 2003 at 39.2 kt than they were in 2000 when they reached 50.5 kt.

Table 7. U.S. imports for consumption of celestite and strontium compounds, by country*

Compound and Country	1999, kg	2000, kg	2001, kg	2002, kg	2003	
					kg	Value, US\$†
Celestite						
Mexico	31,300,000	17,000,000	12,800,000	2,580,000	2,320,000	135,000
Strontium carbonate						
Belgium	0	0	73,700	142,000	61,800	26,100
China	425,000	270,000	931,000	392,000	114,000	45,000
France	0	0	0	79,400	0	0
Germany	2,380,000	2,510,000	2,680,000	1,970,000	2,060,000	900,000
Italy	6,000	6,000	4,000	10,800	1,000	6,620
Japan	100	280	1,260	3,700	0	0
Mexico	41,000,000	46,500,000	39,800,800	39,400,000	35,800,000	17,200,000
Netherlands	0	0	0	0	20,600	8,170
Russia	0	0	20,000	0	0	0
Spain	0	0	0	19,400	200,000	85,300
United Kingdom	35	0	13	10	20	5,390
Total	44,000,000	49,300,000	43,500,000	42,000,000	38,200,000	18,200,000
Strontium metal						
Canada	88,400	90,700	48,600	30,500	39,900	263,000
China	123,000	211,000	76,000	48,700	15,000	72,300
France	0	5,810	11,000	10,000	10,000	67,700
Germany	10	0	15,000	0	0	0
Japan	104,000	0	119,000	62,400	218,000	682,000
Mexico	0	281	0	0	0	0
United Kingdom	0	0	0	4,000	300	2,570
Total	315,000	308,000	270,000	156,000	283,000	1,090,000
Strontium nitrate						
Canada	0	0	0	20,000	0	0
China	195,000	234,000	352,000	399,000	375,000	261,000
Finland	0	57,700	0	0	0	0
France	174,000	209,000	221,000	70,000	0	0
Germany	0	150	0	0	0	0
Japan	98,700	107,000	118,000	160,000	252,000	1,750,000
Mexico	122,000	79,000	140,000	123,000	77,100	56,300
Singapore	0	0	0	0	12	7,250
Switzerland	50	0	0	0	0	0
United Kingdom	0	0	0	0	18	2,210
Total	590,000	687,000	831,000	771,000	705,000	2,080,000
Strontium oxide, hydroxide, peroxide						
Australia	0	0	0	1,050	0	0
China	66,700	71,000	35,100	72,000	0	0
Germany	60,000	3,600	0	9	0	0
Japan	90,500	117,000	29,000	303	0	0
Mexico	30,300	0	0	0	0	0
Switzerland	20,000	0	0	0	0	0
Total	267,000	192,000	64,100	73,400	0	0

Courtesy of the U.S. Census Bureau.

* Data rounded to no more than three significant digits and may not add to totals shown.

† Free alongside ship value.

PROBLEMS AND FUTURE TRENDS

Environmental Problems

Not all strontium is beneficial. Strontium-90, a radioactive isotope of strontium, is a component of nuclear waste from reactors and nuclear fallout. It presents special problems for waste disposal and storage because it generates a significant amount of heat as it decays. When released into the atmosphere through nuclear testing or accidents, it easily enters the food supply via milk and vegetables because it is so chemically similar to calcium. Recent reports on possible terrorist activities have suggested that strontium-90 from spent nuclear fuel rods could be one component of a dirty bomb, in which a conventional explosive device could be used to spread radioactive material, creating a contaminated area that could be difficult to clean up.

Scientists at Argonne National Laboratory developed a process for removing strontium-90 from liquid nuclear waste. The method dissolves more than 99.999% of the strontium-90 from the waste stream in a special solvent. Pure strontium-90 is then removed from the solvent with water or a dilute acid. The recovered strontium-90 could be used in radioisotopic thermal generators that are found in devices such as harbor markers, which require long-lasting, unattended power supplies (Worthy 1990).

Future Trends

Sales of televisions and computer monitors in the United States will continue to influence U.S. strontium consumption significantly, although increased imports of faceplate glass and decreased growth in CRT demand will contribute to lower domestic consumption of strontium compounds. As long as CRTs are used in television and computer monitors, world consumption should continue, but at lower growth rates than those seen in recent years. Ferrite magnet markets are expected to be strong. Growth in other markets will probably continue at the current slower rate. Improved economic conditions worldwide could spur additional growth in demand for strontium carbonate.

Flat-screen display systems for televisions and computer monitors have threatened to replace CRTs for many years, but the cost of the new technology has restricted growth. Flat panels, however, have begun to have an impact on the CRT market, and the flat-panel market is growing at a much higher rate than that of the CRT market. Improvements have increased the likelihood that the large flat screens that use either LCDs or plasma technology will replace bulkier CRTs. LCDs, which are smaller and use less energy than plasma display systems, seem to be filling the market for relatively small, flat displays, such as those required for portable computers. The market for LCD materials is expected to grow at a rate of 16.4% per year through 2005 (Markarian 2002).

Worldwide, about 150 million CRTs per year are produced. In 2001, the last year for which such data were available, about 300,000 plasma displays were sold; by 2005, sales were expected to approach 4 million units, a 13-fold increase (Tremblay 2002). Plasma technology is more common for large, high-definition televisions with screens up to 60 in. and wider (Tremblay 1999). Neither LCD or plasma technology requires strontium carbonate in the glass, but both have been too expensive to make serious inroads in the domestic CRT market until now. In 2000, a 20-in. flat-screen television in Japan cost around \$2,500, significantly more than a comparable device with a CRT. The costs of larger plasma screens (usually between 37 and 60 in. diagonally) were between \$10,000 and \$14,000 (Landers 2000). In 2002, prices were reported to be between \$6,000 and \$10,000 for similar items—a significant decrease, but still quite expensive (Tremblay 2002). Major retailers,

however, were offering some plasma display systems at \$3,000 and below. In 2004 and 2005, the price for similar items was under \$2,000. As these new display systems become more economically attractive to the public, CRTs will become obsolete, and so will the major market for strontium carbonate.

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The sole U.S. strontium carbonate producer voluntarily provided domestic production data to the U.S. Geological Survey. Production and stock data, however, were withheld from publication to avoid disclosing company proprietary data.

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Sulfur

Joyce Ober

INTRODUCTION

Sulfur, a nonmetallic element, is widely distributed in nature and has great industrial and economic importance. It is the thirteenth most abundant element in the earth's crust (0.06%) and an important constituent of animal and plant life (Bush and Semrad 1996).

Sulfur has been known and used since ancient times for several medicinal and industrial uses. In modern times, most sulfur is used to generate sulfuric acid, which is a component of a wide variety of industrial processes, particularly the production of fertilizer. Because of this, sulfuric acid (and hence sulfur) consumption often has been regarded as a good indicator of a nation's industrial development.

In the past, sulfur was mined from surface occurrences in several geologic environments and was used in relatively small amounts. Over time, the uses of sulfur and sulfuric acid expanded, as did the need for larger quantities of these commodities. Sulfur is now mined from underground deposits; a much larger quantity, however, is recovered as a by-product from a number of industrial processes.

Sulfur resources are abundant and widespread, but prevailing prices and extraction technologies constrain the extent to which they can be classified as reserves. At present, sulfur can be economically mined from very few deposits. Most of the sulfur that is currently produced comes from natural gas and petroleum deposits, making it difficult to formulate reliable reserve data.

The sulfur industry is roughly divided into two sectors: voluntary (or discretionary) and involuntary (or nondiscretionary). In voluntary production, mining sulfur or pyrites is the sole objective, and the recovery of the resource is as complete as economic conditions will allow. During involuntary production, sulfur or sulfuric acid is recovered as a by-product and the quantity of the output is dictated by the demand for the primary product and the environmental regulations mandating sulfur removal from the finished products and emissions. Involuntary sulfur is often referred to as recovered sulfur and the acid produced is known as by-product sulfuric acid.

In the early sulfur industry, voluntary sulfur was the sole source of sulfur production. Small quantities of involuntary sulfur in the form of sulfuric acid began to appear early in the 20th century, and by-product elemental sulfur was reported in the late 1930s. Recovery of elemental sulfur from natural gas processing and petroleum refining first overtook sulfur mining as the dominant source in the United States in 1982, and its importance has

increased steadily since that time. Recovered sulfur dominates the world markets. In 2003, mined sulfur was less than 3% of total elemental production worldwide. U. S. sulfur mining ceased completely in 2000. Poland continued to mine sulfur at one location, and some sulfur may have been mined in Iraq.

Sulfur Sources

Barker (1983) describes sulfur sources as follows:

- Combined sulfur—sulfur that occurs in nature combined with other elements, commonly referred to as sulfides and sulfates
- Cupriferous pyrites—pyrite containing minor amounts of copper sulfides. The most common is chalcopyrite, a sulfide of copper and iron with the formula CuFeS_2 or $\text{Cu}_m\text{Fe}_n\text{S}_{(m+n)}$.
- Hydrogen sulfide (H_2S)—a colorless, flammable, toxic gas that may occur in petroleum and natural gas
- Involuntary sulfur—sulfur produced as a by-product in response to legislative or process mandates
- Native sulfur—sulfur that occurs in elemental form in nature
- Nonferrous metal sulfides—copper, lead, zinc, nickel, and molybdenum sulfides that are processed for their metal content
- Organic sulfur—complex organic sulfur compounds that occur in petroleum, coal, oil shale, and tar sands
- Pyrites—metallic-looking sulfide minerals of which iron pyrites (pyrite) is the most common, and includes marcasite, and pyrrhotite
- Sulfate sulfur—sulfur combined as SO_4^{-2} as contained in anhydrite, gypsum, and many other minerals
- Voluntary sulfur—elemental sulfur or pyrites produced in response to market demand

Basic Sulfur Products

Barker (1983) describes basic sulfur products as follows:

- Acid sludge—contaminated sulfuric acid, frequently the result of petroleum alkylation, usually returned to acid plants for reconstitution
- Bright sulfur—crude sulfur free of discoloring impurities; bright yellow in color
- Brimstone—common name for sulfur; synonymous with crude sulfur
- Broken sulfur—solid crude sulfur crushed to -8 in.

- By-product sulfuric acid—sulfuric acid produced as a by-product of a metallurgical or industrial process, generally relating to combined sulfur sources
- Crude sulfur—commercial nomenclature for elemental sulfur that is 99.0% to 99.9% pure and is free from arsenic, selenium, and tellurium
- Dark sulfur—crude sulfur discolored by minor quantities of hydrocarbons, ranging up to 1.0% oil and carbonaceous material
- Elemental sulfur—processed sulfur in the elemental form produced from native sulfur or combined sulfur sources, generally with a minimum sulfur content of 99.5%
- Formed sulfur—elemental sulfur cast or pressed into particular shapes to enhance handling and to suppress dust generation and moisture retention
- Frasch sulfur—elemental sulfur produced from native sulfur sources using the Frasch hot water mining process
- Liquid sulfur—synonymous with molten sulfur
- Liquid sulfur dioxide—purified sulfur dioxide compressed to the liquid phase
- Molten sulfur—crude sulfur at a sufficiently high temperature to keep it from solidifying, thus maintaining a liquid (molten) state
- Prilled sulfur—solid crude sulfur that is cooled in air or water to form small spheroids
- Recovered sulfur—elemental sulfur produced as a by-product of natural gas processing, petroleum refining, water gas, and other fuel gases
- Slated sulfur—solid crude sulfur in the form of slate-like lumps, produced by allowing molten sulfur to solidify on a moving belt
- Specialty sulfur—prepared or refined grades of elemental sulfur that include amorphous, colloidal, flowers, precipitated, wettable, flour, and paste sulfur, usually used in elemental form
- Sulfur ore—unprocessed ore containing native sulfur
- Sulfuric acid—sulfuric acid of commerce as produced from all sources of sulfur, generally reported in terms of 100% H_2SO_4 with 32.69% sulfur content

Ober (2004) estimates that nearly 62 Mt of sulfur was mined or recovered as a by-product in 2003 (Table 1). Production was reported in more than 75 countries, 24 of which accounted for almost 93% of the production, each producing more than 500,000 t. The United States and Canada were the leading producers, each with more than 9 Mt of production in 2003.

Sulfur occurs naturally as a native element in subsurface deposits within salt domes and bedded evaporites (anhydrite and gypsum), many of which were mined in situ using the Frasch mining method. Such deposits are thought to form through the actions of bacteria in the presence of hydrocarbons and calcium sulfate, and are termed *bioepigenetic* deposits. In 1974, the year in which Frasch and other native sulfur production was at the highest historical levels, voluntary elemental sulfur sources supplied 35% (about 18 Mt) of the total world sulfur demand. Since that time, its importance has decreased dramatically, accounting for less than 3% of the total production in 2003 (Tables 1 and 2).

Bioepigenetic sulfur sources constitute most of the voluntary elemental sulfur production. Large bioepigenetic deposits have been exploited in the United States, Mexico, Poland, Iraq, Russia, Ukraine, and other former Soviet republics. Poland is the only major

sulfur producer that continues to produce Frasch sulfur. Iraq could potentially produce significant quantities of Frasch sulfur, but the situation in that country has been difficult to pinpoint since the 1990 Iraqi invasion of Kuwait and the subsequent wars and sanctions.

Native sulfur also occurs in solfatara-type deposits associated with volcanism and recent hydrothermal activity. These deposits are common in volcanic regions such as the western United States, Central America, the Andes, and the Philippines. Volcanic deposits are often contaminated with toxic elements, and so are rarely used except for nonagricultural local consumption.

Sulfur also occurs in combination with base metals as ferrous sulfides (pyrites) and nonferrous sulfides, from which sulfur or sulfuric acid is produced as a primary product or by-product. The importance of this source of sulfur has decreased in recent years, and in 2003 it supplied about 7% (less than 5 Mt) of the total demand for sulfur and sulfur compounds. China and Finland are the only major sulfur-producing countries where the major sulfur source is pyrites (Table 1).

Large quantities of sulfur are present in natural gas and petroleum as hydrogen sulfide and organic compounds from which elemental sulfur is commonly recovered. Sulfur recovered from natural gas and petroleum refining supplied almost 70% (about 43 Mtpy) of worldwide demand in 2003. In the United States, fuel processing plants accounted for 93% of the total output of sulfur in all forms. Ten countries recovered more than 1 Mt of elemental sulfur from fuel processing in 2003. They were, in decreasing order of production, the United States, Canada, Russia, Saudi Arabia, Japan, the United Arab Emirates, Germany, Kazakhstan, Iran, and Mexico.

Sulfur also occurs in organic form in coal, oil sands, oil shale, and tar sands. Canada is the only significant producer from this source, but that production is included with other fuels. Oil sands represent a potentially large source for recovered sulfur, especially in Canada. The province of Alberta has huge deposits of oil sands with estimated reserves of 300 billion bbl of recoverable crude oil that also contain 4% to 5% sulfur (Stevens 1998). The Athabasca oil sands are a mixture of sand, water, clay, and bitumen (a naturally occurring viscous mixture of heavy hydrocarbons). Because of its complexity, bitumen is difficult or impossible to refine at most oil refineries. It must be upgraded to a light-oil equivalent before further refining, or it must be processed at facilities specifically designed for processing bitumen. Oil sands with more than 10% bitumen are considered rich; those with less than 7% bitumen are not economically attractive (Anon. 1999a).

Enormous amounts of sulfur are present as sulfate (anhydrite and gypsum) in evaporite basins throughout the world, but economic methods have not been developed to recover sulfur from sulfate.

Commercial grades of elemental sulfur are classified as crude (run-of-mine, bright, or dark) and recovered. Both types of elemental sulfur are shipped in liquid or solid form, and are guaranteed to be 99.5% pure. The only significant impurity is usually carbon, present as hydrocarbons dispersed throughout the sulfur (dark sulfur may contain up to 0.3% carbon). Most end uses require relatively pure sulfur free of contaminating elements such as arsenic, selenium, and tellurium.

Most elemental sulfur in the United States is marketed in the liquid state. In international trade, sulfur is generally shipped as broken or formed sulfur. Formed sulfur (prills, slates, etc.) is preferred to broken sulfur because it causes fewer dust problems. Fine sulfur dust particles are difficult to contain and can be blown great distances on the wind. In addition to contaminating the area adjacent to the production locations, contamination can be a problem

Table 1. World production of sulfur in all forms, by country and source, kt[†]

Country and Source [‡]	1993	1999	2000	2001	2002	2003 [§]
Albania [§]						
Elemental	10	10	10	10	5	5
Pyrites	6	4	4	4	0	0
Total	<u>16</u>	<u>14</u>	<u>14</u>	<u>14</u>	<u>5</u>	<u>5</u>
Algeria, by-product, natural and petroleum [§]	25	16	12	7	19	20
Aruba, by-product, petroleum [§]	34	50	77	77	77	77
Australia, by-product [§]						
Metallurgy	299	441	654	817	899	863
Petroleum	85	25	30	45	60	60
Total	<u>384</u>	<u>466</u>	<u>684</u>	<u>862</u>	<u>959</u>	<u>923</u>
Austria, by-product [§]						
Metallurgy	9**	5	5	5	10	8
Natural gas and petroleum	8**	9**	10**	9	9	9
Total	<u>17**</u>	<u>14**</u>	<u>14**</u>	<u>14</u>	<u>19</u>	<u>17</u>
Bahrain, by-product, petroleum	54	67 [§]	62	67	67	68
Belarus [§]	na (not available)	20	20	20	25	30
Belgium, by-product, all sources [§]	300	408	410	410	400	400
Bosnia and Herzegovina, by-product, metallurgy [§]	††	1	1	1	1	1
Brazil						
Frasch	22	23	24	24	23	23
Pyrites	2	0	0	0	0	0
By-product						
Metallurgy	184	217	217	280	284	284
Petroleum	59	58	82	80	77	80
Total	<u>266</u>	<u>298</u>	<u>323</u>	<u>385</u>	<u>384</u>	<u>387</u>
Bulgaria [§]						
Pyrites	18	20	0	0	0	0
By-product, all sources	95	151	239	233	200	200
Total	<u>113</u>	<u>171</u>	<u>239</u>	<u>233</u>	<u>200</u>	<u>200</u>
Canada, by-product						
Metallurgy	900	1,159	1,167	1,124	1,109	969**
Natural gas, oil sands, petroleum	7,530	8,656	8,621	8,620	7,816	8,061**
Total	<u>8,430</u>	<u>9,815</u>	<u>9,788</u>	<u>9,744</u>	<u>8,925</u>	<u>9,030**</u>
Chile [§]						
Native, refined and from caliche	1	0	0	0	0	0
By-product, metallurgy	385	1,040	1,100	1,160	1,275**	1,300
Total	<u>386</u>	<u>1,040</u>	<u>1,100</u>	<u>1,160</u>	<u>1,275</u>	<u>1,300</u>
China [§]						
Elemental	330	280	290	290	290	290
Pyrites	5,330	3,860	3,370	3,090	3,240	3,400
By-product, metallurgy	700	1,630	1,900	2,000	2,200	2,400
Total	<u>6,360</u>	<u>5,770</u>	<u>5,560</u>	<u>5,380</u>	<u>5,730</u>	<u>6,090</u>
Colombia						
Native	51	16	16	13	12	12**
By-product, petroleum	12 [§]	18	21	15	12	14**
Total	<u>64</u>	<u>34</u>	<u>37</u>	<u>29</u>	<u>24</u>	<u>26**</u>
Croatia, by-product, petroleum [§]	15	15	15	15	15	15
Cuba, by-product, petroleum [§]	5	5	5	5	5	5
Cyprus [§]	0	1	1	1	1	1
Czech Republic, by-product, all sources ^{§††}	37	35	35	35	35	35
Denmark, by-product, petroleum [§]	10	10	11	11	11	11
Ecuador [§]						
Native	4	4	4	4	4	4
By-product						
Natural as g	5	5	5	5	5	5
Petroleum	5	8**	12**	12	12	12
Total	<u>14</u>	<u>17</u>	<u>21</u>	<u>21</u>	<u>21</u>	<u>21</u>

(Table continued next page)

Table 1. World production of sulfur in all forms, by country and source, kt[†] (continued)

Country and Source [‡]	1993	1999	2000	2001	2002	2003 [§]
Egypt, by-product, natural gas and petroleum [§]	4**	10	60	78	78	78
Finland [§]						
Pyrites	292	380	260	270	359	341
By-product						
Metallurgy	217	299	283	227	308	305
Petroleum	32 [§]	42	46	46	55	60
Total	541[§]	721	589	543	722	706
France, by-product [§]						
Natural gas	829	600	600	600	500	500
Petroleum	278	250	250	250	250	250
Unspecified	150	250	250	250	250	250
Total	1,260	1,100	1,110	1,100	1,000	1,000
Germany						
Pyrites	0	30	30	61	0	0**
By-product						
Metallurgy	33	504	618	684	754	697**
Natural gas and petroleum	1,500 [§]	1,842	1,753	1,749	1,745	1,661**
Total	1,530	2,358	2,401	2,494	2,499	2,358**
Greece [§]						
Pyrites	25	0	0	0	0	0
By-product						
Natural gas	100	na	na	na	na	na
Petroleum	9	na	na	na	na	na
Natural gas and petroleum	na	148	150	153	157	162
Total	134	148	150	153	157	162
Hungary, by-product, all sources [§]	30	30	30	30	30	30
India [§]						
Pyrites	117	32	32	32	32	32
By-product						
Metallurgy	123	261	359	458	458	539
Natural gas and petroleum	31	101	376	526	371	451
Total	271	394	767	1,016	861	1,022
Indonesia [§]						
Native	4	4	4	4	4	4
By-product						
Metallurgy	na	80	100	100	100	100
Petroleum	na	50	50	50	50	50
Total	4	134	154	154	154	154
Iran, by-product [§]						
Metallurgy	50	47	50	50	50	50
Natural gas and petroleum	750	963	963	880	1,200	1,310
Total	800	1,010	1,013	930	1,250	1,360
Iraq, elemental [§]						
Native, Frasch	na	98	300	300	300	50
By-product, natural gas and petroleum	na	2	2	2	2	1
All sources	450	na	na	na	na	na
Total	450	100	302	302	302	51
Israel, by-product, natural gas and petroleum	60	31	38	35	36	45
Italy [§]						
Pyrites	145	0	0	0	0	0
By-product						
Metallurgy	na	193	203	203	142	119
Petroleum	300	485	490	540	560	565
Total	445	678	693	743	702	684

(Table continued next page)

Table 1. World production of sulfur in all forms, by country and source, *kt*[†] (continued)

Country and Source [‡]	1993	1999	2000	2001	2002	2003 [§]
Japan						
Pyrites [§]	29**	41	30	30	25	25
By-product						
Metallurgy	1,383	1,361	1,384	1,319	1,326	1,281**
Petroleum	1,510**	2,060	2,072	2,424	1,865	2,000
Total	<u>2,922**</u>	<u>3,462</u>	<u>3,486</u>	<u>3,773</u>	<u>3,216</u>	<u>3,306</u>
Kazakhstan [§]						
Native	219	0	0	0	0	0
Pyrites	219	0	0	0	0	0
By-product						
Metallurgy	276	245	300	310	260	325
Petroleum	182	1,073	1,200	1,400	1,600	1,600
Total	<u>896</u>	<u>1,318</u>	<u>1,500</u>	<u>1,710</u>	<u>1,860</u>	<u>1,925</u>
Korea, North [§]						
Pyrites	210	na	na	na	na	na
By-product, metallurgy	30	na	na	na	na	na
Unspecified	na	41	41	41	42	42
Total	<u>240</u>	<u>41</u>	<u>41</u>	<u>41</u>	<u>42</u>	<u>42</u>
Korea, Republic of, by-product [§]						
Metallurgy	263	528	572	665	680	690
Petroleum	200	600	600	600	610	610
Total	<u>463</u>	<u>1,128</u>	<u>1,172</u>	<u>1,265</u>	<u>1,290</u>	<u>1,300</u>
Kuwait, by-product, natural gas and petroleum [§]	175	639	512	524	634	714
Libya, by-product, natural gas and petroleum [§]	13	13	15	15	15	15
Macedonia, by-product, metallurgy [§]	6	15	13	15	15	10
Mexico						
Frasch	102	0	0	0	0	0
By-product						
Metallurgy	300	474	474	572 [§]	575 [§]	575
Natural gas and petroleum	804	860	851	878	877	1,034**
Unspecified	30	na	na	na	na	na
Total	<u>1,236</u>	<u>1,334</u>	<u>1,325</u>	<u>1,450</u>	<u>1,452</u>	<u>1,609</u>
Namibia, pyrites	0	0	6	34	2	16**
Netherlands, by-product [§]						
Metallurgy	125	290	123	126	124	119
Petroleum	290	445	428	384	373	408
Total	<u>415</u>	<u>574</u>	<u>551</u>	<u>510</u>	<u>497</u>	<u>527</u>
Netherlands Antilles, by-product, petroleum [§]	32	30	30	30	30	30
Norway [§]						
Pyrites	44	0	0	0	0	0
By-product						
Metallurgy	75	97	92	105	105	105
Petroleum	15	12	18	18	19	20
Total	<u>134</u>	<u>109</u>	<u>110</u>	<u>123</u>	<u>124</u>	<u>125</u>
Oman, by-product, all sources [§]	40	30	30	30	30	30
Pakistan, all sources [§]	27	21	20	21	21	21
Peru, by-product, all sources [§]	60	191	196	203	201	204
Philippines, by-product, metallurgy [§]	261	133	134	170	180	180
Poland ^{§§}						
Frasch	1,861	1,172	1,482	942	760	750
By-product						
Metallurgy	220**	278	279	277	275 [§]	275
Petroleum	29**	74 [§]	70 [§]	133	180	150
Gypsum [§]	10	0	0	0	0	0
Total	<u>2,120</u>	<u>1,524</u>	<u>1,831</u>	<u>1,352</u>	<u>1,215</u>	<u>1,175</u>

(Table continued next page)

Table 1. World production of sulfur in all forms, by country and source, kt[†] (continued)

Country and Source [†]	1993	1999	2000	2001	2002	2003 [§]
Portugal [§]						
Pyrites	5	0	0	0	0	0
By-product, all sources	4	32	28	35	28	27
Total	9	32	28	35	28	27
Qatar, by-product, natural gas	72	155	191	221	221	221
Romania						
Pyrites	170	17	20	20§	20§	20
By-product, all sources	33	45	45	45§	45§	45
Total	203	62	65	65	65	65
Russia ^{§***}						
Native	100	50	50	50	50	50
Pyrites	640	300	350	400	400	450
By-product, natural gas	2,680	4,405	4,900	5,300	5,400	5,600
Other	300	510	600	500	500	500
Total	3,720	5,265	5,900	6,250	6,350	6,600
Saudi Arabia, by-product, all sources	2,400	1,940	2,101	2,350§	2,360§	2,400
Serbia and Montenegro [§]						
Pyrites	1	0	0	0	0	0
By-product						
Metallurgy	130**	15	30	30	30	30
Petroleum	1	2	2	2	2	2
Total	132**	17	32	32	32	32
Singapore, by-product, petroleum [§]	75	190	180	180	175	175
Slovakia, by-product, all sources [§]	6	25	25	25	25	25
South Africa						
Pyrites, S content from gold mines	323	141	146	150	183	176**
By-product						
Metallurgy	80§	125	119	115	362	308
Petroleum	171	139	184	123	137	130
Total	575	406	448	388	682	614**
Spain						
Pyrites	408	388	138	71§	0	0
By-product [§]						
Coal, lignite, gasification	2	2	1	1	1	1
Metallurgy	258	455	454	461	544	560
Petroleum	100	110	115	135	140	145
Total	768	955	708	668	685	706
Sweden [§]						
Pyrites	40	0	0	0	0	0
By-product						
Metallurgy	125	65	91	152	170	180
Petroleum	40	56	61	55	60	57
Total	165	121	152	207	230	237
Switzerland, by-product, petroleum [§]	3	3**	3	3	3	3
Syria, by-product, natural gas and petroleum	35§	12	17	16§	16§	15
Taiwan, by-product, all sources	153	195	206	224	212	225**
Trinidad and Tobago, by-product, petroleum [§]	5	15	15	15	15	15
Turkey [§]						
Native	17	0	0	0	0	0
Pyrites	27**	45**	26**	30	30	30
By-product						
Petroleum	21	47	43	51	50	48**
Unspecified	5	75	75	75	75	72
Total	70	167	144	156	155	150
Turkmenistan, by-product, all sources [§]	60	9	9	9	9	9
Ukraine, elemental [§]	500	80	88	126	124	142
United Arab Emirates, by-product, natural gas, and petroleum [§]	249	1,089	1,120	1,490	1,900	1,900

(Table continued next page)

Table 1. World production of sulfur in all forms, by country and source, kt[†] (continued)

Country and Source [‡]	1993	1999	2000	2001	2002	2003 [§]
United Kingdom, by-product [§]						
Metallurgy	62**	27**	51**	69	33	13
Petroleum	202**	136	140	111	125	115
Total	<u>264**</u>	<u>163</u>	<u>191</u>	<u>180</u>	<u>158</u>	<u>128</u>
United States						
Frasch	1,900	1,780 [§]	900 [§]	0	0	0**
By-product						
Metallurgy	1,430	1,320	1,030	682	772	683**
Natural gas	2,910	2,150	2,230	2,000	1,760	1,940**
Petroleum	4,820	3,210	6,360	6,480	6,750	6,970**
Total	<u>11,100</u>	<u>11,500</u>	<u>10,500</u>	<u>6,470</u>	<u>9,270</u>	<u>9,600**</u>
Uruguay, by-product, petroleum [§]	3	3**	3	3	3	3
Uzbekistan, by-product [§]						
Metallurgy	170	175	160	160	170	170
Natural gas and petroleum	400	280	285	300	350	350
Total	<u>570</u>	<u>455</u>	<u>445</u>	<u>460</u>	<u>520</u>	<u>520</u>
Venezuela, by-product, natural gas and petroleum	135	68	328	322	283	300
Zambia						
Pyrites	33 [§]	27	21 [§]	86	95	100
By-product, metallurgy	86 [§]	39	36 [§]	21	33	35
Total	<u>119[§]</u>	<u>66</u>	<u>57[§]</u>	<u>106</u>	<u>128</u>	<u>135</u>
Zimbabwe						
Pyrites	32	16	23	32	29	25
By-product, all sources [§]	5	3	3	2	2	2
Total	<u>37</u>	<u>18</u>	<u>25</u>	<u>34</u>	<u>31</u>	<u>27</u>
Grand total, world	<u>50,400</u>	<u>58,500</u>	<u>59,700</u>	<u>60,400</u>	<u>60,500</u>	<u>61,800</u>
Of which						
Frasch	2,030	2,980	2,410	966	783	773
Native ^{†††}	1,240	542	762	797	789	556
Pyrites	8,120	5,300	4,450	4,310	4,410	4,620
By-product						
Coal, lignite, gasification [§]	2	2	1	1	1	1
Metallurgy	8,180	11,400	12,000	12,700	13,200	13,200
Natural gas	6,600	7,310	7,920	8,130	7,880	8,270
Natural gas, oil sands, petroleum, undifferentiated	11,500	15,800	16,300	17,000	17,100	17,700
Petroleum	8,440	11,200	11,500	12,000	11,800	12,100
Unspecified	4,280	4,010	4,370	4,540	4,490	4,550
Gypsum [§]	10	0	0	0	0	0

Source: Ober 2004.

* World totals, U.S. data, and estimated data are rounded to no more than three significant digits; may not add to totals shown.

† Table includes data available through July 22, 2004.

‡ The term "source" reflects the means of collecting sulfur and the type of raw material.

§ Estimated.

** Reported figure.

†† Less than ½ unit.

††† May also produce limited quantities of by-product sulfur from oil refining.

§§ Government of Poland sources report total Frasch and native-mined sulfur output annually, undifferentiated; this figure has been divided between Frasch and native-mined sulfur based on information from supplementary sources.

*** Sulfur is believed to be produced by the Frasch method and as a petroleum by-product; information is inadequate to formulate estimates.

†††† Includes "China, elemental."

along rail lines and at port facilities. Of even more concern than the dust contamination is the hazardous nature of sulfur dust. Finely divided sulfur presents explosive and fire hazards, and the sulfur dioxide (SO₂) generated by such a fire is toxic (West 1966). Specialty grades (such as refined sulfur of various shapes and sublimed sulfur) are prepared from commercial grades and distilled sulfur.

Sulfuric acid may be sold at various strengths, but it is generally marketed at 100 %. Acid is generally shipped at 66° Bé (93 % H₂SO₄), as 98% acid, or as 20% to 22% fuming oleum, which is sulfur trioxide dissolved in sulfuric acid (sulfuric acid strength is reported as a function of its specific gravity, reported in degrees Baumé, which is an arbitrary scale). In general, the specific gravity of

Table 2. Sulfur supply (in all forms) from natural resources

Source	Major Methods of Recovery	World Resources, Mt
Native deposits:		
Bioepigenetic	Frasch and surface mining	~2.5
Volcanic	Surface mining, smelting/flotation	~0.5
Pyrites and base metal sulfides	Sulfuric acid and sulfur dioxide from roasting, acid from stack gases	~1.5
Natural gas	Hydrogen sulfide recovered using Claus process	0.7
Petroleum	Desulfurization during refining	0.5
Tar sands	Desulfurization during refining	~2.0
Coal	By-product pyrite and chemical processing	>1.0
Gypsum and anhydrite	Surface mining, sulfate reduction	Very large

Source: Adapted from Nieć 1986a.

sulfuric acid increases as the concentration increases until it reaches 98% acid, at which point the specific gravity remains relatively constant as the concentration continues to increase (Anon. 1961).

HISTORICAL BACKGROUND

Sulfur has been known and used by humans since at least 4000 BC as a pigment, as a fumigant, and for medicinal and religious purposes (Haynes 1959). Earlier peoples throughout the world probably used sulfur as well, but sulfur's rapid oxidation in surface environments tends to remove it from the archaeological record.

As early as 2000 BC, the Egyptians used sulfur as sulfur dioxide to bleach linen textiles (Morse 1991). During the Peloponnesian War, in the 5th century BC, the Greeks may have employed the first chemical weapon when they burned a sulfur-pitch mixture to generate suffocating gases (Bauman 2001). The Romans used sulfur to create incendiary weapons, and they mined much of the sulfur they used from open cuts and shallow underground mines in the evaporite-hosted stratiform deposits in Sicily (Ellison 1971). The Romans also mined sulfur at other sites in their empire, such as in present-day Syria. Alchemists probably produced the first sulfuric acid around 700 AD.

The early uses of sulfur were relatively limited and only small quantities were mined. The invention of gunpowder by the Chinese in the 10th century eventually led to its widespread use in warfare and made sulfur an important mineral commodity. Some accounts suggest that gunpowder first was used in the West at the Battle of Crecy (1346) during the Hundred Years' War between England and France (1337 to 1453), and its introduction led to profound social and political changes in Europe. During this time, the Sicilian sulfur deposits continued to satisfy European demand.

Early in the 17th century, Johann Glauber, a German alchemist, accidentally discovered a process for making sulfuric acid by burning sulfur and niter (potassium nitrate) under a glass bell. Glauber's process was destined to become the cornerstone of the sulfuric acid industry, although at the time, sulfuric acid was generally used only for medicinal purposes. As others reproduced Glauber's efforts, and sulfuric acid production increased, industrial uses for sulfur developed and expanded. An English physician, John Roebuck, began manufacturing large quantities of sulfuric acid using a less expensive lead-lined container, and soon similar acid manufactories appeared. Because it is the cheapest and most versatile of the mineral acids, sulfuric acid became the workhorse of numerous chemical industries. By 1820, there were 23 acid plants in England alone (Haynes 1959). The first American acid production was in 1793.

The Sicilian sulfur deposits continued to supply much of the world's sulfur, but an attempt by French controlling interests in

1838 to stabilize the price of Sicilian sulfur at a high level led to the use of other sources of sulfur for the production of sulfuric acid. In 1833, a French chemist, Michel Perrett, developed a reasonably economical method of obtaining sulfur dioxide by roasting pyrites. His invention led to the development of a rotary furnace in 1870 that made pyrites a profitable raw material for acid. By 1880, sulfuric acid throughout the world was produced from pyrites, except in the United States where import tariffs on iron and copper prevented the shift from native sulfur. These import tariffs were removed in 1890 and 1894, respectively, and by 1900 pyrites had become the principal acid-making material in the United States.

Native sulfur deposits were known in North America, and several attempts were made to mine sulfur from salt-dome cap rock in Louisiana between 1870 and 1890 using conventional underground mining techniques. These efforts were frustrated by the nature of the sulfur ore and the overlying strata. In 1894, Herman Frasch developed a method of mining sulfur in situ using hot water and compressed air. Sulfur was first commercially obtained using the Frasch method in 1895 by the Union Sulphur Company at Sulphur Mines dome, Calcasieu Parish, Louisiana. The Frasch method was also employed in 1912 at Bryan Mound, Brazoria County, Texas, and later at many other domes (Ellison 1971; Halbouty 1979).

Shipping problems during World War I, and a growing preference for brimstone over pyrites in the contact process of acid production (first developed in the 1880s to generate larger quantities of high-strength acid), led to expanded use of Frasch sulfur. By 1919, 48% of American acid production used brimstone; by 1929, 69% came from this source (Haynes 1959).

World War II disrupted sulfur production and transportation outside North America, and recovery after the war was slow. Foreign consumers became more dependent on U.S. Frasch producers as they attempted to rehabilitate and expand their acid industries.

In 1950, Frasch sulfur from the U.S. Gulf Coast and sulfuric acid from pyrite-roasting plants in Europe were the major sources of the western world's sulfur. Competition from low-cost U.S. mines caused a rapid decline in sulfur production in Italy.

A supply shortfall during the Korean War led to short-lived controls imposed on the industry by the U.S. government. The controls were lifted after the cessation of hostilities. New mines were opened at several sites at about the same time. Producers opened new mines in the United States at Garden Island Bay and Damon Mound, and Mexico entered the Frasch market with production from San Cristobal in 1954 (Salas 1991). Also of great significance was the expansion and accelerated growth of recovered sulfur production in Canada, beginning at about this same time. Recovered sulfur production began in France in 1957, and Texasgulf Inc. opened the world's first liquid sulfur terminal in 1958 (Barker 1983; Giusti 1984).

The first Frasch sulfur from the huge deposits in Poland reached the market in 1960. Canadian and French recovered sulfur production continued to expand, and the U.S. share of world exports fell 19% in 4 years to 31%. Mexico surpassed the U.S. export tonnage in 1964. Additional Frasch mines were opened in Poland in 1966 and 1967, and the Duval Corporation discovered the large deposit at the Culberson mine in western Texas in 1967. As time progressed, recovered sulfur output exceeded Frasch sulfur output, even with the opening of the Frasch mine at Mishraq, Iraq, in 1972.

Price offensives by the oil and phosphate cartels in 1974 and 1975 led to recession and the drawdown of existing sulfur stocks. This resulted in a major cutback in the United States and Mexico, and the beginning of a gradual decline in North American Frasch production that continued until 2000, when North American production ceased entirely.

The three historical leaders in mined sulfur production in the United States were Freeport Sulphur Co., Pennzoil Sulphur Co., and Texasgulf (Lou ghbrough 1991). Over time, each company operated multiple Frasch mines and was notable for different reasons. Freeport, the last U.S. Frasch producer when it closed its Main Pass mine in 2000, operated more conventional salt-dome deposits, but was unusual in that the company's last mines were developed on platforms in the Gulf of Mexico. Pennzoil adapted the Frasch process to produce sulfur from bedded evaporite deposits such as its Culberson mine in western Texas, which Pennzoil eventually sold to Freeport. Texasgulf operated the most prolific sulfur mine in Texas, on Boling dome, extracting 82 Mt of sulfur during more than 60 years of production. The mine closed in 1993.

The United States remains the world's foremost producer and consumer of sulfur and sulfuric acid, with production from recovered and by-product sources. The United States is a net importer of sulfur, however, with most of its imports coming from Canada and Mexico. Canada, the second largest producer, is the world's leading exporter. Other countries that produce 1 Mt or more of sulfur in all forms are Chile, China, France, Germany, India, Iran, Japan, Kazakhstan, Republic of Korea, Mexico, Poland, Russia, Saudi Arabia, and United Arab Emirates (see Table 1).

Poland is the only producer of Frasch sulfur, although production has decreased to only about 750,000 t from one mine; it once produced nearly 5 Mtpy from three mines. Frasch production from the Mishraq deposit near Mosul in the Kurdish north of Iraq could resume when conditions there stabilize; Poland's Frasch producer has shown interest in operating the mine but is waiting until circumstances are more favorable. Iraq's status as a major exporter was negatively affected by the United Nations' trade embargo that was enacted as a result of its invasion of Kuwait in 1990 and was lifted only after the start of the second Gulf War in 2003. China is the only major producer that obtains the majority of its sulfur production from pyrites.

GEOLOGY OF NATIVE SULFUR DEPOSITS

Mineralogy and Classification of Deposits

Elemental sulfur occurs naturally by replacement reactions with anhydrite and gypsum in salt-dome cap rocks and bedded evaporites. It is also common in volcanic environments and associated with thermal springs.

Native sulfur is readily oxidized, particularly in the presence of sulfur-oxidizing bacteria, and so is somewhat ephemeral in nature. Surface exposures are relatively rare and are generally restricted to regions of ongoing or very recent mineralization. Most known sulfur deposits are thought to be Tertiary in age or younger, but some fossil deposits (from which the sulfur has been removed) may be older.

The element sulfur occurs as sulfate (anhydrite and gypsum) throughout the world, and in sulfides, both ferrous and nonferrous. All of these occurrences of sulfur are used locally as a source of elemental sulfur and sulfuric acid. Sulfur is present in organic compounds and as hydrogen sulfide in petroleum and natural gas, and in coal, tar sands, and oil shale.

The atomic weight of sulfur is 32.064, and it has an atomic number of 16. Sulfur has four oxidation states (+6, +4, 0, and -2), of which the S^{-2} sulfide ion and the S^{+6} sulfate cation are the most important in nature.

There are four stable isotopes of sulfur— ^{32}S , ^{33}S , ^{34}S , and ^{36}S —that respectively are 95.02%, 0.75%, 4.21%, and 0.02% of the total terrestrial sulfur. The isotopic composition of sulfur is expressed in terms of $\delta^{34}S$ (Faure 1977). The most important cause for variation in the isotopic composition of sulfur in nature is fractionation by sulfate-reducing bacteria. These bacteria split oxygen from sulfate ions and excrete hydrogen sulfide that is enriched in ^{32}S relative to the sulfate. The extent of the fractionation is variable and depends on the rate of reduction, the temperature, the nature and availability of the food supply, and the size of the sulfate reservoir. Native sulfur from salt-dome cap rock and bedded evaporites (as described in the following text) is enriched in ^{32}S , and the residual anhydrite and gypsum and associated sulfate minerals such as barite are enriched in ^{34}S , lending evidence to the origin of sulfur in these environments by sulfate-reducing bacteria (Thode 1972).

Native sulfur is polymorphous; although it commonly occurs in the orthorhombic or alpha (α) sulfur form, it is also known in two monoclinic forms, beta (β) sulfur and gamma (γ) sulfur. The monoclinic forms are unstable at normal surface temperatures and readily convert to the orthorhombic form. Orthorhombic sulfur, when heated to 95.5°C, changes to monoclinic crystals. Natural monoclinic sulfur is rare, but is known from several sites, including Moravia, in the Czech Republic, where it has been given the name of rosickyite (Ford 1949). Native sulfur also occurs in an amorphous state.

Native sulfur crystals are commonly dipyramidal and sometimes thick tabular on c(001) or sphenoidal. Sulfur also occurs in irregular masses, in reniform shapes, as incrustations and earthy masses, and in stalactitic and stalagmitic forms. Cleavage is imperfect, and fracture is conchoidal to uneven. Native sulfur is brittle to imperfectly sectile, has a Mohs hardness of 1.5 to 2.5, and has a resinous luster. Sulfur has a specific gravity of 2.05 to 2.09. The average weight of orthorhombic sulfur is 2.07 g/mL, the average weight of monoclinic sulfur is 1.96 g/mL, and the average weight of amorphous sulfur is 1.92 g/mL (Ellison 1971). The color of sulfur varies from bright yellow to honey yellow, yellowish brown, greenish, or reddish to yellowish gray. The color depends on the temperature and discoloring impurities such as hydrocarbons and clay.

Sulfur is a nonconductor of electricity and a poor conductor of heat. Orthorhombic sulfur melts at 112.8°C, monoclinic sulfur at 119.2°C, and amorphous sulfur at 120.0°C. Molten sulfur is fairly mobile near the melting point, but its viscosity increases with increasing temperature to 188°C, and then decreases to sulfur's boiling point at 444.6°C. The specific gravity of molten sulfur is 1.79 at 132°C, and the flash point (modified Cleveland open cup) is 168.3° to 187.3°C.

Sulfur is insoluble in water and is nonhygroscopic but is soluble in benzene, ether, toluene, alcohol, and carbon disulfide. It is unaffected by most acids. Sulfur is readily ignited in air, burning at 270°C with a blue flame and evolution of sulfur dioxide. Corrosivity is nil for dry sulfur with slow generation of sulfuric acid when wet. Vapor pressure is less than 0.1 mm Hg (mercury) at 20°C.

Rucknick, Wimberly, and Edwards (1979) classify native sulfur deposits according to genesis in the following fashion:

- I. Biogenic deposits
 - A. Bioepigenetic
 - 1. Cap rock
 - 2. Stratabound
 - B. Biosynthetic
- II. Volcanic deposits
- III. Oxidative deposits
- IV. Thermogenic accumulations

The biogenic deposits listed include all types of mineralization thought to originate through the actions of sulfate-reducing bacteria. The bioepigenetic deposits are the most economically significant and include deposits in salt-dome cap rocks (cap rock above) and replacement deposits in bedded gypsum and anhydrite (stratabound above; stratiform is discussed in the following text). The biosynthetic deposits include small occurrences of native sulfur in modern marine or lacustrine sediments generated by bacterial reduction of sulfate. None of the significant sulfur occurrences in the world is known to be biosynthetic.

Native sulfur is common in volcanic terranes, generally as vein and fracture fillings, and is associated with thermal springs. Volcanic occurrences are generally small, but a few have been mined and are locally important. The oxidative classification of Rucknick, Wimberly, and Edwards (1979) refers to widespread, but generally small, occurrences of sulfur formed at the surface or at depth where hydrogen sulfide (regardless of origin) is oxidized. This class of deposit is discussed in more detail in the section on Stratiform Deposits in this chapter where two oxidative deposits are described.

Native sulfur is also known to originate from high-temperature and high-pressure reactions in deep strata, here termed *thermogenic accumulations*. This type of deposit occurs in association with sour natural gas and is discussed in the section on Recovered Elemental Sulfur in this chapter.

Salt Domes

Salt domes, pillows, and anticlines are common in evaporite basins throughout the world. Salt domes host sulfur mineralization at numerous widespread sites, including Tunisia, the Canadian Arctic, and the Gulf Coast region of the United States and Mexico (Figure 1), but only those salt domes in the Gulf Coast are currently known to host economic sulfur deposits. Salt domes are also important traps for oil and gas accumulations, and the presence of hydrocarbons is essential for the development of native sulfur.

Numerous references discuss the origins of salt domes and cap rock, including previous editions of this volume. Additional overviews of salt domes and pertinent Gulf Coast geology can be found in works by Ellison (1971), Halbouty (1979), Seni (1986), Lerche and O'Brien (1987), Warren (1989), Kyle and Posey (1991), and Salas (1991), among others. Many recent papers present data collected as part of the efforts to evaluate salt domes for the storage of radioactive waste, and data pertaining to fluid migration, cap rock development, and metallic sulfide occurrences.

Salt domes are generally described as diapirs of halite that have intruded younger strata in response to early differential loading and subsequent density inversion. It is misleading, however, to believe that salt is capable of intruding many kilometers of strata. Diapirs begin forming early in the sequence of burial, probably as a response to differential loading, and pass to a stage of diapirism as

overlying strata are loaded on the salt bed in thicknesses greatest where the salt is thinning and migrating toward the diapir (Trusheim 1960; Jackson and Talbot 1986; Posey and Kyle 1988). The top of the salt plug maintains a more or less constant elevation relative to the sediment–water interface, although the buoyancy of the salt and continued upward movement may cause minor faulting and deformation in strata above, and the salt may breach the surface.

In the Gulf Coast, the salt that forms the domes has its source in the Jurassic Louann Formation, a thick deposit of halite thousands of meters below the surface. The Louann halite is relatively pure but contains about 5% in-soluble material, mostly anhydrite crystals with small amounts of dolomite, calcite, and quartz, and traces of limonite, barite, and other minerals.

Subsequent sedimentation on the top of the halite deformed the salt and initiated movement, and was eventually directed to distinct salt plugs that grew in response to continued loading. Late in the history of each salt diapir, the top of the salt plug dissolved through the actions of migrating fresh waters. As salt movement continued upward, the halite at the top was removed and the anhydrite residue accumulated, eventually becoming compacted and cemented. Further dissolution and residue underplating resulted in the formation of a banded anhydrite cap rock that is younger downward. The salt dissolution at the upper surface of the salt stock is relatively flat. The location of active dissolution probably migrates across the salt dome with time, and may be only locally apparent. Only those salt domes that penetrate to within about 2 km of the surface exhibit anhydrite cap rock (Halbouty 1979).

The upper (or outermost) portions of the anhydrite cap rock are commonly replaced by calcite cap rock. Figure 2 is a schematic cross section of a typical salt dome. The calcite cap rock is roughly divisible into two parts: an upper variegated calcite cap and a lower banded calcite cap (Kyle and Posey 1991), both of which may be intensely brecciated and veined with crystalline calcite. The calcite cap is separated from the anhydrite by a transitional zone of gypsum. The underlying anhydrite may be locally absent, particularly at the edges of the dome, if calcite replacement has been complete.

Native sulfur may be found throughout the cap rock and adjacent supercap strata in minor amounts, but it is generally concentrated in the lower portion of the calcite cap. The upper portion of the calcite cap is often barren of sulfur, possibly because of non-deposition or subsequent oxidation. The thickest accumulations of calcite cap, and also of native sulfur, are commonly on the basinward sides of the salt domes, which in the U.S. Gulf Coast is predominantly to the south.

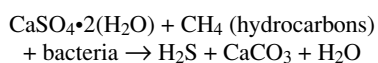
Celestite and barite locally accompany the sulfur as minor accessory minerals. Several recent studies also documented the occurrence of Mississippi Valley type metallic sulfides in both calcite and anhydrite cap rock. Documented sulfide minerals include pyrite, marcasite, pyrrhotite, hauerite, alabandite, sphalerite, galena, chalcopyrite, and acanthite (Price, Kyle, and Wessel 1983; Kyle and Price 1986). Uranium minerals are also found in supercap strata adjacent to salt domes, and realgar has been noted associated with silver values at one dome (G. Wessel, unpublished data 1991).

The origin of sulfur deposits in salt-dome cap rock (and in replacements in bedded evaporites, described as follows) is now widely accepted to be associated with the actions of sulfate-reducing bacteria in the presence of a sulfate source (anhydrite and gypsum) and hydrocarbons. At relatively shallow depths (generally less than 750 m, but locally deeper) and at temperatures below about 60°C, sulfate-reducing bacteria can thrive in the subsurface given an adequate energy source. Sulfate-reducing bacteria are anaerobic, but they are ubiquitous in nature and exist (and probably thrive) with aerobic bacteria in microenvironments.

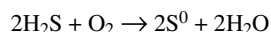


Figure 1. Sulfur-producing domes in the Gulf Coast region of the United States and Mexico

The origin of the sulfur deposits is complex and depends on several parameters. The host anhydrite must be relatively near the surface and exposed to migrating meteoric waters, so that the anhydrite is hydrated to gypsum and put into solution. Into this system, petroleum or natural gas is introduced from depth, generally along faults and joints or permeable strata. Sulfate-reducing and other bacteria introduced with the meteoric water oxidize the hydrocarbons and reduce the sulfate to hydrogen sulfide, represented by the following reaction (greatly simplified):



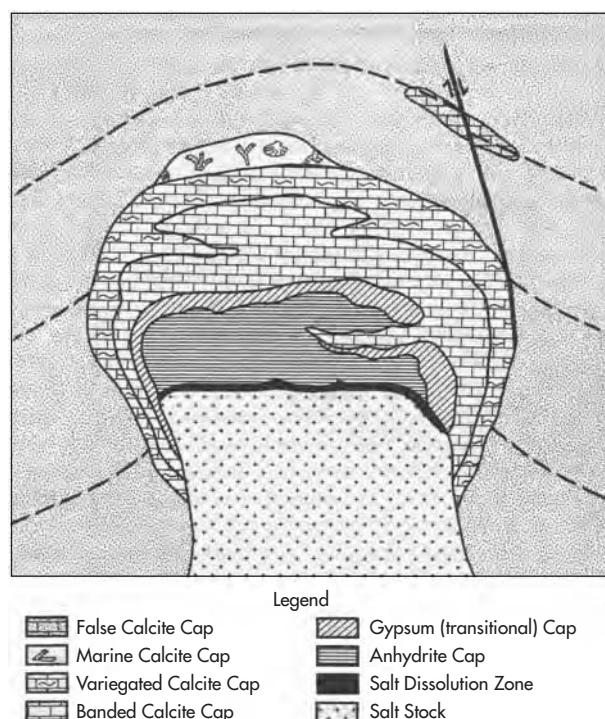
The hydrogen sulfide is oxidized to elemental sulfur with molecular oxygen, presumably present in the groundwater, represented by



Hydrogen sulfide may also be oxidized to sulfur by ferric iron, polysulfide disproportionation, or microbially by colorless and col-

ored sulfur-oxidizing bacteria (Machel 1992). The oxidation of hydrogen sulfide by excess sulfate ions has also been suggested as a mechanism for producing native sulfur (Davis and Kirkland 1979; Ruckmick, Wimberly, and Edwards 1979). In more oxidizing environments, hydrogen sulfide may be oxidized to valences higher than zero and no elemental sulfur may be formed.

These reactions basically represent only the end products of sulfate reduction and sulfur deposition. Numerous intermediate reactions have been omitted for clarity but are important to understanding the nature of sulfur generation. Regardless of the mechanism of oxidation of the hydrogen sulfide, it appears that the confinement of the hydrogen sulfide to a restricted area where the native sulfur may be deposited and preserved is critical to the generation of a significant sulfur deposit. Dissipation of hydrogen sulfide to the atmosphere or elsewhere will prevent the deposition of economic quantities of sulfur. Similarly, subsequent oxidation of sulfur mineralization, especially from the actions of sulfur-oxidizing bacteria such as *Thiobacillus* sp., may leave calcite replacement bodies barren of native sulfur. Overlying impermeable strata such



Adapted from Kyle and Posey 1991.

Figure 2. Schematic cross section of a salt-dome cap rock showing an idealized sequence of cap-rock lithologies

as shales are generally credited with providing a barrier to hydrogen sulfide migration and later oxidation.

One particular species of sulfate-reducing bacteria, *Desulfovibrio desulfuricans*, is commonly credited with being the most significant contributor to sulfur mineralization, but several species of *Desulfovibrio* are probably involved, as are species of *Clostridium*, *Desulfotomaculum*, and possibly others. These sulfate-reducing bacteria are strict anaerobes, but they can exist and thrive in microenvironments distributed throughout oxidized strata containing aerobic bacteria. The sulfate-reducing bacteria do not degrade hydrocarbons but use only simple organic substrates such as acetate, lactate, pyruvate, fumarate, and formate (Kuznetsov, Ivanov, and Lyalikova 1963; Ivanov 1968; Postgate 1979; Skyring 1987). Some are thought to oxidize methane, but for hydrocarbons to be considered an energy source, aerobic bacteria must be present to generate appropriate substrates. The process of native sulfur deposition from sulfate reduction most likely involves numerous types of bacteria in a complex and evolving ecosystem.

The amount of hydrocarbons necessary to produce a significant sulfur deposit is fairly large. It is thought that 2 to 4 bbl of oil must be consumed for each ton of sulfur deposited (Ruckmick, Wimberly, and Edwards 1979). The actual amount of hydrocarbons required probably varies depending on local geologic conditions.

Concurrent with the generation of hydrogen sulfide and the deposition of sulfur, calcite in multiple generations (sometimes referred to as biocalcite) is deposited as a replacement of the anhydrite and forms the calcite cap rock. Early generations of calcite may be massive and fine grained; later calcite filling veins and vugs is often finely to coarsely crystalline, white to tan, and commonly petroliferous. Much of the calcite cap rock is a breccia containing clasts of wall rock and earlier generations of calcite and

associated minerals. The calcite breccia may be barren of sulfur because of nondeposition, later oxidation, and removal, or perhaps because of remobilization and nearby reprecipitation as described by Nieć (1992).

The role of sulfate-reducing bacteria in the formation of sulfur deposits is supported by isotope studies of both sulfur and carbon. Sulfate-reducing bacteria fractionate the sulfur isotopes and selectively concentrate the light isotope. The sulfur is enriched in ^{32}S , and the remaining sulfate is enriched in ^{34}S . The calcite cap rock is isotopically similar to the carbon in associated crude oil and significantly enriched in ^{13}C with respect to sedimentary limestone (Feely and Kulp 1957; Faure 1977).

Currently 167 onshore salt domes and 180 offshore domes are known in the Gulf Coast province of Texas (excluding south Texas) and Louisiana (G. Eager and B. Salisbury, unpublished data, 1991). Of the 167 onshore domes, 90 are shallow enough to be prospective for sulfur, and 24 of these domes produced sulfur (included in Table 3); 12 produced more than 5 Mt, 5 produced more than 10 Mt, and 3 produced more than 20 Mt. Mexico was also a significant producer of salt dome-hosted sulfur, but published data on Mexican production and geology are not extensive (Salas 1991). Two of the most important salt domes in the Gulf Coast, Boling dome and Main Pass, are described in the following sections.

Boling Dome

Boling dome is located in Wharton County, Texas, about 100 km southwest of Houston. Discovered in 1922, Boling operated from 1928 to 1993. Operated by Texasgulf Inc., Boling produced more than 82 Mt of sulfur from more than 8,000 wells (Samuelson 1986, 1992; Seni and Kyle 1986, 1987). When the mine closed, sulfur production was at a rate of about 361 tpd, much less than the peak production in 1948 of 8,510 tpd. A cogeneration plant, opened in 1985, generated electricity that was marketed to a local utility. The cogeneration plant kept Boling dome profitable longer than would have otherwise been possible.

Boling dome is the largest salt dome in Texas with an area of 38 km² at the -1,219 m elevation contour. The minimum depth to cap rock is 117 m, and the margins of the cap rock plunge steeply below a depth of 1,524 m.

The cap rock is divisible into three zones: an upper barren calcite zone, a middle calcite/sulfur zone, and a lower anhydrite zone. The transitional gypsum zone, present at other domes, is poorly developed at Boling. The calcite cap rock is composed of light- to dark-gray, fine- to medium-grained calcite that has been brecciated and veined with crystal line calcite. Rhythmically banded calcite, common at other domes, is rare at Boling except near the base of the calcite cap rock. The anhydrite cap rock is dense, dark gray, and composed of interlocking euhedral anhydrite grains cemented by anhydrite. Uncemented anhydrite sands are locally present at the contact with the underlying salt. The top of the salt diapir is relatively flat (Figure 3).

Relatively large amounts of detrital material are incorporated within the cap rock. Lenses of calcitic sandstone and shale, transported to the surface with the salt, are present in both the calcite and anhydrite cap rock, and locally hamper mining operations.

The main sulfur deposit was within the calcite/sulfur zone in the southeastern third of the dome (Figure 4). The richest areas of sulfur mineralization roughly corresponded to the thickest calcite cap rock, which ranges from 0 m to more than 122 m thick. Some wells in the thickest calcite intersected sulfur mineralization averaging 20% sulfur by volume for the entire 122-m interval.

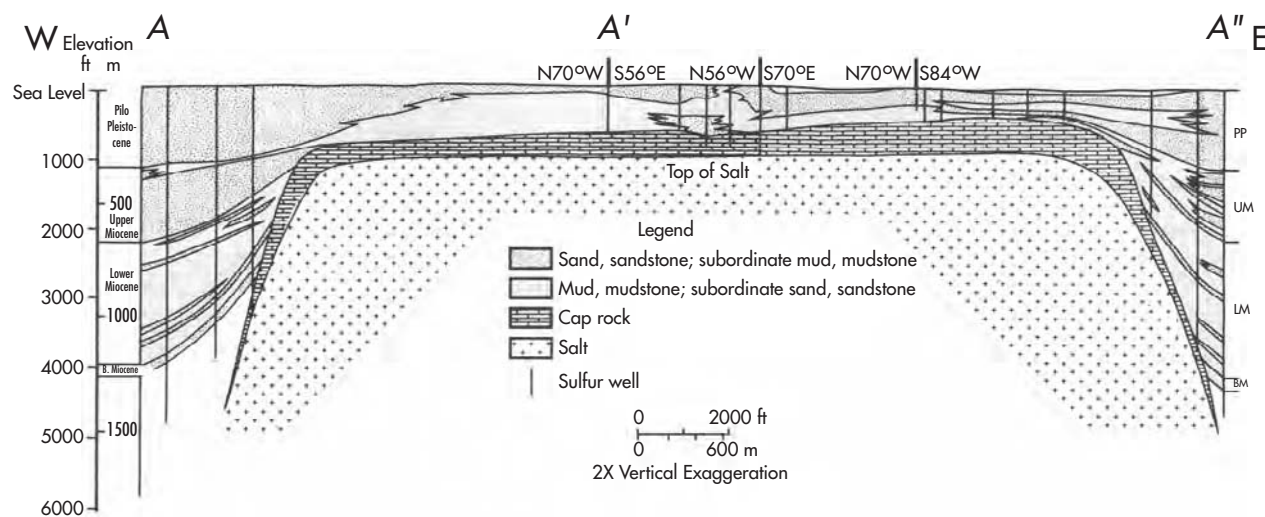
Accessory minerals include barite, pyrite, hauserite, sphalerite, and galena. The barite occurs as filled cavities and as massive

Table 3. Production of Frasch sulfur in the United States and Mexico by mine and company, 1894 through 2000

Mine	Company	Years Operated	Total Output, kt
United States			
Sulphur Mine, Louisiana	Union Sulphur Co.	1894–1925	9,560
Bryan Mound, Texas	Freeport Sulphur Co.	1912–1935	5,080
Big Hill Mound, Texas	TexasGulf Sulphur Co.	1919–1936, 1965–1970	13,100
Hoskins Mound, Texas	Freeport Sulphur Co.	1923–1955	11,100
Palangana Dome, Texas	Duval Corp.	1928–1935	241
Boling Dome, Texas	Union Sulphur Co.	1929–1993	>82,000
Long Point Dome, Texas	TexasGulf Sulphur Co.	1930–1938	408
Lake Peignuer, Louisiana	Jefferson Lake Sulphur Co.	1932–1936	438
Grande Ecaille, Louisiana	Freeport Sulphur Co.	1933–1978	41,000
Boling Dome, Texas	Duval Corp.	1935–1940	580
Clemens Dome, Texas	Jefferson Lake Sulphur Co.	1937–1960	3,020
Orchard Dome, Texas	Duval Corp.	1938–1970	5,580
Long Point Dome, Texas	Jefferson Lake Sulphur Co.	1946–1982	8,710
Moss Bluff Dome, Texas	TexasGulf Sulphur Co.	1948–1982	9,460
Starks Dome, Texas	Jefferson Lake Sulphur Co.	1951–1960	853
Bay Ste. Elaine, Louisiana	Freeport Sulphur Co.	1952–1959	1,150
Spindletop Dome, Texas	TexasGulf Sulphur Co.	1952–1976	9,990
Garden Island Bay, Louisiana	Freeport Sulphur Co.	1953–1991	28,100
Damon Mound, Texas	Standard Sulfur Co.	1953–1957	142
Nash Dome, Texas	Freeport Sulphur Co.	1954–1956	153
Chacahoula Dome, Louisiana	Freeport Sulphur Co.	1955–1962	1,220
Fannett Dome, Texas	TexasGulf Sulphur Co.	1958–1977	3,530
High Island Dome, Texas	United States Sulphur Co.	1960–1962	38
Grande Isle, Louisiana	Freeport Sulphur Co.	1960–1991	26,800
Lake Pelto, Louisiana	Freeport Sulphur Co.	1960–1976	5,710
Sulphur Mine, Louisiana	Union Texas Petroleum Co.	1966–1970	69
Nash Dome, Texas	Phelan Sulphur Co.	1966–1969	174
Chacahoula Dome, Louisiana	U.S. Oil of Louisiana, Ltd.	1967–1970	156
Fort Stockton, Texas	Atlantic Richfield Co.	1968–1985	1,860
Fort Stockton, Texas	Duval Corp.	1968–1970	588
Caminada Pass, Louisiana	Freeport Sulphur Co.	1968–1969, 1988–1994	1,600
Bully Camp, Louisiana	TexasGulf Sulphur Co.	1968–1978	1,750
Culberson, Texas	Duval/Pennzoil Sulphur Co.	1969–1999	45,000
High Island Dome, Texas	Pan American Petroleum Corp.	1969–1971	111
Lake Hermitage, Louisiana	Jefferson Lake Sulphur Co.	1968–1972	448
Comanche Creek, Texas	TexasGulf Sulphur Co.	1975–1983, 1988–1989	1,730
Caillou Island, Louisiana	Freeport Sulphur Co.	1980–1984	803
Phillips Ranch, Texas	Duval/Pennzoil Sulphur Co.	1980–1982	86
Main Pass, Louisiana	Freeport Sulphur Co.	1992–2000	10,000*
Mexico			
San Cristobal	Mexican Gulf Sulfur Co.	1953–1957	165
Jaltipan	Azufrera Panamericana S.A.	1954–1992	>34,000
Salinas	Cia. De Azufre Veracruz	1956–1969	3,930
Noplapa	Cia. Exploradora del Istmo	1957–1960, 1967–1971	681
Texistepec	Central Minera S.A.	1959–1961	9
Texistepec	Cia. Exploradora del Istmo	1971–1993	>12,500
Coachapa	Azufrera Panamericana S.A.	1981–1992	>1,990
Otapan	Azufrera Panamericana S.A.	1987–1992	>89

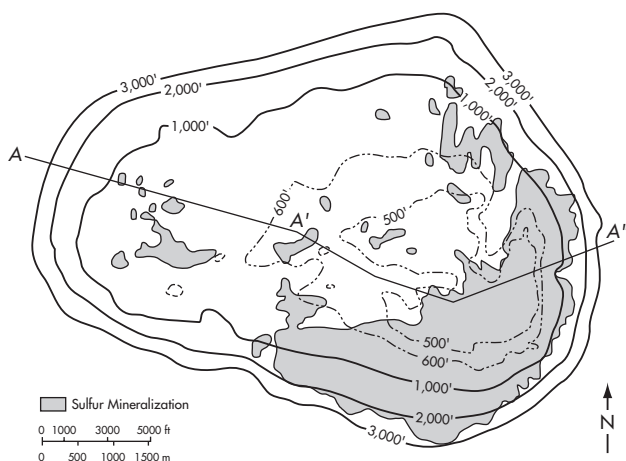
Adapted from Wessell 1992.

* Estimated.



Adapted from Seni and Kyle 1986.

Figure 3. West-to-east cross section of cap rock at Boling dome, Wharton County, Texas (location of cross section is shown in Figure 4)



Source: Samuelson 1992.

Figure 4. Depth to top of cap rock (in feet) and the location of sulfur mineralization at Boling dome, Wharton County, Texas (cross section A-A' is shown in Figure 3)

bodies in the upper part of the calcite cap. The sulfide minerals are concentrated along the east flank of the dome but are not present in quantities of economic interest.

Main Pass

The Main Pass deposit, located in Main Pass Block 299 in U.S. federal waters in the Gulf of Mexico, about 27 km east of Venice, Louisiana, was discovered in 1988 by a joint-venture effort of Freeport-McMoRan Inc., IMC Fertilizer Inc., and Felmont Oil Corp. (which later became Homestake Sulphur Co.). The deposit contained proven sulfur reserves of 68 Mt. The Main Pass deposit is situated in about 63 m of water (Anon. 1991a; Ackerman 1992; Edwards et al. 1992).

Before exploration for sulfur, Chevron discovered oil and gas in strata flanking the salt dome. Freeport's sulfur drilling in 1988 intersected oil and gas reserves within the cap rock and overlying

strata. Freeport purchased Chevron's hydrocarbon reserves and consolidated hydrocarbon and sulfur interests under the Main Pass Joint Venture, which produced sulfur and hydrocarbons. Recoverable oil and gas reserves were 39.4 million bbl and 0.2 Gm³, respectively. The stacked sulfur/oil/gas deposits presented challenging engineering problems for the development staff.

The Main Pass 299 salt dome is roughly circular in plan (Figure 5) with an approximate diameter of 3,000 m at the 900-m subsea contour (Ackerman 1992; Edwards et al. 1992). The top of the dome (about 400 m below sea level) is relatively flat. Cap rock extends over about 680 ha and consists of calcite and anhydrite. Total cap-rock thickness varies from about 40 to 160 m. Sulfur-bearing cap rock up to 70 m thick was intercepted in the exploration program.

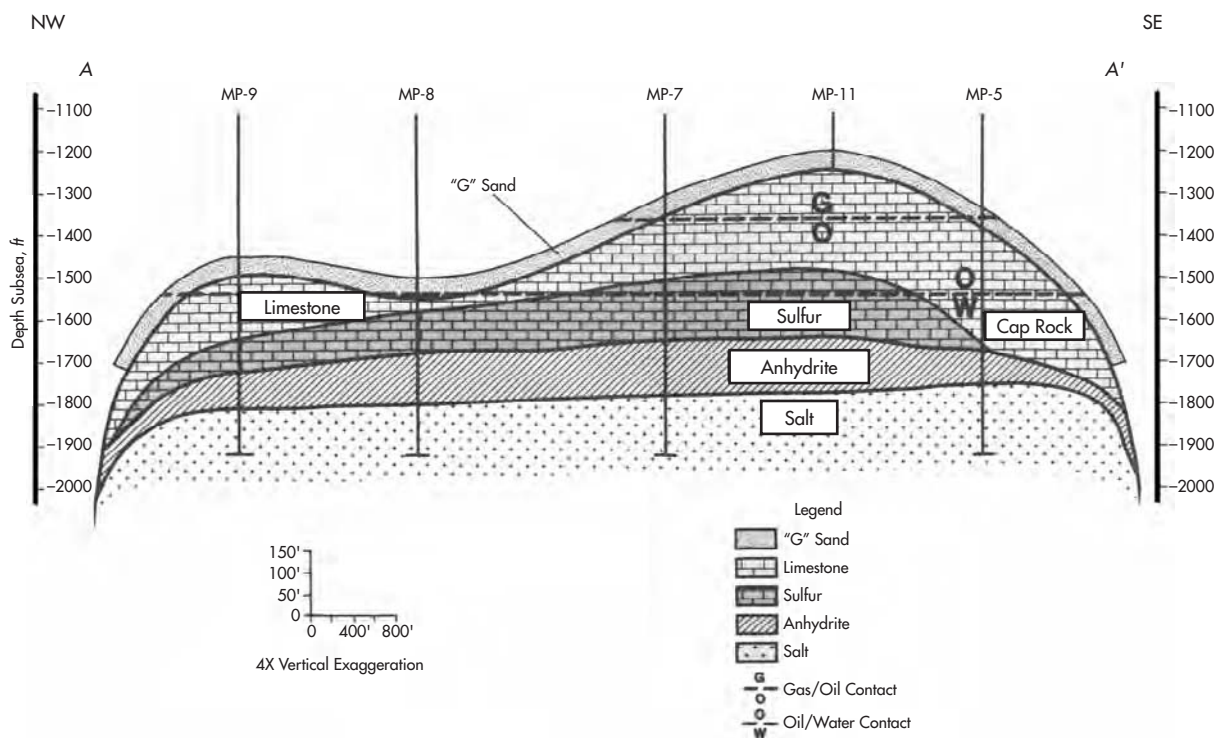
Plans for the mine complex consisted of 15 offshore sulfur mining platforms and related facilities. Production began in 1992 and reached full production in 1993. Production was expected to reach 2 Mtpy over a mine life of 30 years, but developments in the sulfur industry and technical problems forced the closure of Main Pass mine in 2000.

Stratiform Deposits

Stratiform deposits of native sulfur associated with bedded anhydrite and gypsum are relatively common in oil-producing evaporite basins throughout the world, but large deposits suitable for mining are few. Significant stratiform sulfur deposits have been mined in Iraq, Italy, Poland, Russia, western Texas, and Ukraine. Similar occurrences are known in many countries, including Argentina, Angola, Canada, China, Egypt, England, Greece, Iran, Israel, northern Mexico, Romania, Spain, Syria, Turkey, and numerous others. Several deposits that were important operations are described here.

The origin of the stratiform deposits is very similar to that of the salt dome-hosted deposits described previously. Shallow anhydrite or gypsum beds are replaced by biopigenetic calcite and sulfur through the actions of sulfate-reducing bacteria in the presence of oil and migrating meteoric water.

Many of the stratiform deposits are in arid regions where shallow evaporites are more likely to be preserved and are commonly proximal to a major river or other recognized source of meteoric



Source: Edwards et al. 1992.

Figure 5. Cross-section A-A', Main Pass mine, offshore Louisiana (depths shown in feet from sea level)

water. The deposits are usually at the edges of the evaporite basins and are within or adjacent to structures (such as drape folds, anticlines, and faults) that have focused hydrocarbon migration or surface water channeling and evaporite dissolution. As described here, these deposits are difficult exploration targets and are often found by accident during the drilling of oil wells.

Western Texas

Stratiform sulfur deposits are widespread in the Permian Basin of western Texas. Sulfur was the most recently produced from Pennzoil's Culberson mine and also was produced in the past from several smaller deposits. The Permian Basin was the site of intense exploration, most notably in the late 1960s. There are two known sulfur districts in western Texas: the Ft. Stockton District and the Rustler Springs District. The Ft. Stockton District is located on the Central Basin platform that separates the Midland and Delaware basins (Figure 6). The Rustler Springs District and the Culberson mine are located in the Delaware basin portion of the Permian Basin. Sulfur in the Ft. Stockton District occurs with calcite and replaces anhydrite of the Permian Salado, Tansill, and Yates formations. The host formations, as well as formations above and below, drape over the Pennsylvanian-Permian Central basin platform and define a northwest-trending anticline locally termed the Heiner anticline (Figure 7). Structural highs along the axis of the Heiner anticline served as foci for hydrocarbon entrapment and subsequent sites of sulfate reduction and sulfur mineralization (Zimmerman and Thomas 1969; Ellison 1971; McNeal and Hemenway 1972; Hentz, Price, and Gutierrez 1989).

Native sulfur was first noted in the Ft. Stockton District in an oil well drilled in about 1900 (Adkins 1927). Subsequent oil drilling noted other occurrences of sulfur, but it was not until the exploration

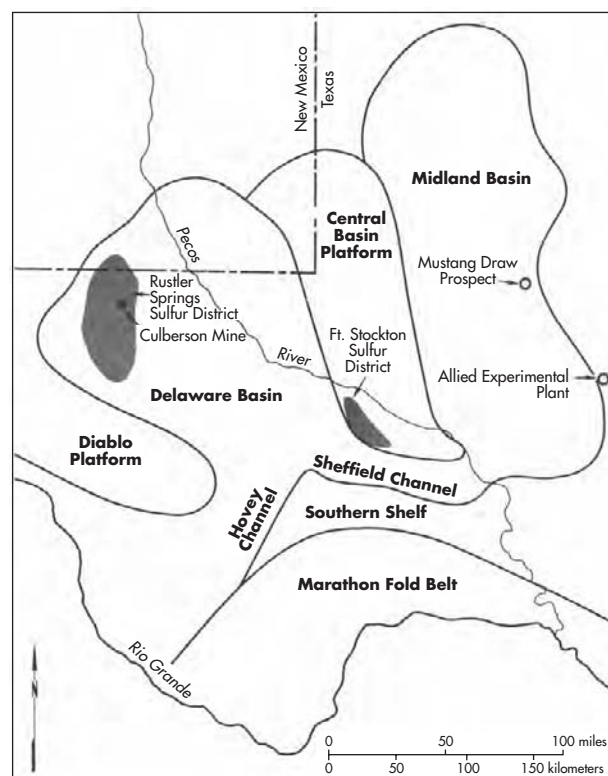
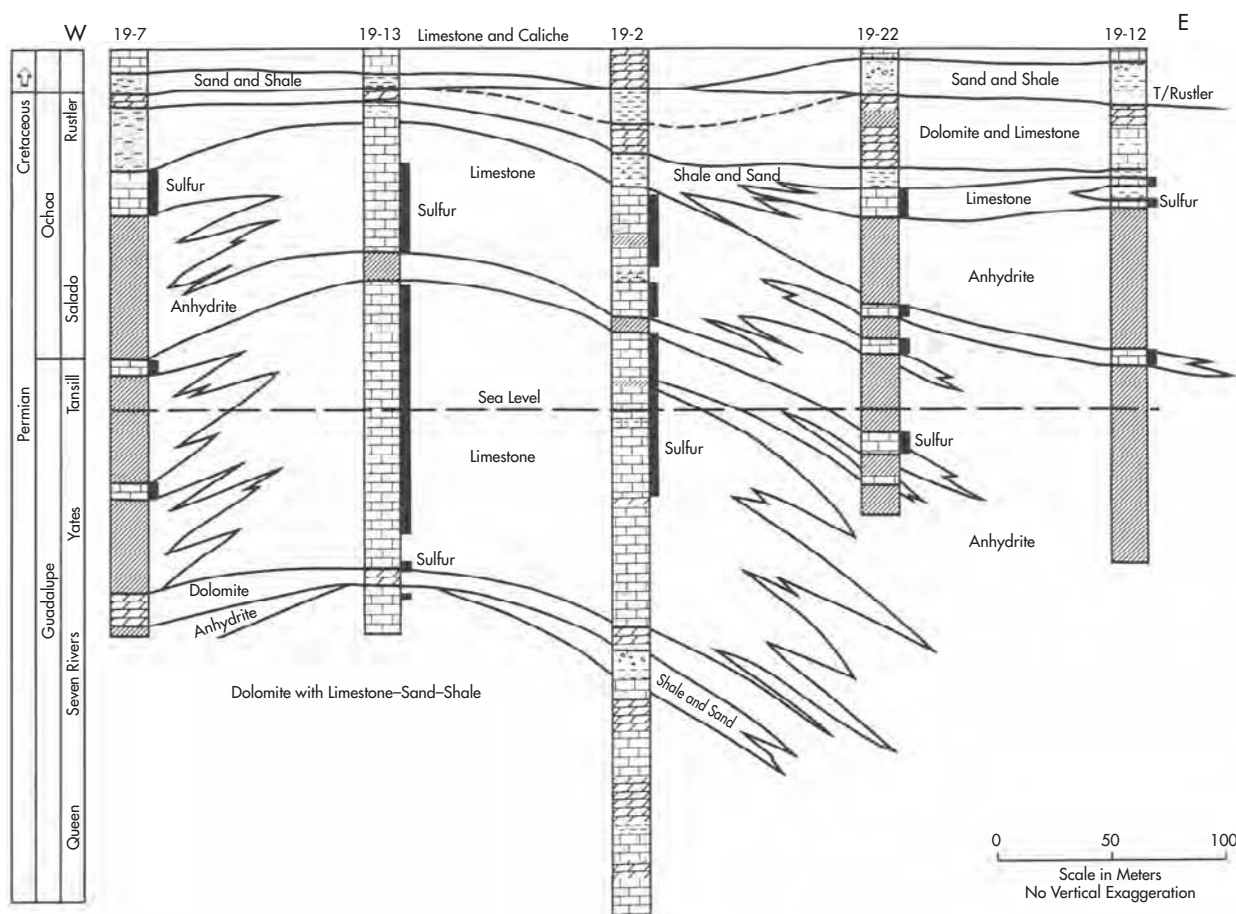


Figure 6. Location of sulfur districts and deposits in the Permian Basin, Texas, with respect to structural and stratigraphic features of Pennsylvanian and Permian age



Adapted from Zimmerman and Thomas 1969.

Figure 7. Cross section showing stratigraphic distribution of sulfur at Ft. Stockton mine, Pecos County, Texas

surge of the mid-1960s that the Ft. Stockton deposit was discovered. The majority of the district is covered by Quaternary alluvium, and the sulfur mineralization is not exposed at the surface.

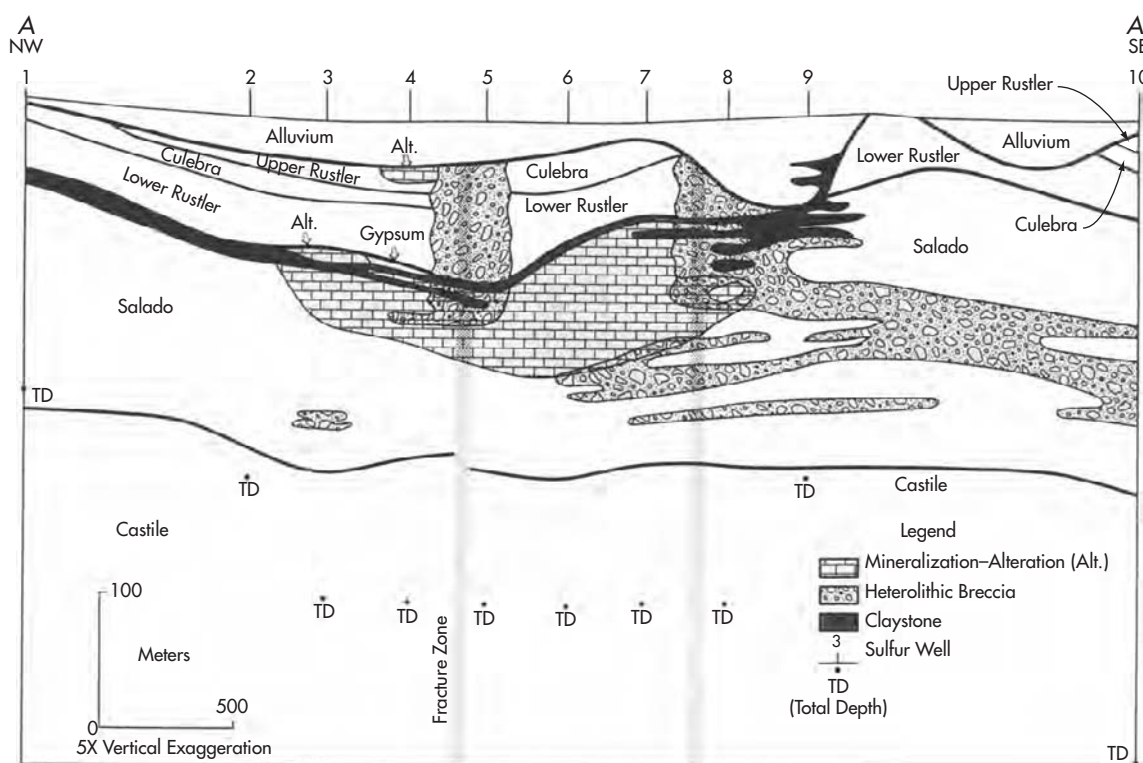
Production from the Ft. Stockton District has been limited to three small Frasch mines: Duval's (Pennzoil's) Heiner mine, Sinclair's (Atlantic Richfield's) Ft. Stockton mine, and Texasgulf's Comanche Creek mine. The Comanche Creek deposit is thought to have been the largest with 7.6 Mt of original in-place sulfur, but none of the deposits produced more than 2.0 Mt.

The Rustler Springs District contains numerous small sulfur deposits, and one very large deposit that produced Frasch sulfur until 1999—Pennzoil's Culberson mine. The Culberson mine had an operating capacity of 2.5 Mtpy, but the production rate toward the end of operation was as much lower (Crawford 1990). About 45 Mt of sulfur were produced from the mine. Other production from the Rustler Springs District was limited to the Phillips Ranch deposit, from which 86,360 t were produced from 1980 to 1982. Addvest Minerals built another Frasch operation at the Phillips Ranch site, but never started production because economic conditions were never favorable (Guilinger and Nestlerode 1992).

Mineralization at the Culberson mine is hosted by bedded anhydrite and gypsum in the Ochoan Castile, Salado, and Rustler formations, but most of the ore is within the Salado Formation (Smith 1980; Mussey and Tyree 1985; Hentz, Price, and Gutierrez

1989; Crawford 1990; Wallace and Crawford 1992). The sulfur occurs with calcite and accessory barite and celestite in three general modes (Crawford 1990): (1) as microcrystalline disseminations in gray diagenetic (replacement) limestone or cave-fill breccias, (2) as orthorhombic crystals lining cavernous voids in the replacement limestone, and (3) as coarsely crystalline crusts or agglomerates that nearly fill all voids in the limestone. The diagenetic limestone (calcite) is a product of biogenic replacement of anhydrite and gypsum solution collapse breccias, and original breccia textures are commonly preserved. Similarly, calcite and sulfur locally replace and preserve varves in the Castile evaporite. The ores commonly contain up to 30 wt % sulfur and average about 25% porosity.

The Culberson ore body is elliptical and extends from 100 to 720 m below the surface. The ores are intimately associated with dissolution collapse and cave-fill breccias (Figure 8) that preferentially occur along selected horizons in the Salado Formation (Miller 1992; Wallace and Crawford 1992). The collapse and cave breccias presumably channeled both hydrocarbons and oxygenated meteoric water, and led to the reduction and replacement of evaporite-bearing breccia clasts and adjacent evaporitic strata. The dissolution collapse and cave breccias appear to be localized along notheast-trending Tertiary normal faults and joints. Rarely visible at the surface, such fractures can be inferred from the linear distribution of collapse sinks, minor offsets indicated by oil-well data and sulfur-related



Source: Wallace and Crawford 1992.

Figure 8. Cross section A-A', Culberson mine, Culberson County, Texas

alteration features. The presence of a residual silty clay cap over the Culberson deposit appears to have been critical to the preservation of hydrogen sulfide and to the generation and preservation of native sulfur (Figure 8).

The presence of sulfur in the Rustler Springs area has been known since 1854. Numerous surface occurrences of sulfur and erosional remnants of bioepigenetic calcite (Kirkland and Evans 1976) are known, and there were several attempts beginning in the early 1890s to mine surface ores (Porch 1917; Evans 1946). Duval Corporation discovered the Culberson mine in 1967 near the site of some old surface works.

Poland

Native sulfur deposits in Poland occur in Upper Miocene strata on the northern (platform) border of the Carpathian foredeep (Figure 9). Sulfur occurs in bioepigenetic calcite replacements of a gypsum unit of Middle Badenian age and is accompanied by barite and celestite. The sulfur deposits are located on uplifted blocks near the northern margin of the Carpathian foredeep at depths from a few meters to about 360 m (Pawlowski, Pawlowska, and Kubica 1979; Anon. 1988, 1990a; Preisner 1991; Nieć 1992).

The sulfur-bearing rocks vary in thickness from a few meters to more than 40 m, and they are subhorizontal. The host strata in nearly the entire region are covered by Quaternary deposits of variable thickness.

The sulfur content of the ore is quite variable and ranges from a few percent up to more than 50% in selected samples. Rocks containing less than 5% sulfur are considered barren. The average sulfur content of individual deposits varies from 22% to 33%. Ore textures commonly mimic textures in the original gypsum.

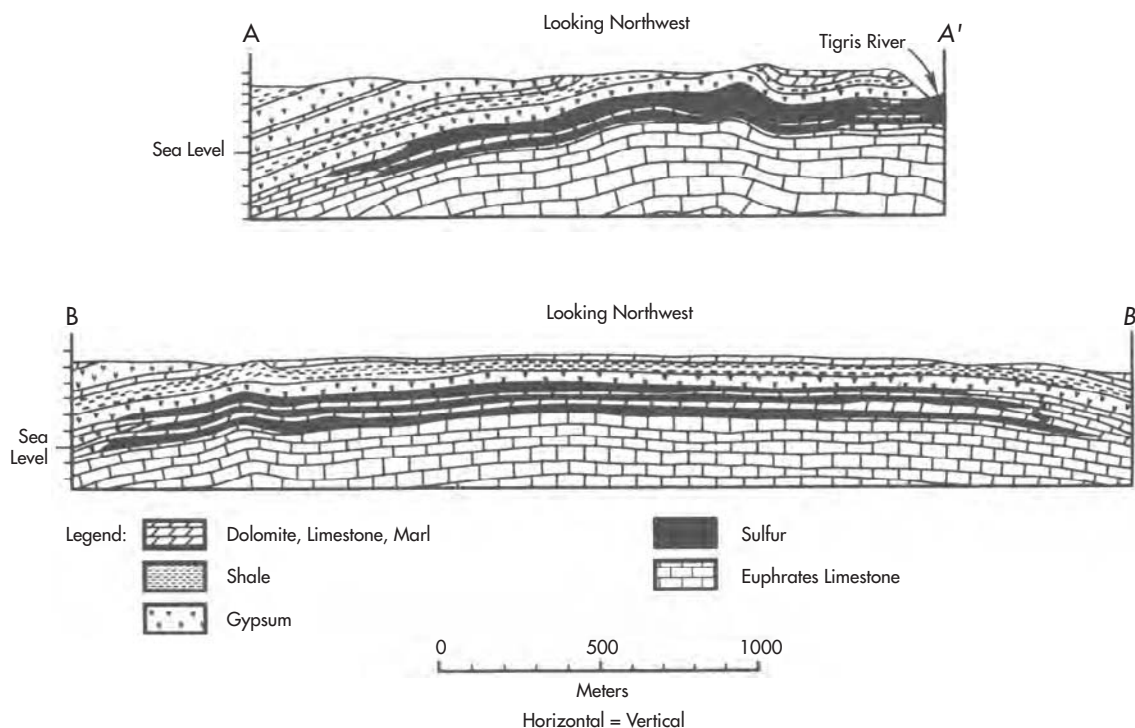
Small surface deposits of native sulfur have been exploited on a limited scale for hundreds of years. The earliest documented sulfur mining in Poland occurred in 1415, but it was not until 1953 that exploration efforts resulted in a discovery of sulfur-bearing limestone in the subsurface near Tarnobrzeg, which became the center of sulfur mining.

There were two main sulfur-producing areas in Poland: the Staszow-Tarnobrzeg region containing four deposits and the Lubaczow Area where one deposit is dissected by the Polish-Ukrainian border. The regional trend of sulfur mineralization follows the northern margin of the Carpathian foredeep into Ukraine, where sulfur was mined at several deposits using both Frasch and open-pit methods. Westward from Staszow-Tarnobrzeg, only small sulfur deposits have been found, some of which were mined before 1921.

The known Polish sulfur deposits together contain approximately 600 Mt of demonstrated sulfur reserves and about 500 Mt of inferred and hypothetical resources (Nieć 1992). Open-pit mining was begun in 1956 at the Piaseczno mine, and Frasch mining modified to fit the unconfined ores of the Polish deposits (the thermohydrodynamic or hydrodynamic method) has been successfully applied since 1966 (Anon. 1986b). One hydrodynamic mine remains in production. At its peak, total annual sulfur production reached more than 5 Mtpy, but the annual capacity at the last active mine is only 800 ktpy. The total recovery from the sulfur deposits varied between 40% and 70%.

Iraq

Sulfur deposits in Iraq are found in the folded portion of the Mesopotamian depression that separates the nappes and the Zagros



Adapted from Barker, Cochran, and Semrad 1979.

Figure 11. Cross section A–A' and B–B', Mishraq deposit, northern Iraq (locations of cross sections shown in Figure 10)

and molten sulfur were observed to be pouring out of the bluff and into the Tigris River, causing severe contamination (Babbitt 1991). Fluids also leaked into adjacent barren structures as far as 3 km away. This indicated excessive costs from fluid loss and overheating of the host rock.

The inclusion of carbon, hydrocarbons, and ash in Mishraq sulfur was a problem in marketing Iraqi Frasch sulfur. Early filtering systems were inadequate and routinely resulted in losses of up to 50%. Efforts by Freeport under contract to MSSE to construct a filtering plant were halted by Iraq's 1990 invasion of Kuwait. The resulting war led to the destruction of some recovered sulfur plants, but there were no reports of significant damage to the Mishraq facility.

During Iraq's war with Iran in the 1980s, production at Mishraq varied widely. In 1981, total Iraqi sulfur production (of which about 80% comes from Mishraq) was 145 kt; in 1987, it was 850 kt (Anon. 1989). Before the invasion of Kuwait, Iraq was producing about 1.8 Mtpy, with Mishraq producing about 1.4 Mtpy. MSSE had previously announced that production at Mishraq would expand to 2.0 Mtpy by 1991, but continuing political and economic instability adversely affected production through 2004. If the country achieves stability, a large increase in sulfur production could occur, possibly with the assistance of the Polish sulfur producers.

Oxidative Deposits

Ruckmick, Wimberly, and Edwards (1979) also included a category of deposits that they termed oxidative. In the strictest sense, almost all native sulfur deposits are oxidative in that they are formed from the oxidation of hydrogen sulfide, but this category properly includes only those deposits not associated with volcanic or biogenic sources of sulfur. They probably are formed as a result of the

oxidation of hydrogen sulfide from a remote source, resulting in native sulfur deposition in existing voids in porous host rock. The hydrogen sulfide may originate in high-temperature diagenetic settings, such as those associated with thermal maturation of crude oil and thermochemical sulfate reduction (Machel 1992), but the source of the hydrogen sulfide is commonly difficult to identify. Oxidative deposits are widespread, but they are generally small and are not currently used as a source of sulfur.

Oxidative deposits of native sulfur have been described in Lechuguilla Cave, located in the Capitan reef at the northern margin of the Delaware Basin (near Carlsbad Caverns, northeastern New Mexico), as well as in western Texas. At Lechuguilla Cave, hydrogen sulfide dissolved in basinal brines was oxidized to native sulfur and is intimately associated with speleogenesis there and at Carlsbad Caverns (Spirakis and Cunningham 1992).

Numerous occurrences of native sulfur in porous carbonate strata of the San Andres Formation, Permian Basin, western Texas, are also probably oxidative deposits of this type. One such deposit, the Mustang Draw occurrence in Glasscock County, Texas, was a site of exploration activity from 1987 to 1990. A resource of 7.4 Mt of sulfur was identified in rock that locally contains 6.5% sulfur by volume (Ruckmick et al. 1992). A similar occurrence in the Permian Clearfork Formation south of Mustang Draw was the site of an unsuccessful pilot Frasch test in 1968 (Zimmerman and Thomas 1969; Ellison 1971).

Volcanic Deposits

Sulfur of volcanic origin is probably the most widely distributed of native sulfur deposits. Deposits of this type are known in nearly all volcanic regions of the world, particularly in the Pacific Rim region: deposits are present in western North and South America,

Central America, the Kamchatka Peninsula, the Kurile Islands, Japan, the Philippines, Indonesia, Taiwan, and New Zealand. Deposits are also present in volcanic regions in western Turkey, Greece, Italy, and elsewhere.

Volcanic sulfur deposits can be subdivided into four types by mode of emplacement (Barker 1983; Níeć 1986a):

1. Impregnation and replacement deposits, usually formed by the actions of hot-acid springs that are rich in sulfurous gases, often in tuffs and volcanic breccias, with sulfur in irregular or lens-shaped or ebbodies aligned along fracture zones; accompanied by sulfides and alteration (aunitization, argillization, silicification) that locally completely replaces the host rock; economically the most important of the volcanic deposits
2. Sublimation deposits, formed by gaseous or fumarolic activity near volcanic craters, where sulfur coats fractures and cavities near the surface in small deposits that are locally mined
3. Sedimentary deposits, formed by precipitation of sulfur in hot crater lakes
4. Sulfur flows, small-flow deposits that probably originated from older deposits that were remelted; of local importance only

Volcanic sulfur deposits are usually found in tuffs, lava flows, and other volcanic rocks but are also found in sedimentary, intrusive, and other rock types in volcanic regions.

Volcanic deposits have been mined in the past in many areas, but significant production of volcanic sulfur has been limited to Japan, Turkey, Mexico, Italy, and the Andean countries of South America. Mining methods used include standard underground and surface mining methods as described here.

Mined volcanic sulfur dominated Japanese production until the mid-1960s, when recovered sulfur challenged its importance (Anon. 1985b). The mining of volcanic ores in Japan ceased completely in the mid-1970s. Sulfur deposits in a highly altered rhyolite dike near Keciöorlu in southwest Turkey supplied much of Turkey's domestic demand in the past. In the United States, several deposits have been mined to supply local needs, including the Leviathan deposit in Alpine County, California, which was mined from 1953 to 1962 to supply sulfuric acid for Anaconda's Yerington, Nevada, copper operation. More recently, numerous projects have been initiated to recover sulfur from volcanic ores, including sites in South America (Anon. 1987a), Romania (Fodor et al. 1989), the Philippines (Anon. 1986a), Utah (Slim 1986), and California (Ward 1992).

In comparison to biopigenetic deposits, volcanic sulfur deposits are generally small. Few contain more than 10 Mt of reserves, but some (such as the Matsou deposit in Japan) are significantly larger. Volcanic deposits are also at a disadvantage because they are sometimes located far from markets and economical transportation. In addition, volcanic sulfur is commonly impure and contains elements (such as arsenic, selenium, and tellurium) that make it unsuitable for some applications. Some ores cannot be economically processed using existing technology. Commercial interest in volcanic deposits is high only when premium or protected markets exist.

EXPLORATION TECHNIQUES

Exploration for native sulfur deposits is a difficult task, especially for Frasch-minable deposits. There is often little indication at the surface of subsurface sulfur deposits, and surface exposures of sulfur are rare because of the instability of elemental sulfur (it is readily oxidized to soluble sulfate). Indirect indicators may be all

the geologist has to suggest the presence of sulfur, and subsequent drilling may be necessary to fully test such blind targets.

For biopigenetic deposits, the genetic relationship between hydrocarbons and sulfur dictates that exploration be directed to appropriate host rocks in areas that contain oil or gas. For this reason, sulfur exploration commonly makes extensive use of oil and gas well data, so much so that sulfur exploration is sometimes almost indistinguishable from efforts to locate shallow oil and gas reserves. The sulfur geologist is essentially looking for a potential oil trap adjacent to or within evaporitic strata that has been biodegraded and is now replaced by calcite and sulfur. Exploration drilling for sulfur sometimes intersects oil and gas accumulations, just as oil wells commonly intersect sulfur shows.

Barker, Cochran, and Semrad (1979) and Níeć (1986a) summarized the general conditions necessary for the generation of stratiform sulfur deposits:

1. Thick anhydrite or gypsum beds, generally in the border regions of evaporite basins
2. Proximity to hydrocarbon accumulations in correlative or underlying strata
3. Hydrodynamic communication between sulfates and hydrocarbons, often along joints, faults, solution-derived porosity, or other structural or stratigraphic pathways
4. A stratigraphic or structural trap (anticlines, monoclines, horsts, etc.) to contain the precursors of the sulfur-forming reaction
5. Serial, coincident, or coexisting reducing and oxidizing environments where hydrocarbons are biodegraded and sulfate is reduced and then oxidized to sulfur
6. An overlying barrier to fluid migration capable of containing reaction products and preventing later oxidation of sulfur

Tools useful in locating stratiform deposits are few and locally unreliable. Standard field and photogeologic techniques are commonly used to identify prospective structures and surface alteration. Detailed mapping such as that described by Wessel (1992) is valuable where surface exposures are adequate. Surface occurrences of sulfur or biopigenetic calcite (verified by isotope studies) are most encouraging, as are occurrences of sulfur and biopigenetic calcite in oil and gas well cuttings. Anomalous occurrences of silica and iron staining or bleaching are sometimes considered evidence of leakage of reactants from below. A number of surface geophysical surveys (including gamma ray spectrometer, spontaneous potential, resistivity, induced polarization, and ground and airborne magnetic) are used to locate hydrogen sulfide plumes and alteration halos (Salisbury 1992). Thermal infrared, remote sensing, and seismic data have been locally useful, and some surface geochemical techniques (soil gas, airborne gas spectrometry, etc.) have been tested.

Gravity surveys are routinely used to locate stratiform sulfur deposits because of the void development and brecciation associated with sulfur mineralization. Unaltered anhydrite has a density of about 2.96, and sulfur ore bodies vary in density from 2.00 to 2.40, yielding a potentially measurable negative gravity anomaly. The amount of variation depends on the nature of the sulfur mineralization, void development, depth of mineralization, and numerous unknown stratigraphic and structural variables. Gravity data are best used in combination with other data, but interpretation is always difficult (Schmoker 1979; Salisbury 1992). Actual use has resulted in few exploration successes.

Downhole logs of oil and gas wells are commonly used to establish formation control and identify low-density zones that may

indicate sulfur mineralization. The use of these logs is limited where well density is low or shallow strata are not logged.

Salt domes present perhaps the most straightforward exploration problem. The locations of most salt domes are known in areas such as the Gulf Coast of the United States and Mexico as a result of past oil exploration efforts. In the United States, the onshore domes have been intensely explored, and little potential remains for exploration success. Many offshore domes, however, remain untested for sulfur, and the likelihood of another discovery like the Main Pass remains high. Given that the location of a specific salt dome is known, the prudent sulfur prospector could evaluate its potential based on the depth and thickness of cap rock, the presence (if known) of calcite cap rock, and the presence (if any) of shows of mineralization or alteration in oil wells. Gravity and seismic data can be used to define the shape of the cap rock. Gravity data can also indicate potential ore bodies in the cap rock, but again, the interpretation of gravity data is often difficult. Oil-well shows of sulfur and bioepigenetic calcite are the most commonly used guides to mineralization. Hydrogen sulfide springs may be present at the surface, but they are not reliable indicators of mineralization. Other surface indications and techniques previously described are often not applicable, particularly in the Gulf Coast.

Exploration for volcanic sulfur follows the more conventional style associated with exploration for hydrothermal deposits. Similar to bioepigenetic deposits, some volcanic deposits are discovered by accident during metals exploration (Ward 1992). Exploration for other sources of sulfur, such as pyrites and sour gas, is uncommon because they generally supply sulfur only as a by-product.

For many sulfur deposits, the most successful exploration tool is the drilling rig. Nevertheless, great care must be taken to correctly describe and interpret cuttings, core, and other drilling data. There is no substitute for an observant and skilled field geologist.

MINING AND PROCESSING OF NATIVE SULFUR ORES

Sulfur mining uses three different mining techniques: conventional underground methods, conventional open-pit methods, and the Frasch mining (or underground melting) method. The last method is specific for sulfur owing to the low temperature at which sulfur melts. Most mined sulfur has been obtained through Frasch mining; most of the remaining sulfur has been recovered using surface mining techniques, and very little has been obtained by underground mining methods (Níeć 1986b).

For surface and near-surface sulfur ores, surface mining methods predominate, but conventional underground methods also are used, particularly in steeply dipping volcanic deposits. Techniques used include open pit, tunneling, room-and-pillar, cut-and-fill systems, and various forms of stoping. These methods are generally confined to shallow high-grade ores with no overlying impermeable barrier that might allow use of the less costly Frasch mining technique. Underground mining techniques are seldom used because of relatively high costs and because of technical problems related to the common abundance of subsurface water and hydrogen sulfide. Ore recovered from surface and underground mines is processed to separate the sulfur from the host rocks and associated contaminants by various combinations of melting, distillation, agglomeration, flotation, and solvent extraction (Dale 1981; Fodor et al. 1989).

Herman Frasch, the research and development director for Standard Oil Co. and the founder of the Union Sulphur Co., devised the Frasch mining process. First used in 1894 at the Sulphur Mine dome in Louisiana, the Frasch technique is now used to extract native sulfur from salt domes in the United States and Mexico, and (with local modifications) from stratiform deposits in western Texas, Poland, the former U.S.S.R., and Iraq.

The Frasch process capitalizes on several characteristics of sulfur—the low melting point (about 115°C), its insolubility and immiscibility in water, and a specific gravity of 1.8. Basically, the process involves heating water to about 165°C and pumping the heated water through the deposit. The heat from the water melts the sulfur, which sinks and accumulates in a pool below the hot water. The sulfur is then lifted with air out through nested pipes in the same hole used to inject the water.

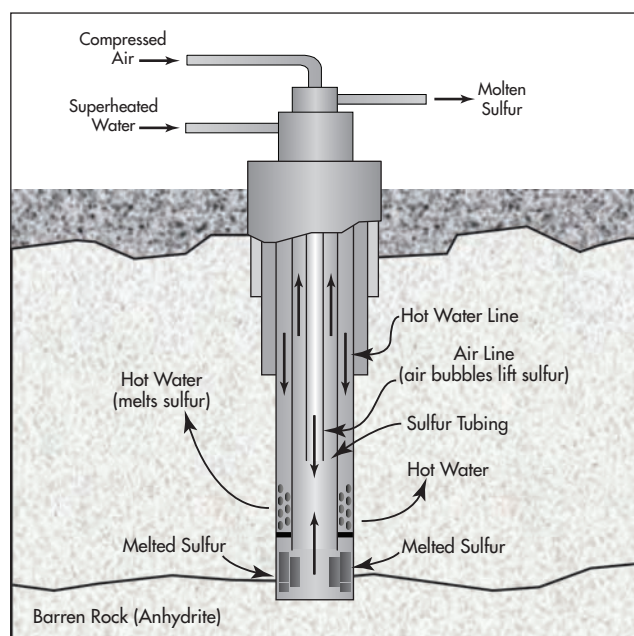
Requisites for the economical production of sulfur using the Frasch process are (1) a large sulfur deposit (preferably more than several million tons) hosted in a porous and permeable formation, generally cavernous limestone breccia; (2) impermeable or partly permeable stratigraphic seals bounding the ore body so that it is hydrologically isolated; (3) a large, dependable supply of water; and (4) an inexpensive fuel supply. An attractive deposit would contain more than 10 Mt of recoverable sulfur, average 20% or more of sulfur over an interval of at least 30 m, lie between 65 and 800 m deep, have a uniform porosity of 10% to 15%, and be overlain by an impervious bed (Donner and Wornat 1973). Deposits less attractive than this may still be very profitable, but deposits exhibiting poor characteristics may be mined only in special cases (Níeć 1986b).

Figure 12 shows a typical Frasch well. A single well consists of four concentric pipes varying in diameter. The outer pipe acts as a protective casing and extends to the top of the barren cap rock. The next pipe extends to the bottom of the ore body and carries the flow of hot water, which is forced into the sulfur-bearing formation through perforations at the bottom of the pipe. As sulfur melts, it percolates down through the porous host rock to form a pool of liquid sulfur at the bottom of the well. Of the two inner pipes, the smaller one in the center carries compressed air to foam and lift the sulfur through the larger pipe to the surface, where the air is removed from the sulfur in a separator before shipment via heated pipeline, barge, or railcar to storage, or to a sulfur-forming device to be solidified in various forms. The volume of the compressed air and hence the rate of production are closely monitored so that the production rate equals the sulfur melting rate in order not to deplete the sulfur pool and cause the well to produce water. If the pool is depleted, production is stopped and additional water is injected until the sulfur pool is reestablished (Donner and Wornat 1973; Anon. 1990b). Bleed wells that extract cooled water from the deposit are generally located at the edges of the mining area. Individual sulfur wells usually recover sulfur from an area of less than 2,000 m² and may be operated only 3 to 4 months before exhaustion. Large operations generally have a continual program of drilling to replace wells that become exhausted. On average, about 70% of the sulfur is ultimately recovered.

The philosophy of Frasch mining is to keep the temperature inside the deposit as close as possible to 150°C, at which the viscosity of sulfur is lowest. At temperatures greater than 160°C, the viscosity dramatically increases and sulfur may become unrecoverable.

The costs and availability of water and fuel are often critical to the economical operation of a Frasch mine. A large quantity of water is injected to mine the sulfur, up to 57 m³ or more per ton of sulfur mined, and a dependable supply of water is desirable. Freshwater is generally preferred, but seawater has been used successfully at several sites in the Gulf of Mexico (Barker 1983), including the Main Pass mine (Ackerman 1992; Edwards et al. 1992).

In areas like western Texas where water is scarce, excessive fluid loss was minimized. Water from the bleed wells, a mixture of spent injection water and connate water that was contaminated with corrosive and scale-forming solutes, was locally treated, reheated, and reinjected. This eliminated environmental problems associated with the disposal of contaminated bleed water.



Source: Ober 2002.

Figure 12. Schematic cutaway view of a typical Frasch well

Fuel-cost increases during the energy crises of the 1970s also led to increased reinjection of spent waters and the development of several new recycling methods (Anon. 1990b) to minimize heat losses. One system developed by Freeport recycled mine water underground by mixing it in place with “new” superheated water. This system reportedly reduced the energy consumption of a well producing over 2 tpd to a third of the original amount. Fuel substitution and cogeneration also circumvented rising energy costs, as at Texasgulf’s Boling dome mine.

In stratiform deposits where the sulfur-bearing rocks are not hydrologically isolated from adjacent strata, fluid loss through underlying or overlying strata can prevent economic sulfur recovery. Such a situation exists in Poland where, in contrast to the salt domes of the Gulf Coast that are at moderate depth and spatially isolated, the sulfur deposits are at shallow depths, are only 10 to 15 m thick, and overlie permeable strata. They are also permeated by meteoric water. For these reasons, the hydrodynamic method (a variation of the Frasch process) was developed and has been used since 1966. The hydrodynamic method was also used in Iraq, and a similar technique was used to exploit the Culberson deposit in western Texas (Anon. 1990b).

The hydrodynamic method uses the same concentric well piping as in the Frasch process, but the wells are arranged in rows along an exploitation front. Because the sulfur-bearing rock cannot retain the heated water under pressure, special measures are used to direct the flow of water underground, including mud injection to seal off areas, judicious blasting to create permeability, and water withdrawal through depression wells placed in advance of the exploitation front. The injected water is thus directed to the depression wells rather than being lost in all directions.

Molten sulfur tends to adhere to the host limestone, leaving about 5% residual sulfur in the ore deposit. For this reason, and because islands of unmelted sulfur remain between production holes, few Frasch operations recover more than about 70% of the sulfur in place, and many sulfur deposits that have been abandoned

yielded considerably less than that (Anon. 1990b). As a result, several secondary and tertiary recovery techniques have been developed, including the Thermofluid technique described by Zakiewicz (1986). Secondary recovery techniques are most popular during times of high sulfur prices.

RECOVERED ELEMENTAL SULFUR

Recovered elemental sulfur as discussed here is largely a nondiscretionary by-product of petroleum refining, natural gas processing, and coking plants. Recovered sulfur is produced primarily to comply with environmental regulations applicable directly to processing facilities or indirectly by restricting the sulfur content of fuels sold or used.

In 2003, involuntary sources of sulfur contributed nearly 97% of the elemental sulfur produced worldwide, a dramatic increase since 1990 when recovered sulfur represented 65% of elemental sulfur production. The combination of recovered elemental sulfur and by-product sulfuric acid was more than 90% of the total world production of sulfur in all forms in 2003, up from 58% in 1990.

The principal sources of recovered sulfur are hydrogen sulfide in sour natural gas and organic sulfur compounds in crude oil. Recovery is mainly in the elemental form, although some is converted directly to sulfuric acid. Smaller quantities of sulfur are recovered from oil sands, oil shale, and coal, although oil sands are increasing in importance in Canada. Of the 24 countries that produced more than 500 ktpy of sulfur in all forms in 2003, recovered elemental sulfur is the dominant sulfur source in 15 of them—Canada, France, Germany, Iran, Italy, Japan, Kazakhstan, Kuwait, Mexico, the Netherlands, Russia, Saudi Arabia, the United Arab Emirates, the United States, and Uzbekistan (Table 1). Table 4 shows salient statistics for the U.S. sulfur industry.

Sour Natural Gas and Crude Oil

The growth in the recovery of sulfur from sour natural gas and crude oil since the mid-1950s has been one of the most significant trends in the sulfur industry. Generally expanding at the expense of Frasch production, recovered sulfur production has steadily increased for reasons independent of sulfur demand. The introduction of stricter environmental controls, combined with increased market demand for lighter petroleum products, a trend toward refining heavier, sourer crudes, and increased use of sour gases led to the availability of greater quantities of recovered sulfur, commonly at a substantially lower price than Frasch sulfur. Recovered sulfur producers usually incur additional transportation costs because many of the production facilities are far from major consumers, but their product is always price competitive. Because it is an involuntary by-product, the cost of production attributed to recovered sulfur is more a question of accounting practices.

Sulfur in oil occurs as organic sulfur compounds such as mercaptans (thiols), alkyl and aryl sulfides and disulfides, thiophenes, and complex condensed aromatic heterocyclic sulfur compounds, which must be converted to hydrogen sulfide before the recovery of sulfur. Sulfur in natural gas is mainly in the form of hydrogen sulfide, which must be removed from the gas at the wellhead because of its toxicity, corrosiveness, and chemical activity. Hydrogen sulfide forms in high-temperature diagenetic settings (such as in deep oil and gas reservoirs) through the thermal maturation of crude oil and through thermochemical sulfate reduction. Thermochemical reduction of sulfate by hydrocarbons is probably responsible for the bulk of the hydrogen sulfide found in this setting (Machel 1992).

Elemental sulfur is also present in high-temperature hydrocarbon reservoirs as a result of oxidation of contained hydrogen sulfide by sulfate and other processes. The elemental sulfur generally

Table 4. Salient statistics for the U.S. industry, *kt*

	1993	1999	2000	2001	2002	2003
World Production						
United States	11,100	11,500	10,500	6,470	9,270	9,600
Rest of world	40,500	47,000	49,200	53,900	51,200	52,200
Total	<u>51,600</u>	<u>58,500</u>	<u>59,700</u>	<u>60,400</u>	<u>60,500</u>	<u>61,800</u>
Components and Distribution of U.S. Supply						
Production						
Frasch	1,900	1,780 [†]	900 [†]	0	0	0
Recovered elemental [‡]	7,720	8,360	8,590	8,490	8,500	8,920
Other	1,430	1,320	1,030	982	772	683
Total, all forms	<u>11,100</u>	<u>11,500</u>	<u>10,500</u>	<u>9,470</u>	<u>9,270</u>	<u>9,600</u>
Shipments						
Frasch	1,480 [§]	**	**	0	0	0
Recovered [‡]	7,580 ^{††}	9,940 ^{‡‡}	9,710 ^{‡‡}	8,470	8,490	8,920
Other	1,430	1,320	1,030	982	772	683
Total, all forms	<u>10,500</u>	<u>11,300</u>	<u>10,700</u>	<u>9,450</u>	<u>9,260</u>	<u>9,600</u>
Exports						
Elemental ^{§§}	656	685	762	675	687	742
Sulfuric acid	46	51	62	69	48	67
Imports						
Elemental	2,040	2,580	2,330	1,730	2,560	2,870
Sulfuric acid	797	447	463	462	346	297
Consumption, all forms ^{***}	12,600	13,600	12,700	10,900	11,400	12,000
Combined producer stocks, Frasch and recovered (December 31)	1,380	451	208	232	181	206

Source: Ober 1994, 2004.

* Data are rounded to no more than three significant digits; may not add to totals shown.

† Estimated.

‡ Includes Puerto Rico and U.S. Virgin Islands.

§ Includes 10 months of Frasch sulfur data. Two remaining months of Frasch data included with "Recovered" to avoid disclosing company proprietary data.

** Withheld to avoid disclosing company proprietary data; included with "Shipments, Total, all forms."

†† Includes Frasch sulfur data for November and December.

‡‡ Includes corresponding Frasch sulfur data.

§§ Includes exports from the U.S. Virgin Islands to foreign countries.

*** Consumption is calculated as shipments minus exports plus imports.

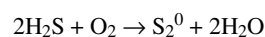
occurs as disseminated droplets of liquid sulfur. Large quantities of sulfur also may be present as polysulfides or dissolved in the hydrocarbon fluids. Lowering of reservoir temperature and pressure (as in a well string) can result in exsolution of elemental sulfur and plugging of rock formations and production equipment. Ruckmick, Wimberly, and Edwards (1979) call such occurrences thermogenic. Hydrogen sulfide originating from thermochemical sulfate reduction may also migrate to near-surface environments and become oxidized to native sulfur. This mechanism may explain some of the enigmatic oxidative occurrences previously discussed.

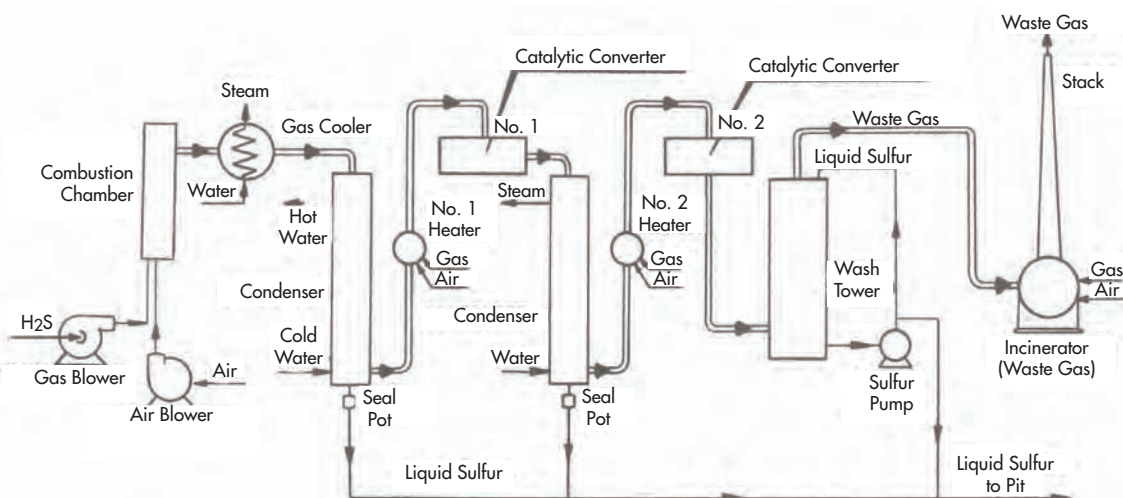
Sulfur in crude oil is recovered during the refining process, and the amount of sulfur recovered depends on the sulfur content of the crude, the amount of crude processed, the refining process, and the products. Refineries in the past were equipped to remove the sulfur only from the lighter refinery products, and much of the sulfur in the crude oil remained in the refinery emission gases or the residual fuel oils and was ultimately emitted to the atmosphere when these oils were burned. Environmental restrictions now limit the quantity of allowable emissions and severely reduced the sulfur content of most finished products from petroleum refineries. The amount of sulfur recovered is increasing because of the increasing

use of heavier and sulfur-rich crudes and more recent requirements to recover most of the sulfur content of the crude oil.

The organic sulfur compounds in crude oil must be removed from the refinery feed and converted to hydrogen sulfide by a hydrogenation process before the sulfur can be recovered. The sulfur in natural gas is already present as hydrogen sulfide, separable from the hydrocarbon gases by a variety of processes (Hyne 1982; Anon. 1987b, 1987c). A process developed by C.F. Claus in Germany in 1883 converts hydrogen sulfide from both sources to elemental sulfur. Over the years, the Claus process has been improved and modified to fit a variety of situations, so that it has become known as the modified Claus process. The basic process is now used in hundreds of sulfur recovery units with different configurations throughout the world, collectively referred to simply as Claus plants. Anon. (1986c) gives an excellent overview of the Claus process in its various forms.

The process was based on the following reaction in which hydrogen sulfide is burned to yield elemental sulfur and water:

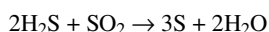
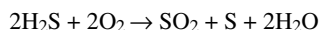




Source: Barker 1983.

Figure 13. Generalized flowsheet of a Claus plant for recovery of sulfur from hydrogen sulfide

Only under ideal conditions does this reaction happen exactly as described. Modern Claus reactors incorporate a two-step process that takes advantage of the following reactions:



In the first step of the process, insufficient oxygen is present to convert all the H_2S to SO_2 , thus also causing elemental sulfur and water to be formed. In the second stage, the reaction product SO_2 from the first reactor mixes with additional H_2S , completing the formation of elemental sulfur and water, usually with the aid of a catalyst. The sulfur condenses and is removed in molten form from the reaction vessel and stored until shipping or use onsite (Lefler 2000). Figure 13 shows the Claus process in a generalized flow sheet.

The efficiency of the Claus process for sulfur recovery from gas streams containing H_2S depends on the concentration of the H_2S being treated. The modifications to the process have improved the recovery of sulfur, although not all the sulfur is recovered. Typical sulfur recovery efficiency at Claus plants is 90% to 96% for a two-stage reactor and 95% to 98% for a three-stage reactor. If the depleted process gas is within acceptable limits, it is then incinerated in the final stage of the Claus process to oxidize all the remaining sulfur compounds, and the remainder, or tail gas, is emitted into the atmosphere. Usually, however, the tail gas must undergo further processing to remove as much of the sulfur as technically possible to meet environmental requirements. In the United States, 99.9% recovery efficiency is required at sulfur recovery plants with a capacity of at least 20 tpd. Amine-based tail gas treatment is the most common tail gas process in the United States, where sulfur compounds in the tail gas are converted to H_2S , separated, and recycled to a Claus plant. Other developed countries have similar requirements. Canada requires sulfur recovery of 98.5% at 50-tpd plants and 99% for 2,000-tpd operations. The European Union (EU) mandates 98.5% sulfur recovery. Germany, a member of the EU, has set higher standards of 99.8% for 20- to 50-tpd plants and 99.5% for those with larger than 50-tpd capacity. Japanese operations must recover 99.8% of sulfur; and Taiwan has the highest standard at 99.95% recovery (Connock 1998).

In 2003, 38 companies in the United States produced sulfur at 106 plants in 26 states and the U.S. Virgin Islands. The number of companies producing recovered sulfur has decreased significantly since 1990, primarily owing to consolidation in the energy industry. Most of these plants are small, with 33 reporting annual production exceeding 100 kt. By source, refineries or satellite plants treating refinery gases and three coking plants produced 78.2% of the recovered elemental sulfur. Natural gas treatment plants produced the remainder. The leading U.S. recovered sulfur producers in 2003, all with more than 500 kt of production were, in descending order of production, Exxon Mobil Corp., BP PLC, ChevronTexaco Corp., ConocoPhillips Corp., Shell Oil Co., and CITGO Petroleum Corp. These companies collectively accounted for 68.4% of recovered elemental sulfur production in 2003 (Ober 2004).

Canada is the second largest involuntary producer of sulfur in the world, with a 2003 production of 8.1 Mt, all from oil and gas (Ober 2004). Canada is also the world's largest sulfur exporter. Canada's ability to export most of its production from Vancouver and its willingness to ship large volumes of sulfur contributed to its dominance of the sulfur market.

Most Canadian sulfur production comes from sour natural gas processing plants in the western Canadian sedimentary basin in Alberta, although production in British Columbia is significant also (Anon. 1991a). Occurrences of native sulfur are also known in Alberta, British Columbia, Nova Scotia, and elsewhere, some of which are oxidative deposits (Hollister 1984; Hora and Hamilton 1992).

Recovered sulfur production in Alberta began in 1952 (Anon. 1984a), but sales did not match production until 1979, when adequate transportation and marketing facilities were established. Before 1979, sulfur was stockpiled, reaching a level of more than 21 Mt in 1977 (Schwalm and Doyle 1987). Strong export sales reduced the Canadian stocks to about 3 Mt by 1992, but since then inventories have increased, reaching nearly 15 Mt in 2002 (Ober 1994; Anon. 2002).

Russia is the world's second-largest exporter and the third-largest producer of recovered sulfur, most of which is a by-product of natural gas processing. The Astrakhan gas processing plant is the largest single source of recovered sulfur in the world. Construction

of Astrakhangazprom's first gas processing plant began in 1981 and production started in 1986. The gas is very sour, containing 26% hydrogen sulfide, and is more than 4,000 m deep. Astrakhan produces gasoline, diesel, furnace fuel oil, kerosene, and liquified gas. Sulfur production has increased significantly since 1995 with the completion of subsequent phases of development. In 1995, production at this operation was 1.7 Mt of sulfur. By 2000, production had more than doubled to 3.8 Mt, and future increases may reach 4.5 Mt (Anon. 2001). Orenburg is another sour-gas operation in Russia, with sulfur recovery of about 800,000 tpy.

The Tengiz oil and gas field is the main source of current sulfur production in Kazakhstan. Located on the northeastern shore of the Caspian Sea in western Kazakhstan, Tengiz has been operated by Tengizchevroil (TCO) since 1993. One of the world's largest oil fields, Tengiz contains high-quality oil with 0.49% sulfur and associated natural gas that contains 12.5% hydrogen sulfide (Connell et al. 2000). An expansion plan at Tengiz to nearly double oil production includes the reinjection of sour gas, limiting total recovery of sulfur at the site (Anon. 2003c). Sulfur also is recovered from the Karachaganak gas-condensate field in Kazakhstan near the Russian border. Because it is close to the Russian gas-processing operation in Orenberg, sour gas from Karachaganak is treated at Orenberg. No gas treatment facilities have been installed at the site (Anon. 2001).

In Western Europe, France, Germany, Italy, and the Netherlands are the leading producers of recovered sulfur from natural gas and refineries. Recovered sulfur production in the Middle East is mostly from associated natural gas. Petroleum produced in this region may have high sulfur content, but much of it is exported, and so the sulfur is recovered in other countries. The largest producer is Saudi Arabia, but significant quantities are also recovered in Kuwait, Iran, and the United Arab Emirates. Japan's elemental sulfur production is entirely attributed to oil refining; Mexican production is from a combination of gas processing and oil refining.

Oil Sands

Sulfur is recovered from synthetic crude oil derived from oil sands in Canada. As conventional petroleum production in Canada has declined, oil sands have become a more important source of petroleum for the North American market (Cunningham 2001). The proportion of Canadian petroleum production from oil sands is expected to increase from 9% in 2001 to 21% in 2005 and 30% in 2010 (Pok 2002). Oil sands represent a large source of recovered sulfur, and they offer potential for huge additional quantities in the future. Alberta has huge deposits of oil sands, with estimated reserves of 300 billion bbl of recoverable crude oil that also contain 4% to 5% sulfur as organic sulfur compounds (Stevens 1998). Known for more than 200 years, the Athabasca oil sands in the Ft. McMurray Area of Alberta are a mixture of sand, water, clay, and bitumen (a naturally occurring viscous mixture of heavy hydrocarbons). Because of its complexity, bitumen is difficult or impossible to refine at most oil refineries. It must be upgraded to a light-oil equivalent before further refining, or it must be processed at facilities specifically designed for processing bitumen (Anon. 1999a). During upgrading and refining the oil sands, significant quantities of sulfur must be recovered using processes designed for conventional oil refining.

The Athabasca deposits crop out locally and are visible at the surface and amenable to conventional surface-mining techniques, but most of the oil sands are buried up to depths of 50 m and require in situ mining methods. Three surface mines are in operation at oil sand deposits, and several other operations are producing small quantities of bitumen using an in situ method that injects steam into

the oil sand, separating the water and bitumen from the sand particles. The bitumen is then removed from the deposit, and the sand remains in place. Many additional projects of both types are planned (Anon. 2004d).

Other large deposits of oil sands are known in Venezuela and Colombia. The United States has deposits in California, Kentucky, New Mexico, Utah, and elsewhere, but they are comparatively small. Interest in recovering oil from sands, and consequently sulfur, is highly dependent on the price of crude oil.

Other Sources

More important than oil sands as a potential source of synthetic crude oil (and by-product sulfur) for the United States are its oil shale deposits, particularly those in Colorado, Utah, and Wyoming (Gray et al. 1982). Several companies developed processes to recover oil from shales between 1940 and 1990, primarily in western Colorado, but the relatively high costs of extraction coupled with the problems of disposal of the spent shale have combined to prevent large-scale use of oil shale. As with tar sands, interest in processing oil shale tends to wax and wane with the economic fortunes of the oil industry, although local conditions, such as political isolation or foreign currency restrictions, may spur the development of oil shale resources.

In the United States in 2003, electric utilities and other power producers burned more than 1 Gt of coal with an average sulfur content of 0.94% (Anon. 2004a). Essentially none of the sulfur in coal is recovered before its combustion, although coal-cleaning technologies are capable of removing a substantial portion of the contained sulfides. Pyrite recovered from coal-bearing strata was an important source of sulfur in China, but its importance is declining (Anon. 1985b). Much of the sulfur contained in coal is recovered from coke oven and combustion gases as described in the Sulfur Dioxide Emission Control section of this chapter.

The organic sulfur compounds in coal can be removed only by processes of hydrogenation, liquefaction, or gasification, which change the form of the coal (Gray et al. 1982). Sulfur is produced from coal gasification in the United States, from coal liquefaction in Europe (principally Germany) and in the Republic of South Africa, and from lignite gasification in Spain. Total production from these sources represents a very small portion of global sulfur production.

COMBINED SULFUR

Sulfur is also recovered from sources where it is chemically combined with other elements, principally as a sulfide or sulfate. Such compounds are processed directly to recover the sulfur as sulfuric acid or other forms, and sulfur is recovered from gaseous pollutants arising from the processing of sulfides in metal ores, coal, and other sources.

Pyrites and Other Metal Sulfides

Metal sulfides, widely distributed in nature, have long been an important source of sulfur. Sulfide ores of commercial interest for their sulfur value alone belong to the ferrous group collectively known as pyrites. The most important of these are the minerals pyrite, marcasite, and pyrrhotite. Pyrites commonly contain traces of nonferrous metals (Russell 1989). Pyrites once were mined in many countries specifically for their sulfur content, but they have decreased in importance globally.

Sulfur is also recovered (ultimately as sulfuric acid) from nonferrous metal sulfides that are mined and processed for their nonferrous metal content. The most important nonferrous metal sulfides include those of copper (chalcopyrite, chalcocite), lead (galena),

zinc (sphalerite), molybdenum (molybdenite), nickel (pentlandite), mercury (cinnabar), arsenic (arsenopyrite, realgar), antimony (stibnite), and silver (argentite and various sulfosalts). Associated iron sulfides are also recovered as a by-product flotation concentrate during the processing of nonferrous ores. This source of pyrite has displaced some voluntary pyrite sources, but it also depends on the market for nonferrous metals.

Ferrous and nonferrous sulfides are the leading source of sulfur production in Australia, Chile, China, Finland, India, the Republic of Korea, and Spain. Large quantities of by-product sulfides are produced in Canada, Germany, Japan, Mexico, Russia, and the United States. China and Finland are the only countries where the major source of sulfur is pyrites; all the other countries listed produce sulfuric acid as a by-product of metal smelting.

Sulfide ore deposits occur in a variety of geological environments. Mineralization occurs in massive lenses, tabular masses, and veins, and disseminated throughout a variety of rock types. Pure pyrite contains 53.4% sulfur and 46.6% iron. Commercial-grade pyrite ores are usually between 40% and 50% sulfur and frequently contain small amounts of arsenic, lead, copper, cobalt, gold, zinc, thallium, and other trace elements. These associated nonferrous metals can be recovered as a by-product, but they can also be a source of environmental problems.

Pure pyrrhotite has varying chemical compositions, but it is poor in sulfur relative to pyrite. When pure, it contains about 38% sulfur and 62% iron. Pyrrhotite is softer than pyrite and weakly to strongly magnetic. Cobalt, nickel, and copper are frequently found in association with pyrrhotite. Silver, gold, platinum, and other trace elements are less common.

Pyrites were the second major source of sulfur in the mid- to late-19th century following the rise in the price of Sicilian sulfur. Pyrites lost predominance to Frasch sulfur in the early 20th century, and pyrite production continues to decline. In 2003, pyrites supplied 7% of the world's sulfur in all forms, down from 17% in 1990.

One of the major reasons for this decline is the capital investment required for a pyrite-based sulfuric acid plant, which is two to three times that required for a comparable plant based on elemental sulfur (Loughborough 1991). Environmental problems have also plagued pyrite producers, because the disposal of cinder residues from pyrite processing is a great obstacle. These factors, coupled with the increasing availability of elemental sulfur, have resulted in less production from pyrites. Several acid plants in Europe and China were converted from pyrite-based to elemental sulfur-based, leaving very little pyrite-based sulfuric acid capacity anywhere except China and Finland. Even in those countries, pyrites continue to decline.

Sulfur is also recovered during the smelting of nonferrous sulfides. Sulfur dioxide in the smelter gases is converted to sulfuric acid, liquid sulfur dioxide, or oleum. The manner in which these concentrates are processed is similar to the way that pyrite is treated, but sulfur recovery can be more difficult because of widely varying sulfur contents in fluctuating gas streams. This source of sulfur has been increasing in significance as a result of progressively tighter antipollution legislation. By-product sulfuric acid represented 21% of all global sulfur production in 2003, an increase of nearly 62% since 1990, when it was 13% of total sulfur production.

In the United States, by-product sulfuric acid from the nation's nonferrous smelters and roasters supplied about 7% of the total domestic production of sulfur in all forms in 2003. This figure has decreased steadily since 1998 because several U.S. copper smelters have closed as a result of poor copper metal prices and preference of lower-cost copper leaching processes. In 1990, seven acid plants operated in conjunction with copper smelters, and eight

were accessories to lead, molybdenum, and zinc smelting and roasting operations; in 2003, three copper smelters and three other smelters reported by-product sulfuric acid production (Ober 2004).

Sulfur Dioxide Emission Control

In addition to being a commercial source of sulfur, sulfur dioxide is also one of the most common synthetic pollutants. Human activity released about 142 Mt of sulfur dioxide containing 71 Mt of sulfur into the atmosphere in 2003. The leading source of this pollution is the burning of coal to produce electric power (Anon. 2004f). Although these fuels often contain low percentages of sulfur by weight, large quantities of fuel are burned by utilities and industrial users, discharging large quantities of sulfur in dilute gases.

Much of the remaining synthetic emissions come from the smelting of nonferrous ores. Pyrometallurgical operations emit higher concentrations of sulfur dioxide than do power plants, but there are many fewer installations worldwide.

The environmental problems associated with sulfur emissions have been known and studied for some time. The downwind deposition of sulfur-bearing compounds, principally sulfuric acid, leads to acidification of lakes and streams, loss of soil nutrients, and damage to plant life. Widespread deforestation has occurred locally in Europe (where it is estimated that pollution-related disease has spread to more than half of the forested land in western Germany) and North America (Anon. 1985a, 1991b).

Sulfur compounds are but one of numerous air pollutants, but they are also one of the easiest to control, and several useful compounds can be recovered. A comprehensive review of flue gas desulfurization (FGD) methods is beyond the scope of this chapter, but the reader is referred to the FGD chapter in this book. FGD methods can be classified broadly as regenerative or throwaway processes, depending on whether the sulfur values are recovered in a useful form or disposed as solid waste. Both recovery methods can be carried out in wet or dry systems. Existing processes use a variety of compounds (lime, limestone, magnesium oxide, sodium carbonate, and others) to neutralize or collect the sulfur dioxide. End products include gypsum, sulfuric acid, liquid sulfur dioxide, and elemental sulfur, all of which can be used if local markets exist. If local markets do not exist, large quantities of gypsum or sulfuric acid may have to be neutralized or otherwise disposed of, which can create other environmental problems.

In the United States, the Clean Air Act Amendments of 1990 successfully mandated reductions in SO₂ emissions. In 2002, the last year for which data are available, sulfur dioxide emissions from power plants totaled 9.9 Mt, a 33% decrease from the 14.8 Mt emitted in 1990 (Anon. 2003a, 2004b). This was achieved by a combination of alternative clean fuels such as natural gas and low-sulfur coal and innovative FGD technology.

Pollution control legislation, by requiring the neutralization and recovery of environmentally damaging compounds, effectively provides additional quantities of sulfur to the market regardless of the economic viability of these activities. As pollution legislation has continued to tighten, increasing quantities of sulfur have been recovered. Despite the predictions of increased tonnages of sulfur recovered from SO₂ emissions at power plants, however, the impact on total sulfur production has not been dramatic. A high proportion of the sulfur is recovered in the form of gypsum, and useful sulfur values are a very small portion of total production.

Sulfates

Sulfate minerals, particularly anhydrite and gypsum, represent the world's largest sulfur resource. Thick deposits of naturally occurring anhydrite and gypsum are found in evaporite basins worldwide, and

large amounts of gypsum are produced as by-product waste materials from a number of industrial and pollution control processes. Nevertheless, sulfates are rarely used as a source of sulfur owing to the high cost of the processing.

Sulfur values (in the form of sulfuric acid and ammonium sulfate) have been recovered from sulfate in only a few countries, including Austria, Germany, India, Pakistan, Poland, Turkey, and the United Kingdom (Anon. 1985b). Sulfuric acid is produced from anhydrite and gypsum using the Muller-Kuhne process, developed in Germany during World War I. Ammonium sulfate is manufactured from natural and by-product sulfate using the Merseberg process in which calcium sulfate is reacted with ammonium carbonate (Barker 1983).

Elemental sulfur can also be recovered from sulfate minerals, including anhydrite and gypsum, but the process has never been economic. Although there have been several attempts to design processes to recover elemental sulfur from sulfate minerals, only one commercial attempt was made in the late 1960s. Located in western Texas, the Elcor Chemical Corp. plant used gypsum from Permian evaporites in a two-step process in which calcium sulfide produced in a kiln was hydrolyzed to hydrogen sulfide, which then yielded sulfur by the Claus process. The process was energy intensive, and high fuel costs combined with technical problems and a drop in the price of sulfur caused the demise of the project (Anon. 1968, 1983; Ellison 1971). Despite occasional efforts by researchers to produce sulfur economically from sulfates, it is unlikely that sulfates will be used extensively because of the increasing availability of recovered sulfur and the relatively low price of the commodity.

Tremendous quantities of phosphogypsum, a by-product of the production of phosphoric acid, have been generated worldwide, and more than 1 Gt are stockpiled in several states in the United States, especially Florida. Much of these stockpiled compounds contain radioactive impurities (Anon 2000). Several organizations, including such groups as the Florida Institute of Phosphate Research and the Institute for Recyclable Materials at Louisiana State University, have conducted phosphogypsum utilization studies, but attempts to devise economically viable alternatives to phosphogypsum impoundment or disposal have not been successful. Recovery of sulfur from phosphogypsum can be economically feasible only if the gypsum is not radioactive and sulfur prices are extremely high, a situation that is not likely in the foreseeable future.

FORMED SULFUR

Before the early 1950s, much of the world's tonnage of export sulfur was handled as crushed bulk. Because of safety, environmental, and economic concerns arising from breakage of the solid sulfur and generation of sulfur dust, sulfur-forming techniques were developed to overcome difficulties inherent in solid sulfur operations.

Basically, liquid sulfur is formed into solid, moderately sized particles of selected shapes. These particles are designed to resist attrition, be unwettable, and handle easily during stockpiling, loading, transport, and unloading.

Early sulfur forming was limited to the production of flakes and slates, but as sulfur output from sources increased in the 1960s, so did the development of new processes for sulfur forming. A variety of forms are now produced, many of which are spherical (Raymont and Hyne 1983).

Production of Formed Sulfur

The main purpose in sulfur forming is to prevent breakage of the solid sulfur particles during handling. Two factors emerge as the most important in determining resistance to breakage: particle size and sphericity (Hyne 1990). The larger the particle size, the greater

the tendency to break apart during handling (friability). The optimum size for spherically formed sulfur is between 1.5 and 3.5 mm. Sphericity is also important in that the more spherical the form, the less likely it is to have easily ruptured protrusions. These factors are especially important in the so-called premium products, where fines (less than 0.3 mm) or dust production is required to be less than 2%. Highly spherical products, however, will have a low angle of repose and angle of climb (the maximum inclination that can be used to lift a product on a conveyor belt without it running back), which may generate other problems during transportation and storage.

Reduced friability also reduces the environmental impact of solid sulfur handling. On exposure to water and air, elemental sulfur reacts to form sulfurous and sulfuric acids, which can create localized environmental problems and lead to excessive corrosion of plant facilities. The reaction is bacterially mediated, and the rate of reaction is inversely proportional to the sulfur particle size. The production of acid can be minimized if dust levels are controlled or bactericides are used.

Sulfur is made into several primary forms: flakes, slates, prills (or pellets), nuggets, granules, pastilles, and briquettes. Flakes are the easiest, but least popular, of the forms to produce. Sulfur is cooled and solidified on the outside of large rotating drums, from which it peels off into small flakes (Anon. 1979b).

Slating, the least expensive process, is widely used but also produces particles having relatively high friability. Molten sulfur is cast onto a continuous conveyor belt and is cooled with air or water so that it solidifies into a thin sheet. As it reaches the end of the belt, the sheet is broken, or breaks naturally, into smaller pieces.

Prilling sulfur is a more complicated forming method, but it also is widely used. There are two fundamental types of sulfur prilling—air and water. In air prilling, molten sulfur is sprayed from the top of a tower against an upward flow of air. As it falls, the sulfur breaks into small droplets and cools into prills. In water prilling, the sulfur is sprayed into tanks containing water, from which the prills are collected and dried. Prilling is also referred to as pelletizing, a legacy from the production of lead shot in towers. Minor modifications to prilling techniques are used to produce nuggets.

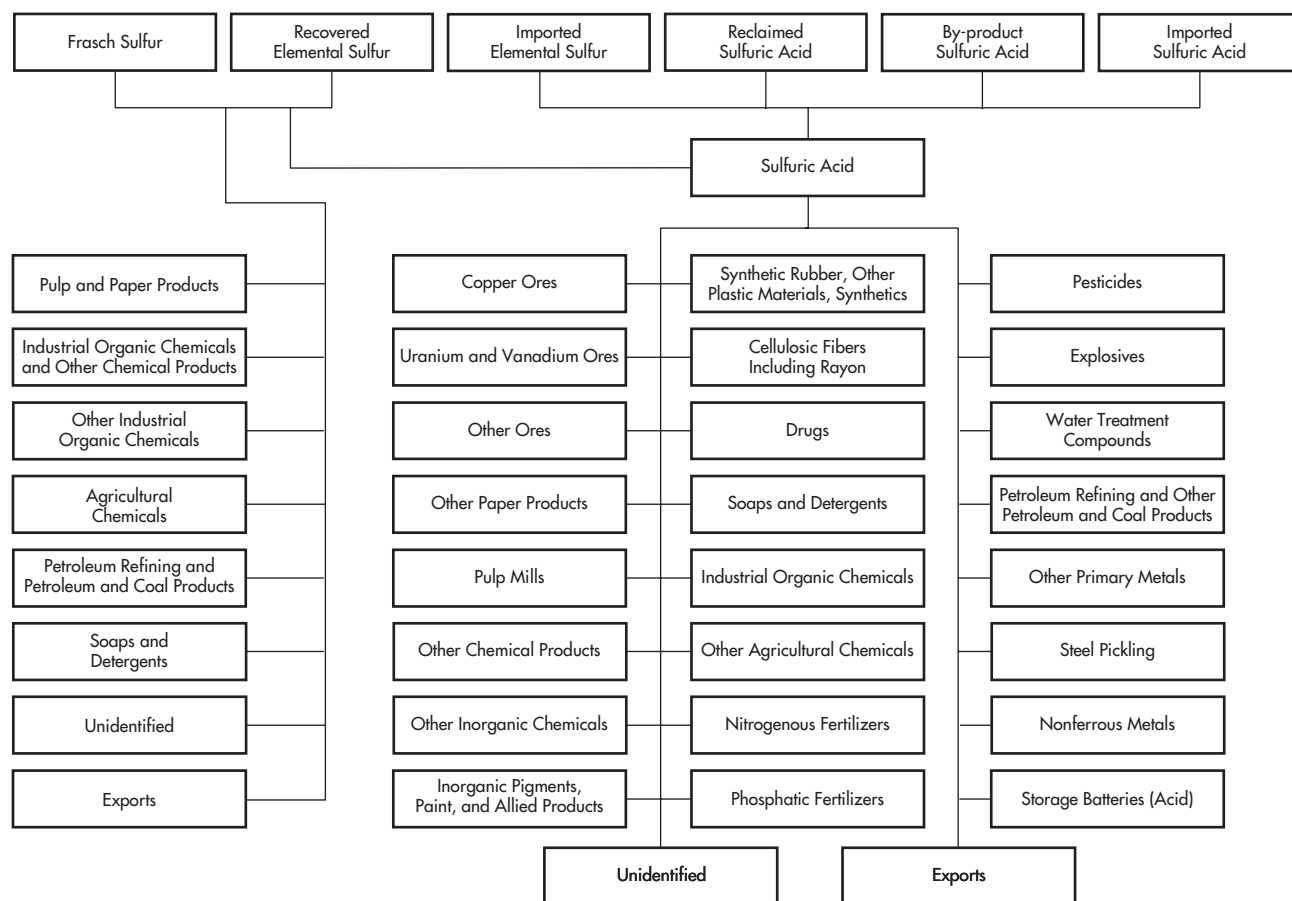
Granulation involves applying successive coats of sulfur to solid particles of sulfur in a granulator until the particle size reaches the required value. In the GX granulation process of Enersul Ltd., liquid sulfur is sprayed into a rotating drum in which small seed particles of sulfur are recycled from the end of the process (Hyne 1990). The product granules are spherical, dry, hard, and free from the voids and structural weaknesses often associated with prills. The end product size can also be varied to meet customer requirements.

Pastilles are individual droplets of molten sulfur that have been dropped on a steel belt and cooled by conduction. Sandvik A.B. has a Rotoform process that uses a patented Rotoformer (essentially a perforated drum) to distribute the sulfur on the belt. At the end of the belt, the pastilles are scraped off and fall onto a collecting conveyor. The resulting pastilles are spherical but flattened on one side.

Characteristics of Formed Sulfur

The characteristics of the sulfur form have a direct bearing on the suitability of the form for transport. Important characteristics include friability, moisture performance, and handling characteristics; friability is probably the most important (Anon. 1979b; Raymont and Hyne 1983). The friability of a sulfur form is influenced by the particle size, surface texture, internal voids, and crystallinity.

Moisture performance is defined by the moisture content of the newly formed product and the moisture uptake and retention when it is stockpiled. Those forms produced by water quenching



Source: Ober 2002.

Figure 14. Sulfur-sulfuric acid supply and end uses

have a higher initial moisture content than forms produced by dry processes, but mechanical dewatering and drying can reduce the moisture content. The moisture uptake and retention of a sulfur form are particularly important because stored sulfur is commonly exposed to the atmosphere. Formed sulfur usually has reasonable water rejection properties because sulfur itself is hydrophobic. The spherical forms exhibit superior water rejection properties; water will often penetrate only the first few centimeters into a stockpile and then drain away.

The handling characteristics of a sulfur form depend on particle size and shape, uniformity, surface texture, density, and hardness. The properties of bulk density and the angle of repose are two of the most important handling characteristics. Normal dry bulk sulfur has a bulk density of between 1,345 and 1,440 kg/m³ and an angle of repose of 35°. Formed sulfur should have a density approaching bulk sulfur and as high an angle of repose as possible, but these values vary considerably, even for forms produced by the same technique. The density and angle of repose are also affected by the moisture content.

REFINED SULFUR

The category of refined sulfur includes a wide range of manufactured products, of which ground sulfur is the most prominent. Sometimes referred to as specialty sulfur, this category also includes wettable, insoluble, precipitated (also referred to as sublimed or flowable sulfur), colloidal, micronized, and double-

refined sulfur, along with special grades used in manufacturing pharmaceutical and photochemical products (Anon. 1979a, 1992).

Although refined sulfur is the oldest end use of sulfur—having been used since antiquity, particularly in pharmacology and alchemy—demand for refined sulfur continues to grow. Nevertheless, of all the sulfur consumed in the western world, only a very small percentage is used as refined sulfur or specialty grades. Even so, it is a business that is important in its own right because it supplies essential and highly specialized products for agriculture and industry.

Although ground and refined sulfur are used to some extent almost everywhere in the world, the manufacture of ground and refined sulfur is confined to a relatively small number of enterprises, most of which are concentrated in areas where the level of economic development is high, such as North America, Europe, and Japan. Other producers are found where there is significant domestic demand, such as Australia, the Republic of South Africa, India, Mexico, Brazil, and Chile, or where large quantities of recovered sulfur are available for export, such as Kuwait and Saudi Arabia (Anon. 1984b).

Ground sulfur must be manufactured in highly controlled conditions to prevent explosions. Because ground sulfur will autoignite at 190 °C, grinding is done in an inert atmosphere with special equipment to minimize the buildup of heat and static electricity.

A healthy international trade in refined sulfur exists because almost all economies need sulfur, but not necessarily enough to justify establishing a domestic industry. In general, the pattern of

Table 5. Sulfur and sulfuric acid sold or used in the United States, by end use, *kt**

End Use	SIC Code [‡]	Elemental Sulfur [†]		Sulfuric Acid (Sulfur Equivalent)		Total	
		2002	2003	2002	2003	2002	2003
Copper ores	102	0	0	707 [§]	421	707	421
Uranium and vanadium ores	1094	0	0	2	4	2	4
Other ores	10	0	0	1	58	1	58
Pulp mills and paper products	26, 261	**	**	122	225	122	225
Inorganic pigments paints and allied products, industrial organic chemicals, other chemical products ^{††}	28, 285, 286, 2816	0	5	27	71	27	76
Other inorganic chemicals	281	**	188	50	97	50	285
Synthetic rubber and other plastic materials and synthetics	282, 2822	0	0	66	82	66	82
Cellulosic fibers, including rayon	2823	0	0	6	1	6	1
Drugs	283	0	0	2	2	2	2
Soaps and detergents	284	**	0	0	2	0	2
Industrial organic chemicals	286	0	0	4	22	4	22
Nitrogenous fertilizers	2873	0	0	105	206	105	206
Phosphatic fertilizers	2874	0	0	6,660 [§]	6,660	6,660 [§]	6,660
Pesticides	2879	0	0	8	11	8	11
Other agricultural chemicals	287	1,650	1,590	29	46	1,680	1,630
Explosives	2892	0	0	8	10	8	10
Water-treatment compounds	2899	0	0	59	98	59	98
Other chemical products	28	0	0	21	45	21	45
Petroleum refining and other petroleum and coal products	29, 291	2,390	3,700	90	140	2,480	3,840
Steel pickling	331	0	0	7	58	7	58
Nonferrous metals	333	0	0	2	3	2	3
Other primary metals	33	0	0	7	9	7	9
Storage batteries (acid)	3691	0	0	3	13	3	13
Exported sulfuric acid		0	0	334	1,420	334	1,420
Total identified		4,040	5,480	8,320[§]	9,700	12,400[§]	15,200
Unidentified		248	678	52	409	300	1,090
Grand total		4,290	6,160	8,380[§]	10,100	12,700[§]	16,300

Source: Ober 2004.

* Data are rounded to no more than three significant digits; may not add to totals shown.

† Does not include elemental sulfur used for production of sulfuric acid.

‡ Standard industrial classification.

§ Revised.

** Withheld to avoid disclosing company proprietary data; included with "Unidentified."

†† No elemental sulfur was used in inorganic pigments and paints and allied products.

trade is from North America to South America in the Western Hemisphere and from Europe and Japan to nonproducing countries in the Eastern Hemisphere.

END USES

Sulfur is consumed mainly in the form of acid and, to a lesser extent, other intermediate chemicals used to manufacture a final product that often does not contain much, if any, sulfur. Approximately 90% of all sulfur consumed in the United States every year is in the form of sulfuric acid for use in a multitude of industries. The balance is used for a variety of nonacid industrial purposes. Figure 14 and Table 5 give detailed end-use information for the United States.

The largest single use of sulfur is in the production of phosphate fertilizers, followed by petroleum refining, other agricultural chemicals, copper ore leaching, and other industrial uses. Combined agricultural uses of sulfur in all forms account for 62% of identified domestic use.

Sulfuric Acid

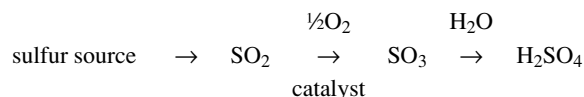
Sulfuric acid, because of its desirable properties, is the most universally used mineral acid and the largest-volume inorganic chemical in terms of the quantity produced and consumed in the United States (Ober 2004). World sulfuric acid production totaled about 159 Mt in 2003 (100% sulfuric acid), of which 41 Mt containing about 13 Mt of sulfur was produced in the United States.

The reasons for sulfuric acid's dominance as the most desirable mineral acid are as follows (Shelton 1980; Barker 1983):

1. Raw materials and acid plant operating costs are low.
2. Shipping, handling, and storage problems are fewer than for other acids.
3. The acid adapts to numerous acidulation and neutralization processes.
4. It has excellent dehydrating properties.
5. It demonstrates effective catalysis in many hydrocarbon and organic chemical syntheses.

6. It readily forms organic sulfates with many hydrocarbons, which are easily hydrolyzed to form other basic products.
7. It has a high boiling point, which limits volatilization losses caused by high temperatures required in many processes.
8. It can be partially used in one process, reused in a second or even a third process, and be readily regenerated, fortified, and concentrated for still further uses.

The basic equations for sulfuric acid production are the same regardless of the process used or the source of the sulfur. The reaction sequence goes as follows



Actual production is much more complicated than this and processes vary significantly, as do requirements for different sulfur sources.

The earliest commercial process for sulfuric acid production, the chamber process, was first used in 1746 (Sander, Rothe, and Kola 1984). In this process, oxides of nitrogen acted as catalysts for the oxidation of sulfur dioxide to sulfur trioxide in a lead chamber reaction vessel. Because the maximum concentration of the sulfuric acid product from the chamber process is about 77% to 78%—lower than that produced in most industrial facilities—the process is considered obsolete, with very limited production from plants of this type (Donovan and Salamone 1983).

The contact process replaced the chamber process early in the 20th century because it could produce the much more concentrated acid (about 98%) needed in the production of synthetic dyes, organic chemicals, and the explosives required during World War I. The first contact process, using a platinum catalyst to oxidize sulfur dioxide to sulfur trioxide, was developed in 1831. It continues to be used with improvements, especially in the type of catalysts used. Eventually vanadium pentoxide replaced platinum as the dominant catalyst, owing to its insensitivity to catalyst poisons and its lower cost; a cesium-promoted vanadium catalyst was a later innovation. A second absorption stage was added in the contact process, optimizing the efficiency of the conversion of sulfur dioxide to sulfur trioxide, reducing sulfur dioxide emissions significantly, and improving the environmental performance of modern sulfuric acid plants. Nearly all sulfuric acid plants in developed countries use double-absorption systems to comply with environmental regulations limiting sulfur dioxide emissions at chemical operations (Sander, Rothe, and Kola 1984). Typical double-absorption plants, as shown in Figure 15, recover 99.5% to 99.8% of the sulfur dioxide produced at the sulfur burner, and some are even more efficient (Donovan and Salamone 1983). Single-absorption contact plants can treat their tail gas, sometimes by producing ammonium sulfate to meet environmental standards.

Smelter-based sulfuric acid plants use the double-absorption process to strip their off-gases of sulfur dioxide. The biggest difference between sulfur-burning and by-product sulfuric acid plants is the lack of a sulfur burner at smelters. Smelter gases have lower sulfur dioxide content and more impurities, requiring slightly different steps and higher gas-flow capabilities to produce comparable quantities of sulfuric acid.

Agricultural Uses of Sulfur

More sulfuric acid is consumed in converting phosphate rock into phosphoric acid and other phosphate fertilizers than is consumed in any other industry. Sulfuric acid converts the insoluble phosphate

minerals into phosphoric acid that can then be used directly or processed into more complex fertilizers. Ammonia and sulfuric acid combine to form ammonium sulfate, another fertilizer that requires sulfur for its production. Elemental sulfur products have been developed to provide sulfur for crop nutrition. Other agricultural uses that require elemental sulfur include nutritional supplements in animal feeds and salt blocks. Finely divided sulfur is also used in agriculture as fungicides, insecticides, and miticides.

In agriculture, refined sulfur in powdered (dry or wettable), micronized, sublimed, and other forms, often combined with metal compounds, is used in direct application on crops, in viticulture, and in horticulture as protection against mildew, powdery mildew, and other fungi. In these end uses, however, crude recovered sulfur increasingly is used without being refined because the quality of recovered sulfur is sufficient.

Refined sulfur, mainly ground, is also used in wine and sugar refining, as a pesticide (since ancient times), in fertilizer as a soil conditioner, and as an additive to compound animal feeds. Plant nutrient sulfur (PNS) products formulated from refined sulfur deliver small sulfur particles that decompose more readily into the sulfate form. The particles can be agglomerated into granules with a binding material that makes the sulfur easier to handle, limiting the sulfur dust, and improving the safety of handling finely divided sulfur. Other products incorporate elemental sulfur with 10% bentonite clay. After application, the clay swells as it absorbs soil moisture, breaking off the sulfur in a variety of particle sizes (Anon. 1999b).

Industrial Uses for Sulfur

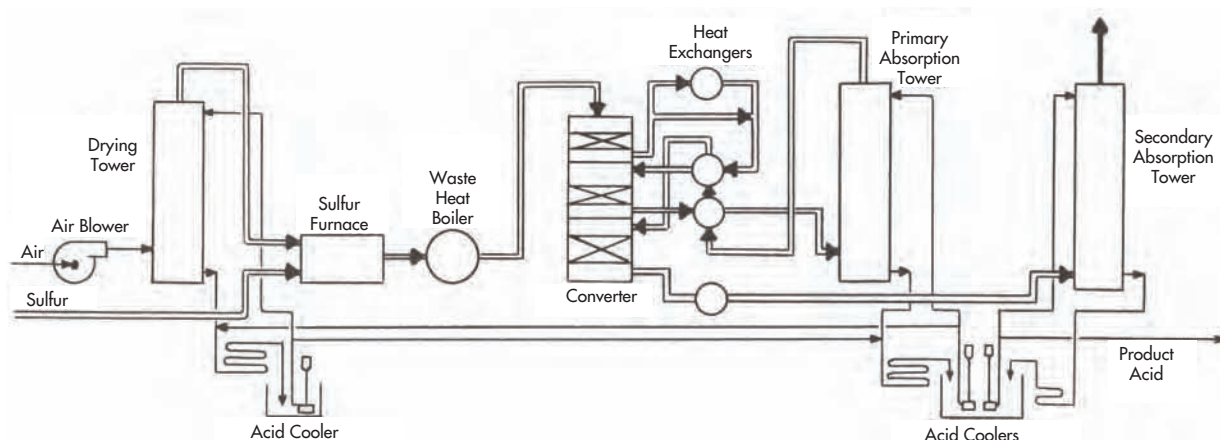
In addition to being the largest source of recovered sulfur in the United States, petroleum refining is a large consumer of sulfur in the form of sulfuric acid. Refineries use sulfuric acid in the alkylation process, which combines specific hydrocarbon materials to produce high-quality gasoline. In nonferrous metals production, processes have been developed that dissolve the various metals from the host rock with sulfuric acid and then recover the desired metals from the solutions. Copper has been produced through a solvent extraction–electrowinning (SX–EW) process since about 1967. Nickel can be produced using a pressure acid leach process.

Another industrial use of sulfuric acid is the source of one sulfur compound used in agriculture. Ammonium sulfate is a by-product from the production of caprolactam, an organic chemical that is a precursor for the nylon-6 polymer that is used in carpets, other textile products, and plastics. Through a series of complex reactions, sulfur, ammonia, and benzene combine to form caprolactam and ammonium sulfate. This process is unusual in that as it consumes sulfuric acid, it produces a usable sulfur by-product—ammonium sulfate, which is used in agriculture.

Although not currently widely used, sulfur construction materials can offer improvements over more conventional materials, especially in specific applications. Sulfur construction materials include sulfur concrete, sulfur-extended asphalt pavements, precast concrete components, extrusions, and cast-in-place forms. Other major end uses for sulfur and sulfuric acid are hydrofluoric acid production, pulp and paper processing, and titanium dioxide production.

Smaller end uses include vulcanization of natural and synthetic rubber tires, production of explosives and other organic and inorganic chemicals, steelmaking, and the production of synthetic rayon fiber. The electrolyte in lead–acid batteries is sulfuric acid.

In industry, the rubber and tire sector is the prime user of special sulfur, using ventilated, micronized, and insoluble forms, all of which are necessary in the vulcanization process. Much smaller quantities of specialty grades are used in the manufacture of such diverse items as pharmaceuticals, matches, fireworks, and textiles.



Source: Barker 1983.

Figure 15. Simplified flowsheet, double-contact sulfuric acid plant

Many other processes use sulfur and sulfuric acid, but listing all of them would be nearly impossible.

Uses for Sulfur with Potential for Growth

Various industrial, academic, and governmental groups have been researching expanded uses for sulfur for some time. The growing supply of sulfur in both elemental and combined forms has led to the development of a number of new products. The use of sulfur in construction applications possesses the largest potential for new sulfur consumption. The practicality of these applications is largely a function of the price of sulfur in relation to competing materials.

Many products have been researched, and some are currently in use. The most promising construction uses are sulfur-extended asphalt paving applications, which give increased durability and performance over a wider range of temperature, and sulfur polymer concrete, a paving or construction material that uses a modified sulfur binder with conventional aggregates. Other construction uses include an extender or recycling agent for used asphalt; foamed sulfur with high compressive strength and insulating properties to be used for insulation, pavement subbases, and possibly lightweight structural applications; an impregnator of various compounds to increase strength, durability, and water resistance; a coating mixed with fibers or modifiers on block or brick buildings, linings for ponds, and other applications where a durable coating is useful; sulfur concretes, mortars, and aggregates with enhanced corrosion and salt resistance; and molded sulfur blocks for tile and brick. Other research has tested using sulfur in electrodes in alkali metal batteries and in sewage and wastewater treatment (Muir 1982; Terrel 1982; Barker 1983).

Paving materials containing sulfur have been shown to possess superior qualities to more conventional paving materials in tests at numerous sites but have enjoyed limited commercial application. In sulfur-extended asphalt, up to 30% of the asphalt binder is replaced with elemental sulfur, making pavement with increased stability, reduced rutting, and increased resistance to cracking at low temperatures (Keenan 2003). Sulfur concrete has several attractive properties that make it superior to portland cement concrete in some applications. These include strength and durability; short setting times and rapid achievement of full strength; impermeability; resistance to corrosion from acids and salts; and high electrical resistivity. Sulfur concrete is particularly effective in high-corrosion environments

such as industrial flooring, acid storage tanks, electrolytic cells, sewer pipes, and bridge decking (Pickren and Mollère 2002).

Copper SX-EW operations are expanding around the world, especially in Australia, Chile, Peru, and the United States. With large reserves of leachable copper ores identified around the world, SX-EW processing holds the potential for significant growth and, with it, significant increases in sulfur and sulfuric acid consumption (Gillen 1996).

In the nickel pressure acid leach (PAL) process, sulfuric acid reacts with nickel laterite ores under high temperature and pressure to dissolve the nickel from the minerals. Large quantities of sulfuric acid are required to recover nickel from the ores, averaging about 30 t of acid per ton of nickel produced. This end use could add significantly to sulfur and sulfuric acid demand, but detailed and specific forecasts are not available.

ECONOMIC FACTORS

Costs

Economic factors and costs of production in the sulfur industry must be considered separately for the voluntary and involuntary producers. As with most industrial minerals, the voluntary sulfur industry is market driven. The degree of use of sulfur and sulfuric acid depends on worldwide economic activity and the health of industries that use sulfur-bearing compounds for the production of other goods. That is not entirely true for involuntary producers who must recover sulfur if their primary operations are to remain active.

What remains of the voluntary sector of the sulfur industry is based on the orderly mining of discrete deposits of native sulfur to obtain as nearly a complete recovery of the resource as economic conditions will allow (Morse 1985). This requires a relatively assured market and a price structure attractive to both producers and consumers. The assured market is commonly based on the relatively close proximity of sulfur users, frequently fertilizer production centers, and the availability of cheap transportation to end users. To a significant extent, stability of sulfur supply and price is accomplished by the maintenance of large stocks of sulfur by the producers.

For the Frasch producers, the main operating expenses are fuel for heating the process water, chemicals for treating the water, and the cost of drilling production wells. Work-force requirements are relatively low. Additional costs include plant maintenance,

royalty payments to landowners (frequently a significant cost), taxes, and transportation. High fuel costs or excessive subsurface water loss can increase the cost of sulfur recovery to a point where it is no longer profitable to operate the plant.

In contrast, involuntary producers are often forced to recover sulfur from their primary product because of environmental restraints or other mandates. The economic desirability of producing sulfur is often subordinate to the necessity of recovering it, and the sulfur revenues may represent only a small portion of the revenues (sometimes not even enough to pay for recovery) from the primary product. In such cases, there may be no ready market for the sulfur or sulfuric acid, and the producer may be forced to dump the product on the market regardless of the cost. The sulfur may also be transported to a market far from the source, and so the transportation charge constitutes a large part of the sulfur cost. Involuntary sulfur production depends on demand for the primary product, and as such is always independent of the need for sulfur.

Sulfur prices can vary greatly by location, source, and terms. In late 2004, *Fertilizer Markets*, a weekly fertilizer industry newsletter, published sulfur prices that ranged from \$50 to \$93/t (Anon. 2004e). *Green Markets*, a similar publication, reported prices ranging from \$12 to \$74/t for other locations (Anon. 2004c). Tampa, Florida, Frasch prices were once the standard against which the prices for all other markets were compared. Frasch sulfur once demanded a premium price because of its superior quality to recovered sulfur, but recovered sulfur has improved to a level comparable to Frasch and its availability to the point that no separate prices are published. As the Frasch industry declined, so has its dominance in sulfur pricing strategy.

By 1990, world sulfur price leadership had shifted from U.S. Frasch producers to the Canadian recovered sulfur exporters. This shift was aided by the ability of Canada to export most of its production from the Port of Vancouver and to ship large volumes from vatted stocks. The abundance of sulfur exporters has diluted the ability of any one industry segment to influence prices. International sulfur trade has become quite competitive, and consumers sometimes have the upper hand in price negotiations.

Markets

The international market for elemental sulfur is active and growing. In 2003, world sulfur trade was 24 Mt, representing 54% of all elemental sulfur produced globally, compared to 1990 when 17 Mt (44% of global production) was traded internationally. The exporters with more than 1 Mt in 1990 were Canada, Poland, Saudi Arabia, and Mexico. The leading exporting countries in 2003 were, in descending order of export tonnage, Canada, Russia, Saudi Arabia, the United Arab Emirates, and Japan, all with more than 1 Mt of elemental sulfur exports.

Countries with more than 1 Mt of elemental sulfur imports in 2003 were China, Morocco, the United States, Tunisia, Brazil, and India. All of these countries use the majority of their sulfur imports to produce sulfuric acid, which is used for phosphate fertilizer production.

Sulfuric acid also is traded internationally, but to a much smaller degree than crude sulfur. Sulfuric acid trade is extensive in Canada, Europe, Japan, Mexico, and the United States (Ober 2004).

Transportation

Sulfur can be transported either in liquid or in solid states. Conversion to sulfuric acid, the principal end use, is easiest using liquid sulfur, so this has become the preferred form, especially when environmental effects are considered. When sulfur cannot be transported to a consumer in the liquid form, it is converted to a variety

of solid forms for transportation or is stockpiled. Stockpiling of sulfur is cheapest by far in large solid blocks (vats) that are broken or melted before shipment. Because sulfur block remelting is expensive, as is liquid sulfur-handling equipment, transport and handling of formed solid sulfur is often more economical except where liquid-handling facilities are in place.

Transporting sulfur in the liquid phase offers certain advantages, including ease of handling, absence of fugitive dust, and reduced losses. Unprotected personnel, however, may be exposed to hydrogen sulfide and sulfur dioxide during handling. Problems associated with solid sulfur include environmental degradation from fugitive dust, possible ignition of sulfur or explosion of sulfur dust, and corrosion of unprotected metal (Morse 1985).

Sulfur transportation costs can be a critical factor in determining the economic viability of a sulfur production facility. For example, sulfur in western Canada must be shipped to Vancouver by rail, adding a significant charge to the cost of the sulfur. Some of the oil sands operations are so remote that transportation costs have limited their availability to international markets of sulfur. The same situation exists in Kazakhstan, but pressure from government officials to reduce sulfur stocks has spurred the installation of forming apparatus to make the Tengiz material more attractive in the global marketplace.

Alternative Materials

For many uses, there are no alternative materials that can replace sulfur or sulfuric acid. In a number of diverse areas, however, hydrochloric or other acids can be substituted for sulfuric acid. The prices of these acids generally dictate which one will be used, and sulfuric acid has been the most widely used because of its relatively low cost. Sulfuric acid has been replaced by hydrochloric acid in the production of titanium dioxide. Because hydrochloric acid production costs have decreased, it could replace sulfuric acid in other applications as well. Sulfuric acid can be replaced by hydrofluoric acid in petroleum alkylation, but sulfuric acid is often perceived as safer than hydrofluoric acid (Anon. 1990c).

Environmental Considerations

Sulfur-bearing compounds, particularly sulfur dioxide and sulfuric acid, are of prime concern in legislation restricting releases of contaminants to the atmosphere and bodies of water. The broad topic of sulfur as a pollutant is well beyond the scope of this discussion, but it should be remembered that sources of sulfur pollutants are now used as sources of recovered elemental sulfur, as previously discussed.

As legislation affecting atmospheric discharge of sulfur oxides or sulfuric acid is tightened, larger quantities of sulfur (generally as acid or calcium sulfate) will be available for use in other industries. Similarly, discharges of sulfuric acid to bodies of water are increasingly prohibited. Dilute acid dumping at sea is now restricted by the European Union, and this measure, coupled with similar efforts elsewhere, has prompted an increase in the recycling of waste acid. Spent sulfuric acid was formerly neutralized or otherwise disposed of; now it is regenerated at numerous sites, where it is reburned with additional sulfur to produce regenerated acid and additional virgin acid.

Environmental concerns also affect sulfuric acid consumption indirectly. Because of environmental pressures, manufacturers of titanium dioxide (a pigment commonly used in paint) have largely converted their manufacturing process from one using sulfuric acid to a chloride-based process.

The environmental impacts of native sulfur mining and transportation are generally minimal and restricted to small areas. Frasch

mining operations commonly experience varying degrees of subsidence from sulfur removal, but at many mines, particularly in western Texas and offshore of the Gulf of Mexico, subsidence is mainly an engineering challenge. Bleedwater recovered during Frasch mining may have to be treated or cooled before it is disposed of, but in some cases water is scarce enough that the bleed water is reused. Native sulfur spilled at the surface quickly reacts to form sulfurous and sulfuric acids, which may lead to acid drainage and corrosion damage, but these effects are generally restricted in area and of short duration.

FUTURE TRENDS

Outlook for Consumption

Demand for elemental sulfur and sulfur-bearing products has continued to grow steadily as the world population and economy have grown, but temporary slumps in the market for sulfur have occurred concurrent with economic recessions. The Sulphur Institute predicts that world sulfur consumption will grow an average of 2.3% annually through 2011, reaching 74.2 Mt at that time. Fertilizer should continue as the dominant end use for sulfur, but other end uses will grow also, especially in metal leaching (Anon. 2003b).

Outlook for Supply

Production exceeded consumption in 2003 for the twelfth consecutive year, although surpluses were smaller than they had been in recent years (Kitto 2004). It appears, however, that much of the surplus is material in those remote locations that inhibit transportation to market. Stocks in Kazakhstan grew, but Canadian stocks declined for the first time in several years.

Recovered sulfur is expected to continue to increase, although reinjection projects at natural gas operations may minimize its effect on the supply/demand imbalance. North American sulfur recovery at natural gas operations has already declined as a result of depletion of deposits, but reinjection projects are likely to remove significant quantities from the market beginning in early 2005. Other reinjection plans may limit the growth in gas-recovered sulfur that could be produced at expanded operations, especially in Kazakhstan. Although not a major force in global sulfur trade in 2003, improvements to sulfur forming and handling facilities were under way, making increased availability of sulfur from Kazakhstan likely.

Sulfur production from Canadian oil sands operations will increase as more projects come on stream, but these deposits also are in remote locations with little of the necessary infrastructure to move large quantities of material to major markets. If markets do not expand in less conventional areas such as construction, oil sands companies may choose to store their sulfur underground until the markets improve. This would limit the effect that large additional quantities of sulfur produced in Canada would have on the world market.

Petroleum refiners have fewer options for disposing of excess sulfur and more potential for growth in production. Refineries are located in populated areas where large stockpiles of solid sulfur are not acceptable, and they are not close to formations amenable to reinjection of sour gases. Even in countries with a short history of environmental protection it is becoming more imperative that they reduce sulfur dioxide emissions from refineries and remove the sulfur from their finished fuels, both of which increase the production of elemental sulfur. In addition to these factors, refineries are increasingly dependent on crudes with higher sulfur content, necessitating additional sulfur recovery capacity. Thus, sulfur production from oil refineries would be expected to increase as the production of petroleum products increases, but more sour crudes, more stringent environmental controls, lower sulfur levels in fuels, and fewer

alternatives for disposing of excess supplies suggest that sulfur from this source is likely to expand at a higher rate than that of other refinery products.

In most industrialized regions, especially Japan, North America, and Western Europe, environmental regulations have resulted in very high sulfur recovery and very low sulfur dioxide emissions. Lower sulfur fuel limits and further reductions in allowable emissions are expected to add relatively small quantities of recovered sulfur. The refining of higher-sulfur crudes will have much more effect on sulfur production at refineries in these regions. In developing countries, however, more stringent environmental regulations and better enforcement of the selective laws represent the potential for very large additional supplies of recovered sulfur. In addition, these producers will face the same challenges with lower sulfur content in fuels and higher sulfur content of the crudes processed. These factors could result in tremendous increases in elemental sulfur supplies from oil refineries. A recent analysis took these factors into account and predicted that elemental sulfur recovery from oil refining could approach 50 Mt within 25 years, an increase of nearly 200% over the 17 Mt recovered from that source in 2003 (Stevens and Hernandez 2003).

Voluntary production of elemental sulfur is expected to remain relatively steady until the remaining mine in Poland ceases production. The possibility exists for Frasch production to resume in Iraq, perhaps with the assistance of the Polish producer, when conditions stabilize there, but the situation is too precarious to make a definitive prediction of what will happen.

Other voluntary production, including pyrites and other native production, is likely to continue to decline. The environmental factors that make pyrites use undesirable will continue to push consumers to alternative raw materials. Small production of native sulfur may persist where it is used for local consumption.

In conclusion, production of recovered sulfur is expected to increase steadily for the foreseeable future. Frasch and native sulfur and pyrites production is likely to continue to decrease in importance and, at some point, cease entirely unless new high-volume end uses become widely accepted.

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Talc

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INTRODUCTION

The term *talc* refers both to the pure mineral and a wide variety of soft, talc-containing rocks that are mined and utilized for a variety of applications. Talc occurs fairly widely in a range of purities, and it is mined on every continent. The commercially exploited ores contain 20% to 99% of the pure mineral, and, although the trend is toward more upgrading and higher purity, many applications require the properties of the minerals that occur with talc.

The terms talc, *steatite*, and *soapstone* are widely used and misused in discussions of talc, its origin, and geology. Steatite was originally considered a relatively pure machinable talc, which was used in ceramic applications. Today there are two widely accepted uses of this term. In geology, *steatite* refers to a relatively pure, massive talc ore. In ceramics, *steatite* refers to a composition containing 80% talc and some fluxes, which is fired and used for electrical insulation—referred to in this chapter as *synthetic steatite*. Soapstone generally refers to a lower-purity talcose ore of mafic or ultramafic origin, which can be sawed or carved.

Talc has been used by humans for more than 3,000 years. The earliest uses were in sculpture and cosmetics. The ancient Chinese carved intricate sculptures from talc rock and made face powders using talc and rice flour. In the first century AD, the Roman philosopher Pliny referred to cosmetics made from *steatitis*. The Vikings used Scandinavian soapstone to carve pottery, many examples of which still survive. Similar artifacts from Native Americans have been found on Santa Catalina Island, west of Los Angeles.

Commercial production in North America dates from 1878 when Colonel Henry Palmer began mining talc for paper and ceramics near Talcville in western New York State. At about the same time, there are reports of small volumes of soapstone being mined in the Sierra Nevada in California for carving. Much of this early production was used for thermal insulating applications, including firebrick, stove insulation, burner tips, and wire insulators. Johnson's baby powder was introduced in the 1880s based on imported Italian powder. Commercial production began in 1904 near Johnson, Vermont; in Southern California in 1914; in Montana in 1935; and in Texas in 1952. U.S. production grew from 83,000 t in 1900 to 1.32 Mt in 1979 (Virta 2003); the major application was ceramic wall tile. A formulation based on tremolitic talc (~60%) and local clays was developed in the 1930s, and this consumed most California, Texas, and New York production well into the 1980s. That application has lessened with changing ceramic tech-

nology, and U.S. talc production has since declined to 817,000 t in 2003. Today, paper and paint are just as important as ceramics, and plastics are the most rapidly growing application.

The first true talc beneficiation plant, built in Johnson, Vermont, in 1937, used multistage froth flotation to upgrade talc ore from 55% to >95% purity. Today, this technology is used in the United States, Canada, Finland, Korea, and Brazil to produce high-grade talc from lower-grade ores.

In the early part of the 20th century, the United States imported talc from Italy and France for use in cosmetics. During World War II, these imports were replaced by domestic talc, and the United States became a net exporter to Europe, South America, and Asia. Over the last 20 years, Canada, and more recently China, have become significant exporters of talc to the United States for paper and plastics applications, respectively. In recent years, the United States again has become a net importer of talc.

In 2002, seven companies produced 817,000 t of talc from nine mines in Montana, New York, Texas, and Vermont, and 250,000 t were imported, mostly from China and Canada. Approximately 180,000 t were exported, mostly to Canada, with Mexico, Belgium, and Japan taking much smaller volumes (Virta 2004). Domestically, ceramics, paper, paint, and plastics are the major uses.

Worldwide, approximately 5 Mt were produced in 2002, with China being the major producer with 1.7 Mt. The United States, Finland, India, France, Brazil, Austria, Spain, Italy, and Australia are other countries producing more than 100,000 t each. Worldwide, paper is by far the major consumer (~40%) of talc, followed by ceramics (~20%), plastics, paint, and cosmetics. In general, world production is declining because of reserve depletion as well as replacement of talc by calcium carbonate in paper filling and by feldspar in ceramics.

The mining, beneficiation, processing, and application of talc is a sophisticated business involving geologists, mining engineers, mineral processing engineers, chemical engineers, surface chemists, and specialists in paper, plastics, ceramics, and cosmetics. In many instances, the processes and applications are unique to talc and even to specific talc deposits. The market for talc is heavily dependent on the scientific research and the technical skills of the producer. Without such applications development, the market declines. This is discussed in more detail in the Commercial Aspects and Future Trends sections later in this chapter.

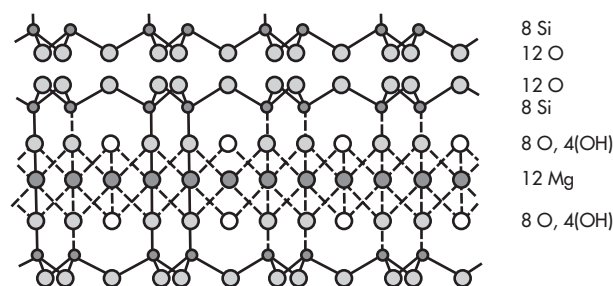


Figure 1. Talc crystal structure

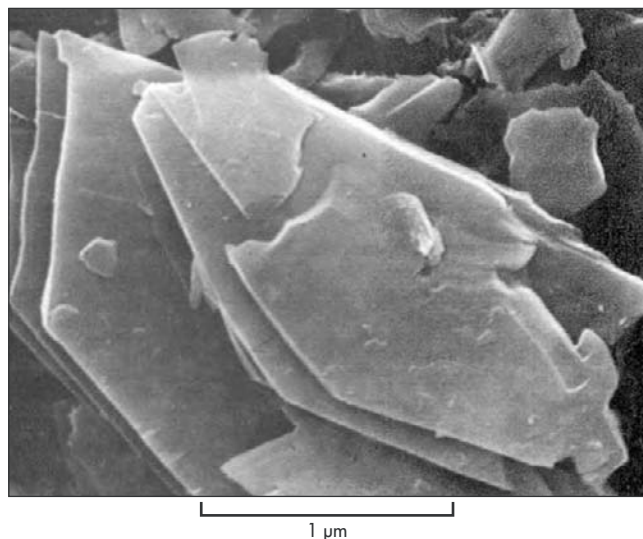


Figure 2. Scanning electron micrograph of talc

The Mineral Talc

Talc is crystalline hydrated magnesium silicate of the general formula $3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$ (see Figure 1). It is one of the layer silicates like kaolin and mica.

The adjacent layers of silica are very weakly bonded with only van der Waals forces, and this allows talc to be easily sheared along this plane. This gives it its natural slippery feel as well as its platy structure and softness (Figure 2). Talc is the softest mineral, with a hardness of 1 on a Mohs scale of 1 to 10.

When talc is split along the silica surface, the surface created is hydrophobic, or antagonistic to water. When it is fractured across the silica-brucite-silica layers, the surface created is ionic (electrically charged) and hydrophilic. Materials that have both a hydrophobic and hydrophilic component are surface active, and this gives talc its unique surface-active properties. Some types of talc are also known as soapstone, because these types are soft and have many soaplike (surface-active) properties.

Talc has a specific gravity of 2.78, a refractive index of 1.58, a specific heat of 0.208 cal/g/°C, and a thermal conductivity of 5 cal/g/sec/°C. It is relatively inert and almost insoluble in conventional acids and bases but soluble in aqua regia and hydrofluoric acid. Talc has a pH in water of 9.0 to 9.5 and very little buffering capacity because of its insolubility. Regulatory authorities consider it a nuisance dust, but it has GRAS (generally recognized as safe) status as a cosmetics and food ingredient.

GEOLOGY

Deposits

The value of a talc deposit is a function of its purity, its color, and its location relative to the market. The purity issue is not related to the absolute percentage of talc present but more a function of specific mineral or metal impurities. Asbestiform minerals and metals such as arsenic and lead are particularly deleterious even at parts-per-million (ppm) levels, and quartz, serpentine, chromium, and pyrite are harmful at levels greater than 1,000 ppm. On the other hand, carbonates and chlorite (magnesium-aluminum silicate) can be beneficial even at levels up to 50%, especially when they are white and the composition is consistent.

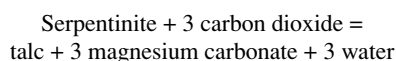
Origin of Talc

Although talc forms by a variety of geological processes, the origins of most talc deposits around the world are clearly defined by the host rock and the accessory minerals found with the talc. Talc deposits are divided into four types of origin: ultramafic, mafic, metasedimentary, and metamorphic. The processes associated with talc formation for each type are outlined in the list that follows.

- Type 1, ultramafic origin
 - Host rock—ultramafic rocks (e.g., peridotite)
 - Step 1—serpentinization of host; high temperature and pressure hydration with little loss of magnesium and silica to form serpentinite
 - Step 2—carbonization of serpentinite; influx of fluid containing 5% carbon dioxide to form talc and carbonate
 - Accessory minerals—magnesite, chlorite, serpentinite, mica, and sulfides
 - Localities—Vermont, United States; Ontario and Quebec, Canada; Norway; Finland; Russia
- Type 2, mafic origin
 - Host rock—mafic rocks (e.g., gabbro)
 - Step 1—serpentinization of host; hydration with little loss of silica and magnesium to form serpentinite
 - Step 2—carbonization of serpentinite; influx of fluid containing more than 5% carbon dioxide to form talc and carbonate
 - Accessory minerals—magnesite, chlorite, serpentinite, and mafic host rocks
 - Locations—Virginia, United States; Egypt
- Type 3, metasedimentary origin
 - Host rock—dolomite or magnesite
 - Process—hydrothermal alteration of host rock by influx of silica-containing fluid
 - Accessory minerals—dolomite, calcite, chlorite, quartz, and feldspar
 - Locations—Montana and Texas, United States; eastern Ontario, Canada; China; Brazil; Australia; India; France; Spain
- Type 4, metamorphic origin
 - Host rock—dolomitic or silica-containing dolomitic marbles
 - Step 1—metamorphism of host rock; subsurface temperature and pressure-driven conversions and recrystallization of the host rocks to form tremolite or actinolite within the host marble

- Step 2—steatization of the tremolite or actinolite; temperature- and pressure-driven alteration of the tremolite to talc and carbonate
- Accessory minerals—tremolite, carbonate, serpentine, actinolite, and quartz
- Locations—New York, California, and Georgia, United States; Italy (Val Chisone)

The formation of talc types 1 and 2 is almost identical. The basic reaction is

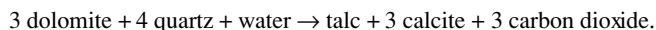


Mafic and ultramafic rocks are dark igneous rocks that are high in magnesium and iron and lower in silica. The products formed are high in iron (5% to 10%), and the magnesite is an iron isomorph. The mafic products are lower in talc content (15% to 35%) and generally useful only for carving or dimension stone. The ultramafic products have 30% to 70% talc and large crystal sizes (>100 µm) and are usually quite platy (high aspect ratio). The latter property results from the folding and fluid movement that takes place during the formation. The stoichiometry of the previous basic talc-forming reaction will give a talc content of 50% to 60%. A further enrichment of talc can take place if the talc-carbonate close to edge of the ore body reacts with silica-rich fluid in the host rock. This process is called “steatization” by geologists and can result in a narrow zone of up to 90% talc near the edge of the ore body. The whole process is called “steatization of serpentinite,” and the ores are often called soapstone or lairdstone. The higher talc content products are often used as is or upgraded to >95% talc purity by froth flotation.

The talc in ultramafic-type ores has high levels of iron and other heavy transition metals (nickel, chromium). Most of these metals substitute for magnesium in the talc lattice and cannot be removed. They are not available and are not toxic, but they do account for the green/blue cast of the pure talc and contribute to the strong brown color when the talc is weathered or fired.

Ultramafic is the most abundant deposit worldwide, but metasedimentary is by far the most widely exploited commercially and accounts for more than 70% of world production.

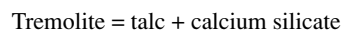
Metasedimentary deposits vary widely in purity and composition from <25% talc in some of the magnesite rocks in Brazil to >95% talc in some of the massive deposits in Montana and China. The basic reaction that forms most deposits is



This reaction would indicate that most talc of this type would be a minor ingredient in a calcite rock. In fact, few deposits have large amounts of calcite associated with them, as the hydrothermal fluids that introduced the silica are believed to have removed the calcite.

A second type of metasedimentary deposit is found in France, Sardinia, and Austria where magnesium-rich fluids altered mica schists to form chlorite, and the silica released during this reaction altered overlying dolomite to talc. These deposits have 25% to 75% chlorite along with the talc and are often referred to as chloritic talc.

Metamorphic deposits were at one time the most commercially important deposit type in North America. The basic reaction is



These deposits are quite variable in talc purity from ~30% in New York State to >70% in Madoc in Ontario. Associated minerals also vary in their levels, with carbonate being the major impurity in

the Madoc deposit in eastern Ontario and tremolite in New York. Tremolite, a calcium magnesium silicate, can occur in either blocky or prismatic forms. The prismatic structure results in a powder that has good dry pressing properties for ceramics. Because the ores are typically very low in iron content, they are white (good for paint) and they fire white (good for ceramics). Tremolite is also a much harder mineral than talc and will build a lower viscosity in suspensions. This property is valuable in paint.

Distribution of Major Deposits

In this section, the focus will be on commercial deposits that are presently being exploited, with lesser emphasis on either historically important or other known deposits.

North America

In the United States, talc is mined in Montana, New York, Texas, and Vermont. In Canada, talc is mined only in Ontario, with minor soapstone production for carving and stove liners in Quebec. Montana has overtaken Texas as the leading producer because of (1) the growth in paper and paint applications, for which Montana products are best suited; and (2) a decline in the older wall tile production technology, which is the biggest market for Texas talc.

Montana. Major massive talc deposits occur in the Gravelly and Ruby ranges of southwestern Montana. The talc is of metasedimentary origin in a carbonate host rock. Deposits range from thin (<1 m thick) veins to massive (100 m thick) pods of steatitic talc. The deposits were first mined under ground in the late 1930s as a source of machinable steatite ore for defense purposes. Today three major open-pit mines produce approximately 400,000 tpy of mostly high-purity talc for paper, paint, ceramic, and plastic applications. Waste-to-ore ratios are quite high at greater than 6:1 in all cases.

The talc was formed by the hydrothermal replacement of magnesium-rich marble. Silica-rich fluids penetrated the marble, reacted with the dolomite, formed talc, and swept away most of the excess calcium carbonate. Cross-cutting fault zones and joints serve as ore-forming fluid conduits and often contain minor blooms as subsidiary veins of talc.

The talc in the Yellowstone mine in the Gravelly Range southwest of Ennis is very fine grained and white to light green in color with yellow staining in the weathered or oxidized zones. Dolomite and quartz are the major impurities, with minor amounts of chlorite, pyrite, iron oxides, and dendrites of manganese minerals.

The talc can occur in high-purity thin (<1 m) veins in dolomite or as thick (>200 m) pods of botryoidal form. The talc was formed during the Proterozoic era or approximately 1,700 million years ago. Economic reserves at the Yellowstone mine are in excess of 40 years at present rates of production.

The other major mines are the Regal and Treasure mines in the Ruby Range in Madison County near Dillon. This ore is not as fine-grained as the Yellowstone mine ore, is white to gray in color, and occurs in lenses of 1- to 5-m thickness in a dolomite host rock. Chlorite is a major impurity along with dolomite, quartz, and magnesite. Pyrite, graphite, mica, and titanium are minor components.

New York. Metamorphic talc ores are mined from the Precambrian Grenville Province in northwestern New York near the towns of Gouverneur and Balmat. In the early years of these mines, which have been exploited since 1878, underground mining was mainly used, but operations are now consolidated into two open-pit mines. The ores are highly tremolitic; typically 60% tremolite, 30% talc, and 10% serpentine. They are very white, low in iron, and occur in both thin veins (2 to 5 m) and thick seams (40 to 80 m) over a

13-km-long, 150-m-wide belt. The host rock is a marble with some gneiss. Zinc deposits also occur in the vicinity, and talc contamination was a major problem in the beneficiation of the zinc ores.

Product applications are focused on paint, with ceramic tile, once a major market, now declining in volume because of technology changes. That, along with health concerns about tremolite, accounts for the decline in production in this area over the last 20 years.

Texas. The major talc production in Texas is from the Allamore Formation near Van Horn in west Texas. The formation is approximately 32 km in length and 8 km wide with talc occurring very close to or at the surface, in thick (10 to 500 m) seams in a host marble and phyllite rock. The talc is of metasedimentary origin and quite unique in that most of it is very dark gray or black. The ore is typically 80% to 85% talc, 10% to 12% carbonates, 2% to 4% quartz, and 0.1% to 0.7% graphite, which accounts for the black color. It is very low in iron content (<0.3%) and thus fires white. Smaller zones of pink to white talc occur and are mined for color-sensitive applications.

The major market for west Texas talc has always been ceramic tile. Because low-cost natural gas is available for firing, the tile industry has become concentrated in the southwestern United States and across the Mexican border in Monterrey. Although tremolitic talcs—well suited for pressing into tile—had been available from California and New York, the low cost and proximity of the Texas talc made these deposits more attractive. It was found that if some of the talc was calcined in lump form and then milled with the raw ore, a much more pressable mixture was produced. This became the standard for west Texas talc.

In recent years, production has steadily declined as ceramic tile technology changed, and talc is used now more as an additive than as a major component of tile body raw materials.

Vermont. Vermont has produced talc for more than 100 years. In the late 1800s, soapstone was mined in Vermont and New Hampshire and cut into blocks for stoves and heating utensils. Production of talc powders began in Johnson, Vermont, in 1904. At one time, seven mines were active in the state, but production is now limited to one, the Argonaut, near the town of Ludlow in central Vermont. The Vermont deposits are part of the Appalachian Orogenic belt, which extends north into Quebec and the Superior Province of eastern Ontario. Similar deposits are found in Norway, Finland, and the province of Karelia in Russia.

Talc was formed from the alteration of peridotite (ultramafic) rocks of Precambrian age, first into serpentine and then to talc and magnesium carbonate by reaction with carbon dioxide. Talc-carbonate mineralization generally is found as an alteration zone rimming a serpentinite core. The deposits vary in size from 1 m wide by 200 m length to 150 m wide by 1.5 km length. The margins of the deposits usually have a thin blackwall containing a biotite-chlorite schist in contact with the surrounding host peridotite. Subsequent shearing has complicated the structures and created zones of high-grade platy talc. Grades typically run 45% to 70% talc, with magnesite, chlorite, serpentine, quartz, and mica being the major impurities. Minor amounts of magnetite, chromite, nickel sulfides, and manganese minerals are scattered in the deposits.

Along with the Ludlow deposit, talc has been mined near Johnson, North Troy, and Waterbury in northern Vermont and in Windsor and Chester in southern Vermont. Vermont talc is crushed and milled as a whole ore for use in rubber, roofing, flooring, and other construction products. Some talc ore was also purified by froth flotation for use in cosmetics and reinforcing plastics, but that is now uneconomic. Environmental activism, directed at both the mining and transport of talc, is strong in Vermont and has hurt the industry in the past 20 years.

Other U.S. Production

Over the years, California and Georgia have also been major talc producers, and Arkansas, Alabama, Maryland, Nevada, North Carolina, Oregon, Virginia, and Washington have had limited production, but other than some intermittent campaigns on old mines and tailings piles, production in these states has ceased today. Only limited discussion of these deposits will be given here, but the reader is referred to a report by Greene (1995) for a more complete description.

In southeastern California, the Inyo or Talc City district was a major producer of high-purity steatite talc from underground mines from 1914 until 1978. This metasedimentary-type deposit produced a very white and very machinable grade of talc. Further east, the Southern Death Valley–Kingston District produced, from the late 1920s to the late 1980s, a very white tremolitic talc, valued for its properties in ceramic tile and industrial coatings, especially marine paints. In the northern Sierra Nevada foothills, small, altered ultramafic deposits were mined until 1997 for roofing and construction products. Similar small deposits have been mined in Oregon and Washington states for soapstone blocks.

In Georgia, deposits of the metamorphic type were mined underground in the Chatsworth Area until 1990. Roofing and construction were the major uses, and a froth flotation plant was built in 1987 to make products for paper and plastics. The project failed because of the inability to produce a high-brightness product and the failure to effectively remove tremolite from the talc. In Talladega County, Alabama, a small metasedimentary-type deposit was mined from 1954 until 1998, and a flotation plant upgraded the product for cosmetics markets. Near Murphy, North Carolina, small metamorphic-type deposits, which produced high-brightness talc for cosmetics and paints, were mined until the early 1980s. In Maryland and Arkansas, altered ultramafic deposits were mined for roofing and ceramics markets.

The mineralogy and chemistry of the commercial North American deposits produced today are summarized in Tables 1 and 2. Tables 3 and 4 present the mineralogy and chemistry of the major international talc ores.

Canada

Canada has deposits of talc in almost every province, but today production is limited to Ontario, with minor soapstone production in Quebec. Canadian production in 2000 was approximately 80,000 t. Major altered ultramafic deposits occur in Quebec, Ontario, Newfoundland, and British Columbia similar in nature to the Vermont deposits. Mining of soapstone, which was sawed for use in lining paper digesters, was a major business in the Broughton Area, dating back to World War I. Powder production began in the 1960s with a dry mill in Broughton and a flotation plant near St. Hyacinthe near the Vermont border. These operations have since shut down because of environmental and health (asbestiform contamination) concerns, and now only minor soapstone cutting for stove liners and sculpture carving continues.

Mining of the metamorphic deposits near Madoc in eastern Ontario, which dates from 1896, is now the only North American underground talc mine. The ore ranges from 30% to 80% talc, with dolomite, calcite, tremolite, and mica as the major impurities. It is white to gray in color and milled without beneficiation for applications in plastics and paints.

An altered, ultramafic deposit in Penh orwood Township in northeastern Ontario near Timmins was developed by open-pit mining in 1975, and a froth flotation plant was built adjacent to the mine. The ore is about 45% talc, with magnesite, magnetite, chlorite, and serpentine the impurities. It is now the major talc producer

in Canada and makes products for the paper, plastics, paint, and ceramic industries.

Central and South America

There is minor talc production in Mexico, Argentina, Peru, Colombia, and Uruguay. The major South American producer is Brazil, which mines about 300,000 tpy from deposits in Parana, Bahia, Sao Paulo, and Minas Gerais states. Parana is the major producing state with 200,000 tpy of talc from meta sedimentary deposits used primarily in the ceramic tile industry. The ore is 60% to 90% talc, with carbonate, chlorite, and quartz as the major impurities. It is gray to black in color but fires white because of a low iron content. In Bahia Province, a higher-purity white talc is produced by floating talc from a magnesite ore that is mined for steel refractories. Also in Bahia, some highly platy, mica-type talc ores are selectively mined in small quantities for the cosmetics market.

Europe

The major talc producer in Europe is Finland, with almost 500,000 t, followed by France (350,000 t), Italy (140,000 t), Austria (135,000 t), and Spain (100,000 t). There are major modified ultramafic deposits in northern Europe across northwestern Russia, Finland, Sweden, and Norway. The Finnish paper industry resorted to using these ores as fillers during World War II, when Cornish kaolin could not be obtained. A large paper company, United Paper Mills, developed the Lahnaslampi deposit in central Finland in 1969. A huge flotation facility was built nearby at Sotkamo, and production began to supply filler for papermaking. Two more major deposits at Horsmanaho and Lipasvaara, each with nearby flotation plants, were opened in 1977 and 1985, respectively. These are now consolidated under Mondo Minerals and produce talc primarily for paper coating, filling, and pitch control.

The deposits are all 55% to 65% talc with magnesite as the main impurity. Nickel sulfides occur in the Lahnaslampi ore and are recovered separately in the float circuit and sold as a by-product. The float plant upgrades the talc to ~95% purity with the balance being chlorite and magnesite.

In France, Talc de Luzenac has mined a talc-chlorite deposit of metasedimentary origin at the Trimouns mine in the Pyrenees in southern France for 100 years. The ore vein is 10 to 80 m thick, more than 1,500 km long, and dips at 20 to 60 degrees. The talc was formed when magnesium-rich fluids altered footwall silica and alumina-rich mica schists and gneisses. Chlorite, which makes up 30% to 60% of the ore, was formed in the micaceous and feldspathic footwall during magnesium enrichment, and the silica that was released during chloritization transformed the overlying dolomites into talc. Unmineralized dolomite forms the hanging wall of the deposit. Although the average ore is about 60% chlorite and 35% talc, through selective mining and hand sorting, grades with up to 90% talc are produced. Carbonates (0% to 3%), quartz (0% to 3%), and iron (0% to 2%) are the other impurities. Because of the elevation (2,500 m), mining is campaigned from May through October. After the ore is graded in lump form, it is transported by an overhead cableway down the side of the mountain to the mill located in the village of Luzenac. Paper and plastics are the major markets.

A very similar type of deposit comes from Austria's main producing mine in Rabenwald in the province of Styria. The talc-chlorite ore is mined in an open pit on the top of a mountain, and, after sorting, lump and screened ores are transported down the mountain to the mill in Oberfeitz by an overhead cableway. In the nearby village of Lassing, 10 underground talc miners in 1998 were killed when the mine was inundated with mud after a heavy rainfall. That mine is now closed.

Table 1. Typical mineralogy of North American talc ores

Mineral	Montana	Texas	Vermont	New York
Talc	95	80	60	30
Carbonates	2	15	35	<2
Tremolite		trace		60
Serpentine			trace	10
Chlorite	1	1	3	
Quartz	0.5	3	trace	1

Table 2. Typical chemistry of North American talc ores, wt %

Oxide	Montana	Texas	Vermont	New York
SiO ₂	61.0	56.8	37.0	60.0
MgO	31.0	31.3	34.0	27.0
CaO	0.3	2.3	1.0	8.0
Al ₂ O ₃	<1	<1	2.5	<1
Fe ₂ O ₃	1.5	0.3	6.0	0.3
LOI*	5.3	8.1	20.0	4.0

* LOI = loss on ignition.

Table 3. Typical mineralogy of international talc ores, wt %

Mineral	Finland	France	China	Australia
Talc	55	55	93	95
Carbonates	40	2	3	2
Chlorite	5	40	3	1
Quartz	trace	1	0.5	0.5

Table 4. Typical chemistry of international talc ores

Oxide	Finland	France	China	Australia
SiO ₂	37.5	45.1	61.0	61.1
MgO	34.0	31.0	32.2	31.1
Al ₂ O ₃	3.5	11.0	2.0	1.0
Fe ₂ O ₃	6.5	2.1	0.7	1.0
LOI	22.0	9.0	5.9	5.5

In Italy, IMI Fabi operates two large underground mines in the Sondria region of northern Italy. The ore, a metasedimentary type with high levels of dolomite and poor color, is used mainly in roofing and noncolor-sensitive plastics applications. Luzenac Val Chi sone operates another underground mine at Fontane, near Pinerolo in northwestern Italy. The ore, of metamorphic origin, is particularly platy and white and is prized in cosmetics and plastics. Luzenac also operates a small open-pit talc-chlorite deposit in Sardinia.

Spain

High-purity steatite talc is mined in Leon, and a low-grade ultramafic deposit is mined in Malaga. The Leon ore is from a high-grade metasedimentary deposit with good brightness and low iron content and is especially useful to the large Spanish ceramic tile industry. The Malaga deposit is used mainly in roofing and agricultural applications.

Other European Production

The other major producer in Europe is Norway. Mondo Minerals operates two talc-magnesite deposits (ultramafic origin) in

Altemark and Framfjord. Because of reserve issues, production has fallen significantly in recent years. The ore is mined at plants in Norway, England, and the Netherlands and sold primarily for industrial paint applications. Other small ultramafic deposits are mined in Sweden, the Shetland Islands, and Karelya in western Russia. A quite famous but small, high-purity steatite-grade talc deposit was mined at Gopfersgrun in Bavaria until 2002. The first machinable steatite used by industry was from this deposit, and the first synthetic steatite composition was produced by Thurneaur in 1932 with talc powder from this ore.

Africa

Relatively little talc is produced in Africa, with Egypt, Morocco, and South Africa having the only meaningful amounts of production. Egypt has deposits of both ultramafic and metamorphic origin in the southeastern deserts in the Precambrian metamorphic rocks of the Nubian-Arabian shield. Production has tended to be intermittent because of logistical, economic, and ownership issues. Some high-quality, cosmetics-grade talcs are mined near Agadir in Morocco. South African production is from mainly lower-grade mafic deposits that are milled for low-value uses in rubber dusting, fertilizers, and putties.

Australia

In Australia, three relatively high-grade metasedimentary deposits are mined. In Western Australia, the large Three Springs mine is in a massive, finely crystalline, white, high-purity talc deposit that has been mined by open-pit methods since 1961. The ore body is approximately 500 m long by 350 m wide by 20 m thick and is cut by a series of diabase dikes. Most of the ore is exported in lump form to Japan and Europe for paper and ceramic applications. Luzenac purchased the Three Springs deposit from Western Mining in 2001.

Also in Western Australia, the Mt. Seabrook deposit is a smaller, macrocrystalline, high-purity talc deposit that was opened in 1971. Although operation has been intermittent because of ownership changes and its remote location, the ore is valued in cosmetics markets for its plateness. In southern Australia, the Mt. Fitton deposit is the main source of talc for the Australian domestic market. The talc occurs in narrow (1 to 5 m thick) veins in a dolomitic rock, and both high- and low-purity grades are produced and shipped to a mill in Adelaide.

Asia

Asia is both a major talc-producing and -consuming region. China is the world's largest producer and exporter with 1.7 Mt, while Japan (450,000 t) and South Korea (200,000 t) are major importers. India (450,000 t) is the other major producer with most talc consumed domestically (Roskill Information Services 1997; Harris 2001; Virta 2004).

China

China has approximately 120 working talc mines located in three provinces: Liaoning and Shandong in the north and Guangxi in the south. Almost all the talc is of metasedimentary origin, and much of it, especially in Liaoning and Guangxi, is of high purity and has high brightness. Ownership is distributed among a range of provincial, district, and local village governmental bodies with limited private ownership.

The Liaoning deposits formed as metasomatic replacements of magnesitic and dolomitic carbonates of the Late Proterozoic Liaohe-Dashiqiao Group. The carbonates are dominantly magnesite with some tremolitic deposits within dolomite and calc-silicate rocks. The rock orientation is east-north east. High-purity veins are gener-

ally podiform and sheared. Mined widths range from 2 to 15 m with strike lengths from 10 to 500 m. Deposits are mined both underground and in open pit. The ore is sorted in lump form at the mine or in nearby villages, and about 50% is exported to Japan, Taiwan, and Korea.

In Shandong, the deposits belong to the Late Proterozoic Jueten-Zhanggezhuang Group. The talc is formed by metasomatic replacement of magnesium carbonates. Most ore is mined underground in veins of 7 to 30 m in width, often extending for hundreds of meters. The ore is of lower grade (<85%) talc, with the balance being magnesium carbonate and dolomite. Most ore is milled and used locally in the paper and ceramic industries.

In Guangxi, the talc deposits belong to the Middle Proterozoic Banxi-Heong Group and are the largest, highest-purity veins of talc in China. The principal mines are located along a N30°E fracture zone within a belt 2 km wide by 8 km long. The host rock is an off-white dolomitic marble that is contorted into high-amplitude isoclinal folds.

The talc veins are concordant, lenticular bodies that average 5 m in thickness and are 200 m long. The veins widen to 80 m and have sharp but irregular contacts with the host marble. The ore is typically light green to gray and locally very white. Chlorite, dolomite, magnesite, and quartz are the main contaminants.

Almost all mining in Guangxi is in open pits. Most high-brightness ore is exported to Europe and the United States in lump form. Reserves of high-brightness talc and production have been reported as diminishing in recent years.

India

The major Indian reserves and production are in the state of Rajasthan where the Golcha Group is the dominant producer. Most deposits are of the metasedimentary type, mined by open-pit methods, and sorted and processed locally for the domestic market. Approximately 5% of production is exported to Europe, Southeast Asia, and western Africa.

Production of talc is limited elsewhere in Asia, with Korea, Japan, and Iran having significant deposits and some production. At one time, Korea was a major producer, but output has fallen because high-quality, low-cost ore is available from China.

TECHNOLOGY

Exploration

Despite the availability of many modern geophysical techniques, the most effective talc exploration techniques are traditional field diagnostic, sampling, and mapping methods. Although talc is physically weak, it is chemically very stable, and the presence of talc in outcrops and in the overlying soils is the best diagnostic tool. After the deposits are sampled and mapped, if the quality is acceptable, the deposit is drilled, the quality confirmed, and the reserve estimated.

The value of any talc deposit is a function of its color, purity, and location, along with the availability of appropriate markets. Nowhere is this more true than in Finland, where relatively low-purity and low-color ultramafic deposits were developed successfully to serve the local paper market and replace expensive imported kaolin.

Mining

Most talc is mined today by conventional open-pit, drill-and-blast, shovel-and-truck techniques. The major difference from conventional technology is that blasting is minimized to reduce breakage of soft talc ore, and all shovel work is accompanied by a high level of selectivity to minimize cross contamination of high- and low-grade material. Many producers analyze blast-hole cuttings

to delineate ore grades and select blast patterns accordingly. Shovel operators can select ore or waste by color or texture for different grades. Equipment such as 10-m³ shovels and 150-t trucks are common in North America and Europe, while 1-m³ shovels, 20-t trucks, and even hand-carried baskets are used in Asia and Brazil.

A typical western talc deposit is drilled on 30- to 50-m spacing, and the ore body is characterized by mineralogy, color, and chemistry. From this, the ore body is defined and a computer-aided mine plan is generated. Overburden is removed and stored elsewhere for eventual use in mine reclamation. Mining is typically done on 5- to 10-m benches. Before each blast, drill holes are analyzed and, if necessary, the shot is reconfigured to remove potential waste or segregate a better quality of ore. After the blast, the shovel operator will selectively scoop the rock into haul trucks and designate it as waste or as a low or high grade of ore.

Waste-to-ore ratios are often quite high, especially for massive steatite deposits. Typical values range from 5:15 for massive ores and 1:3 for the lower-purity ultramafic grades. Underground mining is now less common and is declining rapidly in importance. Pure talc is a very soft, noncompetent rock, which is often highly fractured, of varying thickness, and in steeply dipping bodies. Where veins are thin and the surrounding rock is competent, openhand mining is acceptable with limited timbering. In thicker veins, underhand mining is necessary; where the veins dip steeply, shrinkage stoping is used. Some low-grade deposits can be mined by room-and-pillar methods, for which equipment is much smaller, blasting and mucking much more selective, and waste-to-ore ratios much lower than in open-pit mining. Continuous miners can be used on softer high-grade veins.

Reclamation

In contrast to past practice, reclamation is now an integral part of all talc mining in developed countries. Waste piles are graded, covered with topsoil, seeded, and monitored for a return to natural vegetation. For both surface and underground mining, both surface and subsurface water flow is measured, monitored, analyzed, and if necessary treated to meet local and national discharge standards. Some pits are backfilled or converted to a beneficial long-term use, such as recreation.

Beneficiation

Two major types of ore beneficiation are used for talc: sorting for massive talc ores and froth flotation for ultramafic and lower-grade ores. The sorting technology includes hand sorting of lump ore, mechanized optical sorting of pebble-sized ore, and slide sorting of lump ore to separate talc from dolomite and other impurities. Hand sorting usually takes place in sheds at process plants. Screened ore (5 to 25 cm in size) is run across belts, and, if low grade, talc is picked from the ore; if high grade, waste is picked from the talc. A slide-sorting process to replace this function was patented by Cyprus Industrial Minerals (now Luzenac America) in 1988. Talc has a much lower coefficient of friction than dolomite or quartz, so when dropped on a rotating plate, talc will quickly slide off while the other ore will be carried around and removed by a scraper. This type of sorting is particularly useful for high-grade talc that occurs in narrow (<1 m) veins in a carbonate host rock.

Optical sorting processes usually require talc to be washed and screened into narrow pebble size (1–2 cm) range. A camera scans each particle as it falls through a testing zone, and then jets of air either remove ore (for low grade) or waste (for high grade). This type of sorting is suitable for higher-value products such as required for cosmetics or plastics applications.

An important factor in the sorting and color beneficiation technology is that blending of low- and high-color ore is not linear. If equal parts of an 80 and a 60 brightness ore are mixed, the color is not 70 but much closer to 60. Conversely, if a small fraction of high-brightness ore is sorted out of a low-brightness ore, the effect on the color of the remaining low-brightness ore is minimal.

Ore beneficiation by froth flotation is usable for almost any ore, but it is particularly useful for ores where the talc is intercalated with the waste, such as talc ores of ultramafic origin. Ore is crushed and then milled to liberation size, typically about 50% passing 325 mesh. It is slurried in water at about 25% solids, and a frother, such as methyl isobutyl carbinol, is added. It is then passed through two to five stages of flotation where the talc content is upgraded to >95% purity. Carbonates, quartz, chlorite, and tremolite are selectively removed by this process. If a problematic level of dark magnetic minerals is present, high-energy magnetic separation is used to remove them from the floated product. The concentrate is thickened, filtered, and flash dried. Some producers mill in conjunction with the drying process.

Analytical Techniques and Measurements

A tiny fraction of talc is sold in lump form for carving, machining, or decorative applications. A significant volume of Chinese, Australian, and U.S. production is exported in lump form to the consuming countries. The vast majority of the ore must be reduced to a powder for end use. The size needed ranges all the way from –10 mesh (top size 2.5 mm or 2,500 μm) to 1,250 mesh (top size 10 μm). The distribution of the particles, sometimes called the granulometry, is also important. Some applications require a narrow particle-size distribution and some a broad distribution. Finally, the shape of the particles is critical in some applications and is affected by the grinding method.

In describing milled products, a number of measurements are used, most notably median particle size and top size. Median particle size is most often measured by sedimentation techniques using an instrument called a sedigraph. The sedimentation technique assumes that all particles are spherical, which talc particles are not. A sedimenting talc platelet will behave like a much smaller sphere, skewing the reported distribution toward the fine end. The technique is generally used only for subsieve-size particles (100% finer than 100 mesh [150 μm]). The technique will give a full particle-size distribution and is accurate down to ~0.3 μm . The other major subsieve technique is laser particle size analysis with instruments made by a number of companies including Coulter, Alcatel, and Horiba. Unlike the sedimentation technique, the laser analyzer measures the long dimension of the talc platelet, and thus the distribution reported by the laser will be quite a bit larger than that by sedigraph.

For top-size measurement, sieving and Hegman drawdowns are used. Sieves of 40 to 325 mesh are common. The Hegman bar, also called the fineness-of-grind gauge, is a technique borrowed from the paint industry. A small quantity of talc powder is dispersed under high shear in a vegetable oil. A small portion of the talc in oil dispersion is placed on the Hegman bar, which has a very accurately machined groove with a depth of 100 μm at the top end and zero at the bottom. When the talc in oil dispersion is drawn down through the groove, the coarsest particles will show up somewhere in between, and the material is given a Hegman rating based on the largest particles in the sample. For instance, particles of 70 μm give a 3 Hegman, and particles of 25 μm would give a 6 Hegman.

Other critical properties that are measured include surface area, bulk density, and color. Surface area is measured by the Brunauer, Emmet, and Teller (BET) method. It consists of adsorbing

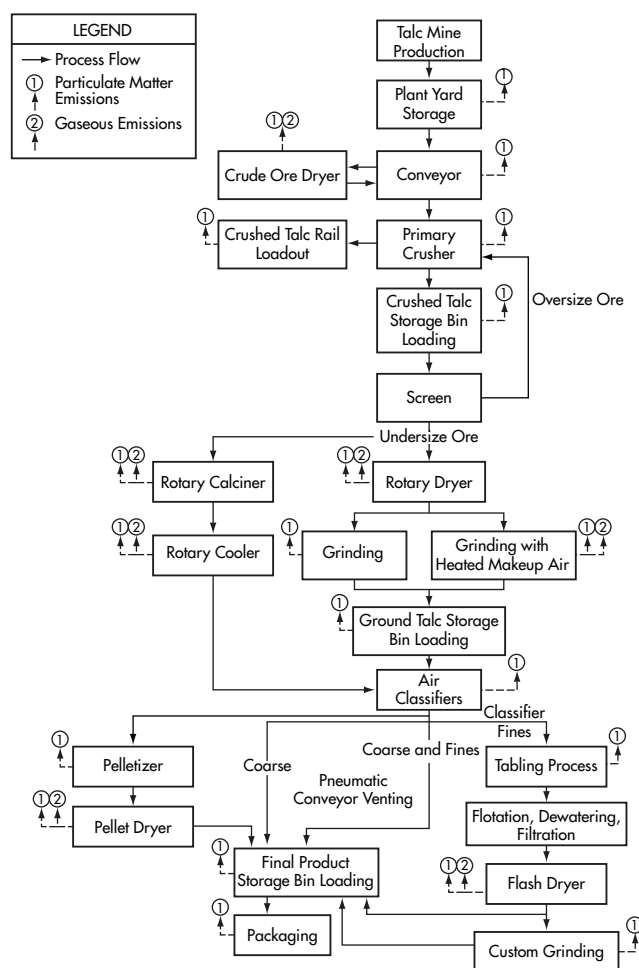


Figure 3. Flow scheme of a typical multiproduct talc plant

a monolayer of nitrogen on the surface of the sample and weighing it. Values vary from 1 m²/g for the coarsest, macrocrystalline products to 20 m²/g for the finest microcrystalline products. Bulk density is reported as either loose bulk density (LBD) or packed bulk density in grams per cubic centimeter. LBD is measured in a very simple piece of equipment called a Scott volumeter, in which the powder is cascaded over a series of glass plates into a 1 in.³ cube. After the cube fills, it is smoothed off and weighed. LBD values go from 1 to 1.2 gm/cc for coarse roofing products to <0.15 g/cc for the finest paint and plastic grades. LBD strongly correlates with median particle size and in many plants is used as a primary control parameter because it is quicker to run than a median particle size.

The science of color measurement as it impacts talc is quite complex and constantly evolving. Most producers measure powder color, which is achieved by pressing the powder into a pellet at standard conditions (3 bar pressure) and then measuring the color and brightness on the surface. There are a wide variety of measurement systems. The most commonly used is the General Electric brightness (GEB) method. GEB is measured on a simple scale of 0 to 100 on a brightness tester. Products vary from about 60, for low talc content, coarse products, to 96, for the finest, whitest talc products. Almost all ways, as talc products are milled finer, dry brightness improves.

The Hunter L-a-b scale measures color on three scales: *L* ranges from 0 to 100 on a white/black scale; *a* from red to green on a similar scale; and *b* from blue to yellow. A typical talc product with a GEB of 80 might have an *L* value of 86, an *a* value of 0.5, and a *b* value of 3. The *b* value, sometimes called *tint*, is the most critical as it is often reflective of iron staining. A lower *b* value is almost always better.

The powder brightness does not always reflect how the product performs in an end use. In plastics, for instance, the brightness of talc is typically lowered significantly as the talc surface is wet out by resin, which changes the optical image. To measure this, the powder is wet out in mineral oil and the color measured on the paste. In paint, the color is affected by hiding or opacity characteristics. In this application, platy talc, despite having lower powder color, is usually superior. This is measured by preparing a thin film over a black and white surface.

The other major analyses involve mineralogy and chemistry of the ore and products. In its simplest form, talc mineralogy is estimated from LOI data. The pure mineral talc loses its (4.75%) water of crystallization at 960°C. Thus the closer the 1,000°C LOI is to this, the purer the talc. If the major impurity such as dolomite or magnesite is known, the purity can be accurately estimated.

Mineralogy is measured more accurately by x-ray diffraction (XRD) techniques. An x-ray beam is sent through a pressed sample of the powder, and the beam is scattered at a specific angle by each mineral present. The location and intensity of that scattered beam is characteristic of the mineral and its level in the sample. Talc, chlorite, carbonates, asbestiform minerals, and quartz are readily identified and quantified down to concentrations of approximately 0.1% (1,000 ppm) by this technique.

A method to quantify the crystalline nature of talc was proposed by Holland and Murtagh (2000). They measured the intensity of the 004 and 020 XRD peaks and combined them in an equation (*I* represents beam intensity):

$$MI = I_{004} / (I_{004} + 2 I_{020}) \quad (1)$$

Their morphology index (MI) varied from 0.98 for the more macrocrystalline and platy Vermont talc to 0.45 for the microcrystalline Montana ores.

Chemistry is determined by either x-ray fluorescence (XRF) techniques or by more detailed wet chemistry techniques, such as inductively coupled plasma (ICP) and atomic adsorption (AA). XRF, done on a pressed powder sample, is accurate for silica, magnesium, calcium, iron, and aluminum down to perhaps 0.2%. The wet chemistry techniques are much more accurate but require that the samples be digested in a very strong acid, like aqua regia or hydrofluoric acid, before they are run through the ICP or AA instruments. This makes the technique much more expensive and time consuming.

Talc Milling

Talc is an extremely soft mineral and generally very easy to mill or to reduce in particle size, although the aspect ratio or platy nature of the talc can complicate matters. Preserving that aspect ratio is difficult in some milling processes, and a fine talc platelet is very difficult to handle and “manage” in an air stream, where almost all talc milling occurs. Very little wet milling is used.

If the ore is wet, the process will typically start with drying (Figure 3). Direct-fired rotary dryers are the most common. The coarsest talc products can be produced by crushers run in closed circuit with vibrating screens. Roofing products are produced in this fashion by running crusher discharge over a 35-mesh screen.

The most common milling machine in the talc industry is the ring roller mill, with the Raymond roller mill being the most popular type (Figure 4). In this mill, ore up to 50 mm in size is swept into a grinding zone between a set of rotating rolls that mill the talc between them and a horizontal ring. The fine product is swept out of the milling zone up to an air separation zone. Here a set of horizontal blades, called a whizzer, creates an airflow in a horizontal direction to the sweep air and forces the coarse particles out to the side and back down the circumference of the cylinder into the grinding zone. The fine product continues with the sweep air and is removed by centrifugal action in a cyclone. The air is recirculated with a large fan back into the grinding zone. A slipstream of air is pulled off after the fan into a dust collector. This keeps the whole system at a slight negative pressure and removes fines that are too fine for the cyclone to remove.

Roller mills are effective devices for milling softer (up to 3.5 Mohs hardness) materials down to 325 mesh top size (44 μm). They appear to preserve the aspect ratio and, if heat is applied, have the capability to do limited drying of wet feed. The primary control mechanism on the mill is the whizzer speed, with a higher speed giving a finer top size and a finer median particle size.

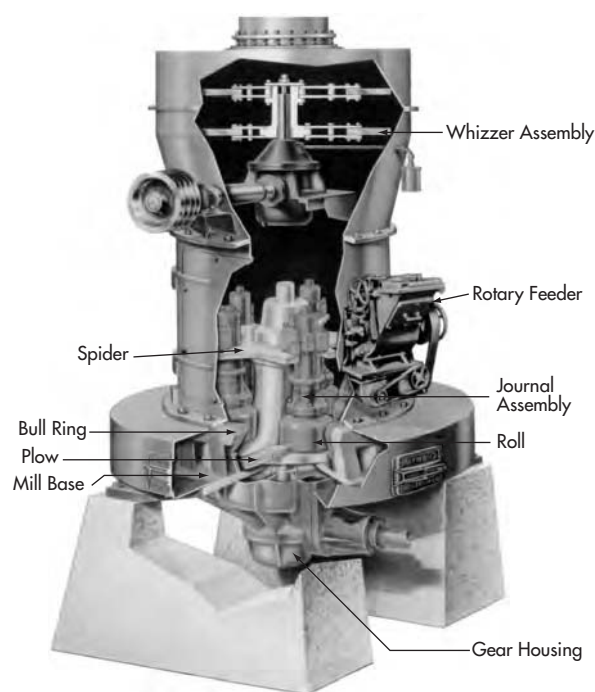
Newer mills use the more-sophisticated cage classifiers in place of the whizzer, which is not an efficient separation device. Cage classifiers require a higher pressure drop and usually a bigger fan but will enhance both throughput and top-size control. Products as fine as 5 Hegman can be made with enhanced classifier systems. Some producers use ball mills in closed circuit with air classifiers, especially for harder tremolitic talc or ore with high carbonate content.

To mill from a 325 mesh to a 6 Hegman, the most efficient machines are hammer mills with built-in classifiers, such as the Raymond vertical mill or the Hosokawa Micron air classifying mill, or ACM. The ACM is a compact hammer mill with an integral highly efficient cage classifier. The hammers are mounted on a plate in a cylindrical housing, and the rotation forces the particles to impact a serrated liner. They are then air-swept into the cage classifier zone where the coarse are knocked back and the fines are sent on to collection in a baghouse. The ACM can accept feed up to approximately 6 mm. The primary control mechanism in the ACM is classifier speed, with a higher speed giving a finer top size and a smaller median particle size.

For ultrafine grinding, often called *micronizing*, fluid energy mills are used. In this process, high-pressure (>10 bar) air or steam is expanded through nozzles into a grinding chamber. In some of these, the grinding chamber is a doughnut-shaped system, and the high-speed air flowing around the chamber in a centrifugal motion causes the powder to grind against itself. In the Aljet type, the fine product is taken off on a slipstream on the inside of the doughnut. In the Alpine type, the grinding is done by streams of opposing nozzles that inject pressurized air and powder into the base of a cylinder (Figure 5). The fines are taken by the milling air into the classification zone on the top of the cylinder where multiple cage classifiers reject coarse particles back into the mill. Product from all these systems are collected in baghouse filters, with care being taken to ensure that any cooling does not approach the dew point of the steam effluent.

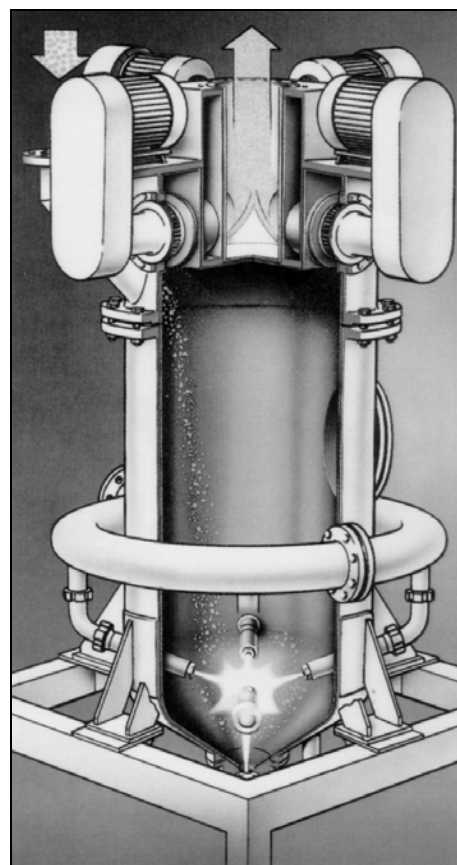
Fluid energy mills are effective for milling from approximately 4 down to 7 Hegman top-size products. At the same top size, they will give a much finer median particle size than the ACM, and the centrifugal-type mills are believed to be better delaminating devices than the ACM.

The primary control mechanism in fluid mills is the integral or external classifier speed, with a higher speed giving a finer product. For mills without a classifier, the product can be made finer with a higher fluid-to-talc ratio or a higher fluid pressure.



Adapted from Combustion Engineering sales brochure.

Figure 4. Raymond roller mill construction features



Adapted from Hosokawa Alpine sales brochure.

Figure 5. Alpine fluid energy mill

Size Classification

The separation of products by particle size is just as critical a part of process technology as milling and, in most cases, is integrated into the milling circuit.

Screens are excellent absolute size separation devices, but their capacity and efficiency decline rapidly with finer meshes, and they are subject to rapid blinding and high maintenance with fine powders, platy materials, and agglomerates. In general, conventional screens are effective for separation of talc powders down to about 60 mesh. Below this, the powders agglomerate and blind the screens. For scalping-type applications (<0.5% oversize), air-swept screens can be used for powders down to 100 μm .

Air classifiers are devices in which a stream of air that contains fine particles (usually <100 mesh) is subjected to a velocity perpendicular to the direction of flow. This will cause the coarse particle to be deflected, allowing the fine particles to pass through. Two types of devices are used to create the perpendicular flow—blades (sometimes called whizzers) and cages that have a fanlike design. The latter are much more efficient, especially at fine particle sizes, but have higher pressure drop, lower capacity, and more potential problems. Typically the flow is upward, and the cage or whizzer is mounted vertically. When the separation points get finer (<20 μm), however, it is often advantageous to mount the unit horizontally.

Classifiers do not make a clean cut, and a platy particle behaves like a much smaller sphere. In addition, there are problems with bypassing, dispersion, and airflow control. In the most sophisticated units, all the accepted (fine) particles are forced through the vanes of the cage and exit through a hollow shaft on which the cage rotates.

The primary control parameter is the speed of the whizzer or cage, but other variables like airflow, air-to-solids ratio, and particle surface energy have significant effects. For any classifier, the higher the air-to-solids ratio, the better the classifier will work. But the operating cost is higher and the capacity is proportionally lower. Higher surface energy will have a detrimental effect in encouraging agglomeration, and this energy is an inevitable by-product of the milling process.

Densification and Compaction

The fluffy nature and low bulk density of fine talc products makes packaging and shipping difficult and expensive. To overcome this, producers use de-aeration and agglomeration technology to increase the bulk density of fine products.

The standard de-aeration technology uses a Carman densifier to pull air out of powders. The powder is transferred through a horizontal screw, which is surrounded by a filter cloth. A vacuum is pulled on the outside of the cloth, increasing the bulk density of a fine product by more than 100%, from 0.15 to 0.3 g/cc. The process has little effect on the talc itself as the powder reflows with minimal agitation. It does allow the product to be packaged in smaller sacks or to get 100% more talc in a regular sack.

In compaction the fine talc is wetted with about 20% water in a continuous mixer, and this paste is forced through a circular die to form pellets. These pellets are then dried to ~2% moisture for paper applications and <0.5% moisture for plastic and rubber. Bulk density is increased from 0.15 to 1 g/cc for fine products.

Other Processing Technology

A limited amount of talc is surface treated to improve its performance in specific applications such as plastics, rubber, and cosmetics. Amino-silane, polyethylene glycol, and stearates are some of the materials used. In general, the level of coating on talc products is rel-

atively low, in many cases less than 1%. This is in contrast to carbonates, where stearate coatings reach 3 wt % for ultrafine products.

A major development, especially in northern Europe, is the delivery of fine talc to paper mills in slurry form for use in paper coating. Fine talc, which has high surface energy and hydrophobicity and a platy structure, is difficult to wet in water and extremely difficult to make into a stable, high-solids slurry. Nevertheless, close to 350,000 tpy are now produced in this form in Europe. The talc is dry milled and then made down into slurry using high-energy mixers and a proprietary package of dispersants and stabilizers. The slurries have solids content of 61% to 65% and a viscosity of ~200 centipoise. A limited amount of talc is also shipped for pitch-control applications in slurry form, but the solids content is much lower and no chemicals are used.

Packaging and Shipping

Talc products are shipped in super sacks (400 to 1,200 kg) and in paper bags (usually 25 kg), stacked on wooden pallets. Transportation to the customer is a significant portion of the total cost of talc products, averaging 25% to 30% of the cost and, in some cases, more than 50%.

Most talc products are now shipped by truck. The combination of faster, more-reliable delivery and lower costs for most customers continues to favor this mode. Rail is used for larger-volume bulk customers when the haul distance is more than 500 km. Most trucks will deliver coast to coast in 4 or 5 days while rail delivery will typically take 2 to 3 weeks.

Bulk trucks are very popular with customers, because the truck driver unloads the material with a compressor on the truck, in contrast to bulk railcars where the customer has to supply the compressor and unload the material. Most product is shipped directly to customers. Smaller customers typically purchase through chemical distributors, who buy the product from the talc mills and store it locally.

PRODUCT APPLICATIONS

The section that follows is not intended to be scientifically complete or to cover all the applications and potential applications in different industries, but is more heavily weighted to major applications, major developments, and technological changes that affect talc consumption. This section also attempts to evaluate talc's position in the market compared to competitive minerals and chemicals.

Almost all of the talc markets are mature and thus are characterized by limited growth (at or below gross domestic product [GDP] rates), customer consolidation, competitive substitution from other minerals, and downward pressure on prices. This is certainly true of the pulp and paper, paint, rubber, joint compound, putty, flooring, roofing, cosmetics, and agricultural markets. The exceptions are plastics and ceramics. Although plastics is a mature business, it is enjoying a growth spurt as talc-reinforced polypropylene replaces more expensive engineering polymers in automotive applications. New applications in ceramic pollution-control devices are also showing significant growth.

In most markets, talc competes with other minerals, such as calcium carbonate, kaolin, and silica. In some markets, however, most notably pitch control, talc competes with alternative pitch-control technologies, including dispersant and detackifying chemicals, periodic solvent washes, or improved processing procedures.

Another critical piece of the application picture is the usability of the talc product. In paper, for instance, although customers prefer slurry, producers find it more convenient to supply a dry product. In plastics, customers prefer a dense, dustless, easy-to-disperse pellet. Plastic compounders are now supplying concentrates of 70% to 80% talc in plastic resin.

Paper

Pitch Control

Beginning as an accidental development of Sierra Talc Company in the northwestern United States in the late 1950s, the pitch-control market has grown steadily to become the largest market for talc in North America today, consuming close to 160,000 t in 2000 (Table 5). The pitch-control market has consistently been dominated by Montana-based products, and although the talc has become coarser over the years, the market continues to accept microcrystalline products from Montana as the industry standard.

Wood is made up of three components—fiber, cellulose, and resins—that are liberated from each other in the pulping process. In thermomechanical pulping, the wood is broken apart by a combination of heat and energy, and all the components are left in the final pulp. In chemical pulping, a combination of mechanical, physical, and chemical separation processes are used to produce essentially pure fiber. It is in chemical pulping that talc works best, helping to produce a cleaner and more valuable fiber. Talc has also had good success in recycle mills, where previously used paper is repulped, and contaminants, such as ink and adhesives, are removed by physical means. In both cases, talc is used more or less as a scavenger for the residual oil droplets or resin particles that are left in the pulp. It prevents them from adsorbing on machine surfaces, screens, and felts, and the talc/contaminant mixture is retained in the pulp as an inert filler.

The mechanism by which talc works is not totally clear, except that it effectively sorbs on to the pitch, detackifies it, and limits its ability to deposit. Some of the mechanisms that appear viable are migration of the talc into the oil phase, the peptizing of pitch particles by the surfactant-like talc, the adsorbing of pitch onto the larger planar surfaces of talc, and the steric stabilization of the pitch dispersion by the talc. One or more of these mechanisms is likely to be effective in different situations.

Where talc is ineffective, as in thermomechanical pulp, the mechanism is clear. The anionic trash (lignin products) left in the pulp preferentially adsorb on the surface of talc and render it ineffective. Even 1,000 ppm of anionic surfactant will completely negate the ability of talc to work in this environment.

In earlier years, talc was added to the process in repulpable 50-lb bags. Talc producers, such as Cyprus, developed talc dispersion units (TDUs) that can take talc from a super sack or bin and produce a dilute (~5%) suspension of talc in water. Typical addition rates are 5 to 10 kg of talc per ton of pulp. The standard product for the application is a microcrystalline Montana talc product milled to a 3.5- μ m median particle size and a surface area of 13 m²/g.

The main competition for talc is from specialty chemical companies. Traditionally, these companies sold dispersants for this application, but dispersants sent the pitch to the waste treatment plant where it added to chemical oxygen demand (COD), whereas talc kept the pitch in the pulp. The specialty chemical companies have now revised their products and sell materials with trade names such as Surround and Detac, a competitive recognition of the peptizing and detackification properties of the talc product.

Paper Coating

The concept of talc as a paper-coating pigment was developed by the Finnish United Paper Mills and its subsidiary FinnMinerals in the early 1980s. Partially driven by a need to control the costs of imported English coating kaolin, the company found that talc significantly improves print quality and cuts down on core burst problems when used as a component of rotogravure grades of lightweight coated paper. Today, more than 300,000 t of talc are

Table 5. Talc usage by major market area, ktpy

Market Area	North America	Europe	Asia
Paper	195	605	1350
Plastics	160	280	170
Paint	150	155	105
Ceramics	130	150	90
Putties	120	90	50
Cosmetics	35	25	25

used for this purpose in Europe. North American coating talc use is minuscule because of the relative economics of talc and kaolin. In Europe, most kaolin is imported from the United States or Brazil and is more expensive than talc. In North America, high-quality delaminated kaolin is available from Georgia at half the price of talc.

The coating product used in Europe has a 2.5- μ m median particle size and 85 GEB and is sold in a highly stable 63% to 64% solids slurry. Most is produced in Finland from a macrocrystalline ore made by froth flotation and dry micronizing.

Paper Filling

Talc has been used in paper filling for more than 80 years, especially where it was inexpensive and where kaolin was not available locally, such as in southern Europe, China, Japan, and Finland. At one time, more than 1 Mtpy was probably consumed worldwide for this application. With the increase in alkaline pulping throughout the world, usage has declined, but the market still exists for certain grades in Europe, China, and Japan. The typical product is 99.9% –325 mesh, and 80 to 85 GEB. Because of its surface and larger particle size, talc has better retention in paper than kaolin, improves drainage and print properties, and generally makes a stronger and smoother sheet.

Little talc has been consumed in North America for this application since Georgia kaolin became plentiful and inexpensive in the 1930s. In the rest of the world, the application is declining because of the availability of less-expensive ground and precipitated calcium carbonate fillers.

Paints

Talc and other mineral pigments such as calcium carbonate have been used in coatings for more than 100 years. Initial use was based on local availability, acid solubility, and whiteness. Over time, talc has been recognized for its good anticorrosion and moisture barrier properties, weathering and antisetling properties in oil, hiding and color extension, and flattening properties. Today approximately 150,000 tpy are used in paint in both North America and Europe.

Basically, two grades are sold. The coarser 3 Hegman grades are used for general purpose extension in architectural (household) coatings and as a functional additive in alkyd primers and industrial coatings. Finer 5.5 to 6.5 Hegman grades are sold for flattening in alkyd coatings, barrier applications, and corrosion prevention in maintenance coatings; for pigment extension in color concentrates; and for viscosity build in gel coats. The coarser products represent 60% of the overall volume. Other than top size, the most important properties of a talc in coatings are color or brightness and its contribution toward the paint viscosity. The viscosity build property is loosely related to oil adsorption (ASTM D281), and a high or low value can be beneficial depending on the system employed.

Although most of the products sold are made from high-purity, platy ores, the tremolitic New York State talc and the natural

talc-carbonate ores are favored for certain applications because they have lower viscosity and better scrub resistance than pure talc. The 3 Hegman grades are made on roller mills or ball mills in closed circuit with air classifiers. The 6 Hegman grades are made on fluid energy mills and air classifying mills.

In water-based coatings, talc is a good spacer for prime pigments such as titanium dioxide; it reinforces the film, contributes to low shear rheology (antisetling), and helps to roughen the surface, which reduces gloss and promotes interlayer adhesion. In oil-based coatings, talc wets out easily, reinforces the film, reduces permeability, and has inherent corrosion-resistant properties. The gray epoxy paint on U.S. naval vessels is pigmented with mostly Montana talc and a little lampblack.

Talc competes with calcium carbonate, kaolin, and mica in the paint market. Although it is more expensive and generally not as bright as calcium carbonate or kaolin, it has better weathering and anticorrosion properties and a lower "b" value or yellowness than kaolin. Because of its higher cost, however, it is rarely used (only when its functional properties justify the extra expense) as an inert "filler." As the production of oil-based coatings continues to decrease, the paint market is relatively static for talc because the limited overall market growth just about compensates for the loss of talc share.

Plastics

Plastics is the fastest-growing market for talc in North America, with growth rates of more than 6% per year with close to 140,000 t consumed in 2000. The main application is reinforcing and nucleating polypropylene, especially for automotive uses. Lesser amounts are used as film antiblock additives and in engineering and thermoset polymers.

The polypropylene (PP) application is driven by a basic technology shift in automotive production. Talc-reinforced polypropylene replaces a number of more expensive and exotic engineering polymers, especially acrylonitrile butadiene styrene (ABS) and polyurethane in the interior panels and exterior bumpers of cars. The engineering polymers sell for \$2 to \$4/kg; polypropylene sells for \$0.7 to \$0.9/kg. But PP itself does not match the strength, heat resistance, dimensional stability, or molding properties of the more expensive polymers. PP is a semi-crystalline polymer, and talc surface has the ability to improve the crystallization rates to the point that dimensional stability is improved, mold shrinkage is reduced, and stiffness is improved. Fine talc is used at 2% to 10% concentration in large parts like bumpers for this purpose. Talc is also capable of reinforcing PP, increasing stiffness 150% at 30% to 40% loading. This property is used in interior panels and dashboards. Molded color is extremely critical in this application because the parts are color matched. Under the hood, black parts such as ducts and covers are also made from talc-reinforced PP. Here, heat resistance and long-term heat stability are critical. In the PP resin, 325-mesh talc products are used at 30% to 40% concentration.

The shift to PP has been driven by Japanese manufacturers, who have reduced the number of parts and the total cost of their cars by using this and other technologies over the last 10 years. As more Japanese auto companies have begun manufacturing in North America, they have been followed by Japanese compounders for talc-reinforced polymers. These compounders tend to use the finest and whitest talc products, and their technology is now being transferred to U.S.-based companies.

Talc-reinforced products are also used in appliances such as washing machines and refrigerators, in plastic trays for fast-food restaurants, and in fire-retardant applications where talc will increase low shear viscosity and prevent the hot plastic from dripping.

In polyethylene film, talc at about 0.5% will act as an anti-block. It detackifies the resin so that adjacent layers of film will not stick together, but it will not negatively affect film clarity or strength. Talc is also used to nucleate and reinforce nylon and polyester for electrical and packaging applications.

A major handicap to talc use in polymers is the difficulty of mixing it into resin. Most of this is done by specialty compounders, who use high-energy extruders or rubber mixers. These compounders now generally sell their products as 40% to 80% talc in resin concentrates to the manufacturers who actually mold the parts. These master batches are mixed with virgin plastic pellets and extruded or molded at the proper talc loading, usually less than 30%.

Even though talc has a major position in plastics and its use will continue to grow as domestic auto producers switch to PP, it is losing market share to calcium carbonate, especially stearate-coated fine 1- to 3- μ m products, elsewhere in the plastics market. Carbonates provide impact resistance but little stiffness. They work well in applications where the finished product is low in price and disposable, such as plastic grocery bags. Carbonates have always dominated the thermoset portion of the market but now are growing dramatically in film, polyvinyl chloride (PVC), and general construction products. With the exception of nylon, kaolin finds little use because of its surface properties. It does not mix well with polymers and will degrade the polymer during compounding.

Talc is also widely used in a related industry: rubber. Micronized talc is used as a reinforcing agent in mechanical rubber goods such as hoses and belts and as an insulating agent in wire and cable coatings. It will also function as a process aid in extruded rubber profiles such as the seals on automobile doors and windows.

Coarser 325-mesh talc is used as a dusting agent on molded products such as tires and elastomeric thread. These markets, however, are declining.

Ceramics

Ceramics remains a major use for talc in the Americas, especially in the floor and wall tile industries of the United States, Mexico, and Brazil. At one time, tile consumed 50% of U.S. talc production, at more than 600,000 tpy. The tremolitic and white firing talcs from Death Valley in California and from New York, and later the white-firing ore from west Texas, were particularly preferred. The typical body was 60% talc and 40% ball clay, pressed and slow fired to form a porous bisque, which was then glazed and refired to make the final tile. Until the 1970s, when new glazes were developed, this was the only way to make a tile on which the glaze did not crack.

This technology is no longer economically viable. Most tile products today are either single-body porcelain tiles or pressed, glazed, and fired only once. Feldspar, silica, and ball clay are the major body components, with talc reduced to the role of a fluxing additive to reduce porosity and increase strength. As such, it is used at levels of 3% to 7% in the body. This is still substantial, as the ceramic tile industry is very large and growing at more than 5% per year.

In tile applications, talc purity is not critical, but low iron content (<0.5%) is. Most of the product used in the United States and Mexico still comes from west Texas, with minor amounts from New York. Many producers purchase lump ore and co-mill the talc with feldspar and other ingredients. Where powder is used, coarse products with 99% passing 100 mesh are typical.

A major growth market for talc is the honeycomb cordierite substrates used in automotive catalytic converters and diesel particulate filters. As clean air regulations become more stringent and extend to include light- and heavy-duty trucks, this market is

expected to grow dramatically. Cordierite is a magnesium aluminum silicate, which is formed at 1,350°C by firing a mixture of talc (35%), kaolin (40%), and alumina (15%). Cordierite has an extremely low coefficient of thermal expansion, which allows it to go through thousands of heating and cooling cycles and maintain its mechanical strength. This market is dominated by two suppliers: Corning of the United States and NGK of Japan. High-quality talc from North America is used worldwide in this application.

The traditional electrical porcelain markets in synthetic steatite and cordierite are declining rapidly. Synthetic steatite can be made by pressing or extruding a mixture of 80% talc, 10% plastic kaolin, and 10% feldspar and firing to 1,250°C. Although synthetic steatite was used in high-temperature and high-frequency insulators in the automotive industry and in appliances, today better plastic products are replacing the synthetic steatite in lower-voltage applications. Other markets in whitewares and kiln furniture are declining because of technological changes.

Talc does not compete with any other mineral in ceramics.

Construction Products

This area, which includes roofing shingles, vinyl flooring, joint compounds, caulking compounds, and automotive body patching, is a huge market for minerals, most of which are low in price. More than 100,000 tpy of talc are sold into this market, most of it low brightness and low purity. The major mineral used in this market is limestone, with close to 10 Mt utilized each year.

In the manufacture of asphalt roofing shingles, coarse platy talc is applied to the back of the shingle to prevent sticking during the manufacturing process, storage, and shipping. A platy talc with 100% passing a 30-mesh sieve and <40% passing a 200-mesh sieve is preferred. Talc competes with sand and coal slag in this application. In the manufacture of rubberized asphalt sheet roofing, 200-mesh roller-milled talc can be used as a filler to reduce the loss of lighter hydrocarbons in the asphalt and improve weathering. Talc also competes with limestone in this market.

In vinyl flooring, talc is used in the felt backing to prevent cracking when the felt is bent during installation. In sheetrock joint compounds, 200-mesh talc is added to build body, prevent cracking, and promote sanding properties. Such compounds are typically 85% carbonate, 10% talc, and 5% resin and other additives.

In caulking compounds, talc and synthetic silica are used together to obtain the right combination of flow (low high-shear viscosity) and sag resistance (high low-shear viscosity). Both coarse and fine products are used at 5% to 25% levels in the formula. In automotive body patch, talc makes up about 45% of the formula, with polyester resin as the balance. Talc builds viscosity and creaminess and allows for good sanding after the polyester cures. The mixed talc-carbonate Vermont ores milled to 200 mesh are preferred.

Cosmetics and Pharmaceuticals

Baby and body powders are one of the more traditional and best-known uses for talc, but it is a market in continuing decline. In developing countries, talc is used extensively in bar soaps and detergent powders, but elsewhere body powders are being replaced by stick and spray deodorants, and many powders are now starch or starch-talc blends. About 35,000 tpy are used in this area, and, although the average selling price is one of the highest in all industry segments, both pricing and volume continue to decline.

The major products are pure 200-mesh roller-milled talc made to tight chemical, microbiological, and loose bulk-density specifications. The market has now gone primarily to high (>0.5 g/cc) loose bulk-density products that flow and fill better and are sold pri-

marily as superstore brands. Only a few brand name marketers such as Johnson & Johnson participate now, and their share continues to decline. Elsewhere, 200-mesh talc is also used as a minor ingredient in "speed-stick" type underarm deodorants, whereas finer talc is used in pressed powders, creams and lotions, and chewing gum.

The market for talc in cosmetics and personal care is still very much under a cloud because of potential action from the National Toxicology Program (NTP) on the health aspects of talc.

Other Applications

Agricultural Products

Talc has traditionally been used as a carrier for all kinds of pesticides, herbicides, fungicides, and crop dusts, although these uses have declined except for seed potato dusts. It is also used as a parting agent for granular fertilizers and ammonium nitrate, but this application has been replaced largely by oil-based soaps. Talc is used as a flow improver for hygroscopic feeds like soy meal, as a process aid in certain types of olive oil production, and as a lubricant in many seeder machines, where it competes with graphite.

Friction Products

Coarse talc is used in the manufacture of brake pads, primarily to adjust the coefficient of friction in conjunction with graphite. Talc is also used as a lubricant in some dry lube and grease formulations.

Wastewater Treatment

Talc can act as a flocculant for the mixed bacteria in biological oxidation systems that are widely used to remove soluble organics from both municipal and industrial wastewater or as an absorber of oil and grease in primary treatment. The application has been patented by Luzenac and commercialized in Europe.

HEALTH AND SAFETY

In the last 30 years, health and safety concerns have become a major issue in the talc industry. The initial problems, dating to the 1970s, were related to asbestiform fibers, but in the last decade, they have extended to crystalline silica and even the talc mineral itself.

Talc powder is considered a nuisance dust and has a threshold limit value (TLV) for an 8-hr exposure of 2 mg/m³. All manufacturers now require workers handling talc powders to wear dust masks if the exposure is close to this level.

The geology of talc makes it apparent that certain types of talc deposits will be associated with asbestiform fibers (metamorphic and ultramafic types). The major commercial type, metasedimentary, is associated with silica. When a asbestos carcinogenicity became an issue in the 1970s, much of the talc-producing industry was affected. Fibrous tremolite was recognized as being a carcinogen and tremolite was a component of talc produced in California, Georgia, New York, and North Carolina. All these deposits, with the exception of New York, were shut down. Tremolite occurs in two forms—blocky and fibrous—and R.T. Vanderbilt, the major New York producer, challenged the regulations that treated all tremolite as a carcinogen. In 1994, the federal government agreed and subsequently regulates only the fibrous form.

Although the legal labeling requirement is 1,000 ppm of asbestiform mineral, the analytical techniques for analyzing asbestos have now improved, allowing for its detection by electron microscopy at 10 ppm. Luzenac shut down a mine in Quebec in April 2001 when asbestos fibers were detected at well below the legal limit.

In 1985, respirable crystalline silica was named a probable human carcinogen by the International Agency for Research on

Table 6. World talc production and trade statistics, ktpy

Country	Production	Exports	Imports
China	1,700	950	~2
United States	817	180	250
Finland	475	125	<10
India	465	25	<10
France	330	150	30
Brazil	300	6	10
Australia	180	145	10
Italy	140	75	65
Austria	135	110	40
Spain	114	63	64
Canada	80	45	50
Japan	45	5	550
South Korea	45	2	280
Mexico	12	2	68
Germany	10	3	210
The Netherlands	0	78	160
Belgium	0	74	92

Source: USGS, Industrial Minerals, Roskill and Finnish, Spanish and Brazilian government statistics.

Cancer, triggering labeling requirements required by U.S. government regulations. *Respirable* is basically defined as the 0.5- to 10- μ m particle size range. These regulations require all products containing more than 1,000 ppm (0.1%) of a known carcinogen to be labeled. Although almost all talc products exceed this 1,000 ppm of total crystalline silica, most of the silica is not in the respirable range.

Many producers also maintain that there is a long history of safe talc use, and that because these mixtures of talc and silica have been found safe in extensive use tests, there is no need to label. The Occupational Safety and Health Administration of the U.S. government has now accepted this logic.

More recently, a number of epidemiological studies have shown a weak association between perineal talc use and ovarian cancer. There is a strong difference of opinion within the scientific and medical communities as to the validity of these studies, both because the association is weak and because no fundamental scientific basis exists for the association. In 1998, the NTP placed talc on a review list for possible listing as a cause of ovarian cancer. After peer review and public comment, the NTP panel of experts voted 7 to 3 in late 2000 not to list talc in this category. Nevertheless, the debate continues, and much fundamental and applied science, as well as political pressure, is now being applied by both sides. In 2004, NTP announced that it will reexamine the issue and that review is under way.

COMMERCIAL ASPECTS

Worldwide, talc is approximately an \$800 million per year business at the finished product level. Some 5.0 Mt of product are sold at an average of \$160/t. Virta (2004) estimates the value of U.S. production (0.857 Mt) at \$23.3 million at the ore level, at an average of \$27.18/t. On a worldwide basis, this appears to be low, and where ore is traded, statistics suggest a value of ~\$65/t f.o.b. mine.

Table 6 summarizes world production. The major producer, China, has a very diverse ownership, mostly state and local governments. Most exported ore is handled by traders such as Dailen Haicheng Talc Trading, Gongrong International, Minmet, and South

China Trading Company. Well-known producers are Liaoning Ahai Talc with an output of 180,000 tpy, Haicheng Beihai Minerals (100,000 tpy), and Pingdu talc mine (100,000 tpy).

Worldwide, the major private producer is the Luzenac group of Rio Tinto plc, which produces approximately 450,000 tpy in the United States and Canada; 600,000 tpy in France, Austria, Spain, Italy, and Belgium; and 150,000 tpy in Australia. Other major producers and their production totals are

- Mondo Minerals: 550,000 tpy in Finland, the Netherlands, and Norway
- Golcha Group: 250,000 tpy in India
- Costalco: 200,000 tpy in Brazil
- Barretts Minerals of the United States (subsidiary of Minerals Technology): 150,000 tpy in Indiana, New York, and Ohio
- Gouverneur Talc (subsidiary of R.T. Vanderbilt): ~120,000 tpy in New York
- IMI Fabi: ~120,000 tpy in Italy and the United States
- Wold Resources; ~120,000 tpy in west Texas.

Over the past 20 years, there has been a major consolidation of production both in the United States and worldwide. In 1982, the United States had 14 producers with 26 active mines, and at least 5 were underground. Today, there are only seven producers and 9 mines, all open pit. Production in formerly major producing states such as California and Georgia has almost ceased because of environmental and economic factors. There is less production of lower grades such as the higher tremolite and carbonate products and much higher production of the higher-purity Montana, Chinese, and floated grades.

International trade in talc is very large, with some producers such as China, Australia, and Austria exporting most of their talc and some consumers such as Japan, South Korea, and Germany importing to meet their needs. In the Far East, China and Australia are the major exporters, and Japan, South Korea, and Taiwan are the major importers. Most imports are ore, which is then milled domestically for paper and plastics markets.

In Europe, the major exporters are France, Finland, Austria, Italy, the Netherlands, and Belgium. The major importers are Germany, the Netherlands, the United Kingdom, and Belgium. In contrast to Asia, most trade is in finished goods, except for Belgium and the Netherlands, which import mostly ore.

In the Americas, there is significant cross-border trade between the United States and Canada in finished talc products, and a significant export of ore and finished products from the United States to Mexico, primarily from west Texas to Monterrey, Mexico, for ceramics. The United States is a major importer of ore, especially from China, which is milled in the United States for plastics and cosmetics markets.

This trade is now manifested in an increasing reliance in Europe and the United States on talc ore imports from Asia and Australia—both now net importers of talc. Along with this trend is the growth of mineral processors, which mill and market purchased and mostly imported ore. This growth has been facilitated by two factors. First, significant quantities of high-quality ore are available at reasonable prices, mainly from China and to a lesser degree from Australia and India. Second, the sale of talc requires a high degree of product application expertise and marketing acumen, skills that are not always present in mining companies.

The pricing environment for talc has been extremely poor over the last 10 years. There has been an excess of both ore production and milling capacity, and pricing of equivalent products has either not kept pace with inflation or declined in real terms. Although the

average price for talc product has increased, this is somewhat deceiving, as lower-cost materials such as silica sand and calcium carbonate have displaced talc in lower-value applications and left talc with a smaller number of higher-value-added markets. The poor state of the major consuming markets, especially paper and construction products, has not helped. Industries such as paper, ceramics, roofing, and paint have suffered from excess capacity, poor pricing, consolidations, and shutdowns in the same time frame.

Overall production of talc worldwide appears to be falling significantly. Production was estimated to be 7 Mt in 1990, 6 Mt in 1995, and 5 Mt in 2000. This appears to be driven by less demand for lower-grade tremolitic and carbonate ores in construction markets along with a conversion of European and Asian paper-filling markets from talc to calcium carbonate.

The industry has also struggled with environmental and health issues, and the legal problems experienced by asbestos producers and users cast a heavy shadow over investment and business prospects.

FUTURE TRENDS

These trends—increases in demand for higher-purity products in plastics and paper coating, decline in demand for construction and paper filling, and consolidation and continued environmental concerns—are likely to continue. Future talc applications will be concentrated in the high end of the value chain, where the price is more elastic. Volumes are unlikely to grow and may continue to decline. Revenue growth, however, may be more positive because of the growth in higher-value applications.

The prospects on the pricing front appear better. Chinese production is declining, especially in the higher-purity bright ores. Ocean freight rates from China to Europe and North America have increased significantly in recent years. The quality of the available lower-priced carbonate and tremolitic ores in Europe and the United States is not sufficient for the paper coating and plastics market.

Unless a major new low-cost source of high-quality ore is developed, then, pricing should remain firm and at least keep pace with inflation. Of course, technology changes can always have an impact on demand. The construction market for talc has largely been lost to lower-priced carbonates, kaolin, and silica sand. If more economic alternatives to talc are found in paper coating and plastics, demand will continue to decline. The challenge remains for talc producers to develop new applications for their product, but this effort has declined significantly in the past decade with consolidation and lower profitability.

The environmental climate for talc mining is also challenging. Permitting, even for dry milling and smaller mining operations typical of talc, is very difficult. With some operations located in environmentally sensitive locations, existing facilities are subject to a high degree of scrutiny. The health concerns with talc and its associated minerals are likely to become more acute. Although existing producers are committed to ensuring that sound science is applied to the issue, health issues are an emotional subject and difficult to deal with in a public forum.

Generally, then, the future for talc is at best cloudy, with significant challenges to be addressed for the remaining producers. The key competitors will not be from within the community of talc producers and marketers but from the minerals or technologies competing for a position in the portfolio of available applications.

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Titanium

Philip Murphy and Louise Frick

INTRODUCTION

Titanium occurs in the earth's crust in two predominant commercial minerals, ilmenite and rutile. Ilmenite, occasionally known as titanoferrite, was named in 1827 after a locality in the Ilmen Mountains, Southern Urals, Russia. Ilmenite is a common accessory mineral in many igneous and metamorphic rocks and forms a solid solution with hematite above 600°C. Below 600 °C, ilmenite commonly occurs with hematite. The name for rutile originates from the Latin *rutilis*, in reference to the red color that is observed when the mineral is viewed in transmitted light. Rutile is a common accessory mineral in many igneous rocks and some metamorphic rocks.

The principal application for titanium minerals is as a feedstock for the manufacture of titanium dioxide (TiO₂) pigment, which accounts for more than 90% of global titanium mineral consumption. As the most widely used white pigment, TiO₂ is employed mainly for its opacifying properties in a wide variety of consumer goods such as paint, paper, and plastics. The titanium feedstock industry as a whole, all the way down to the exploitation of titanium mineral deposits, is therefore predominantly driven by trends in the TiO₂ pigment industry and the specific technical requirements of TiO₂ pigment manufacturing processes.

PRODUCTION AND TRADE; RESOURCES AND RESERVES

Titanium Mineral Supply

Titanium feedstocks for the production of TiO₂ pigment, titanium metal, welding electrode flux, and other, minor uses include the minerals ilmenite, rutile, and leucoxene, and the beneficiated products synthetic rutile and titanium slag. Feedstocks are classified according to their suitability for either chloride or sulfate processing in the TiO₂ pigment industry, and are categorized as follows.

Chloride-grade feedstocks:

- Chloride-grade ilmenite, typically 60% TiO₂
- Leucoxene, typically 75% to 91% TiO₂
- Rutile, typically 95% TiO₂
- Chloride-grade slag, typically 86% TiO₂
- Upgraded slag (UGS), typically 95% TiO₂
- Synthetic rutile (SR), typically 90% to 93% TiO₂

Sulfate-grade feedstocks:

- Sulfate-grade ilmenite, typically 44% to 57% TiO₂
- Sulfate-grade slag, typically 75% to 80% TiO₂

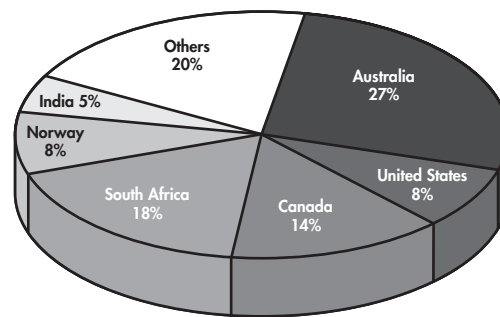


Figure 1. TiO₂ feedstock production by country (2003)

Table 1. World titanium mineral production in 2003 by country and product, in thousand TiO₂ units*

Country	Ilmenite for Pigment	Leucoxene	Rutile	Synthetic Rutile	Slag	% of World Supply
Australia	504	73	160	615	0	27
Canada	0	0	0	0	677	13
India	163	0	14	66	0	5
Malaysia	51	0	0	24	0	1
Norway	247	0	0	0	143	8
South Africa	27	0	102	0	790	18
United States	295	31	25	94	0	9
Other	846	1	64	0	30	19
Total	2,133	105	364	798	1,640	100

* TiO₂ units are calculated as ton of feedstock multiplied by the proportion of TiO₂ contained.

Total titanium feedstock production in 2004 is estimated at 5.14 million contained TiO₂ units, the standard measure for comparison of feedstocks, which is calculated as a ton of feedstock multiplied by the proportion of TiO₂ contained. This compares with 5.04 million contained units in 2003.

Australia remains the world's largest producer, providing approximately 27% of total supply in 2003 (Figure 1, Table 1). Australia is the leading producer of SR, and a major supplier of

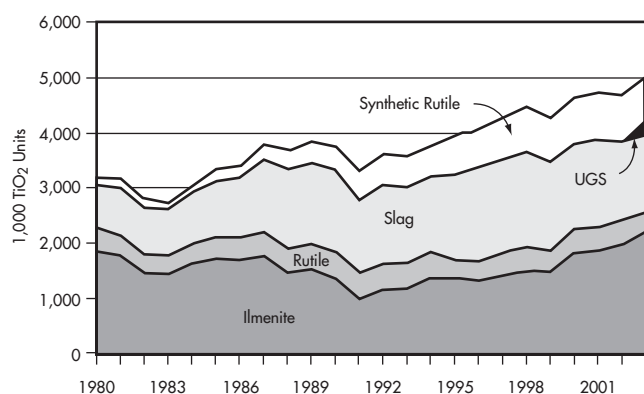


Figure 2. Global titanium feedstock supply by product (1980–2003), in thousands TiO_2 units

sulfate- and chloride-grade ilmenites. South Africa was the second largest feedstock producer in 2003, supplying mainly chloride-grade slag. The other significant titanium feedstock producing countries are Canada, the United States, and Norway.

Ownership in the titanium feedstock industry is highly concentrated, with the top three producers responsible for 47% of global feedstock production in 2003 and the top nine producers accounting for 75% of world output. Iluka Resources Limited (including its 51%-owned Consolidated Rutile Limited subsidiary) headed the producer rankings in 2003 with total production of 992,000 TiO_2 units, a market share of 20%. QIT-Ferret Titane Inc. (QIT) was the second largest producer with a market share of 14%, closely followed by Richards Bay Minerals with 13%, which was unusually low because of temporary production cutbacks.

Titanium slag has dominated feedstock production since 1990, when it first surpassed ilmenite as the major feedstock category (Figure 2). In 2003, slag (including chloride slag, sulfate slag, and upgraded slag) accounted for 33% of titanium feedstock production. Ilmenite (both chloride and sulfate grades) accounted for 42% of the total because of the rapid expansion in China. Sulfate ilmenite is the largest single feedstock category, accounting for 30% of total production.

GEOLOGY

Mineralogy

The chemical formula of ilmenite is FeTiO_3 , often expressed as $\text{FeO} \cdot \text{TiO}_2$. The composition is 36.8% iron, 31.6% titanium, and 31.6% oxygen, or 52.6% TiO_2 . This analysis, however, is an ideal, and rarely seen in nature. In practice there will be some impurities present, including iron as Fe_2O_3 . Often iron is substituted by elements such as Mn and Mg with the result that naturally occurring ilmenite has a variable composition with a generic formula of $(\text{Fe}, \text{Mg}, \text{Mn})\text{TiO}_3$. Much of this variation in composition relates to the chemistry of iron, in particular the solid solution that exists between bivalent FeO and trivalent Fe_2O_3 , which is a function of geological history.

Ilmenite exists within the TiO_2 - Fe_2O_3 -FeO phase system. Although the terminology of end-member minerals of the TiO_2 - Fe_2O_3 -FeO phase system consisting of rutile, hematite, and wustite is generally well known, it can be difficult to find common definitions for intermediate minerals within the system, including ilmenite. Further, the definition of their alteration products is sometimes unclear.

The extent of solid solution of Fe_2O_3 in ilmenite is a function of the original geological origin. In many instances, Fe_2O_3 can be precipitated as hematite, which is typically the case in many east-African ilmenite deposits. In addition, even individual “ilmenite” grains can often contain a range of mineral types.

A clear distinction must also be drawn between what can loosely be termed “ilmenite-containing products” and the various individual minerals present, which may include the mineral ilmenite. Depending on the specific methods used to separate this product, the spectrum of minerals present may include nontitanium minerals having similar physical properties to ilmenite and a variety of titanium and iron-bearing minerals, including the weathered products of those minerals.

For the purpose of this chapter, ilmenite is defined as a product consisting of a combination of minerals, predominantly containing titanium and iron in various states of weathering, and having a TiO_2 content in the range of 35% to 65%.

It is therefore important to clearly understand the definitions of titanium-bearing minerals, which also involves an understanding of their relationship with iron minerals.

Definitions of Major Titanium-Bearing Minerals

The 1996 classification scheme of Buddington for describing the minerals of the TiO_2 - Fe_2O_3 -FeO system has been adopted. The mineral nomenclature follows, and Table 2 summarizes the geological source of the minerals.

- Rutile is an optically homogeneous, essentially pure, common form of TiO_2 . It forms tetragonal crystals.
- Anatase is a polymorph of rutile forming a blue or black tetragonal phase at low temperatures.
- Brookite is a rare metastable form of rutile and anatase, formed by the alteration of other titanium minerals, with a nonorthorhombic crystal structure.
- Ilmenite is a homogeneous, hexagonal phase consisting of $\text{FeO} \cdot \text{TiO}_2$, with less than 6% Fe_2O_3 in solid solution.
- Ferrian-ilmenite is a homogeneous, hexagonal phase consisting of $\text{FeO} \cdot \text{TiO}_2$, with 6% to 13% Fe_2O_3 in solid solution.
- Magnetite is a nonoptically homogeneous, spinel phase with a formula close to Fe_3O_4 , containing less than 5% TiO_2 .
- Titanomagnetite is a single-phase, homogeneous, cubic mineral, with Fe_3O_4 as the dominant phase, but containing more than 5% TiO_2 .
- Hematite is a hexagonal-trigonal phase with a formula approaching Fe_2O_3 , containing less than 5% TiO_2 .
- Titanohematite is hematite with greater than 5% TiO_2 , usually as $\text{FeO} \cdot \text{TiO}_2$ in solid solution, with a little excess TiO_2 .
- Pseudorutile is a hexagonal mineral, originally referred to as arizonite, formed by the alteration of ilmenite, with a composition approximating $\text{Fe}_2\text{Ti}_3\text{O}_9$ or $\text{Fe}_2\text{O}_3 \cdot 3\text{TiO}_2$.
- Altered ilmenite is a general term used to describe the alteration products of ilmenite, having a chemical composition between ilmenite and pseudorutile. Altered ilmenite need not be optically homogeneous and is essentially amorphous, although submicroscopic intergrowths of ilmenite and pseudorutile may be present.
- Leucoxene is a general term for the higher TiO_2 alteration products of all titanium-bearing minerals. Leucoxenes are distinguished optically from rutile by their characteristic internal reflections, although they may consist almost entirely of cryptocrystalline rutile or anatase in the final stages of alteration.

Table 2. Naturally occurring common titanium minerals and their geological occurrence

Mineral	Formula	TiO ₂ , %	Geological Occurrence
Ilmenite	FeTiO ₃	45–53	Common accessory mineral in most igneous and metamorphic rocks. Common detrital mineral.
Rutile	TiO ₂	95–100	Common accessory mineral in medium- to high-grade metamorphic and igneous rocks. Common detrital mineral and alteration product of ilmenite and other titanium minerals.
Anatase	TiO ₂	95–100	Low-temperature polymorph of rutile. Usually secondary, formed by the alteration of other titanium minerals.
Brookite	TiO ₂	95–100	Metastable polymorph of rutile and anatase. Found in cavities, fissures, and veins. Weathering product of other titanium minerals. Relatively rare.
Pseudorutile	Fe ₂ Ti ₃ O ₉	60–65	Alteration product of ilmenite in sediments. Common phase in altered ilmenite concentrates.
Altered Ilmenite	FeTiO ₃ –Fe ₂ TiO ₉	53–70	Term for the alteration products of ilmenite consisting of mixtures of ilmenite, pseudorutile, and leucoxene. Common in heavy mineral sands.
Leucoxene	High TiO ₂	70–100	Term for high TiO ₂ alteration products of ilmenite and occasionally sphene, usually consisting of microcrystalline rutile, or anatase, with minor pseudorutile, ilmenite, hematite, or goethite.
Titanite (sphene)	CaTiSiO ₅	40	Widely distributed accessory mineral in intrusive igneous, low-grade metamorphic rocks and as a detrital mineral.
Perovskite	CaTiO ₃	58	Accessory mineral in metamorphic and igneous rocks.
Pseudobrookite	Fe ₂ TiO ₅	33	Accessory mineral in igneous rocks. Forms as an oxidation product of ilmenite and titanomagnetite.
Ulvöspinel	FeTiO ₄	36	Accessory mineral in basic igneous rocks, usually found as exsolution lamellae in magnetite.
Titanomagnetite	(Fe,Ti) ₃ O ₄	0–34	Term for optically homogeneous Fe–Ti spinel containing magnetite and ulvöspinel in solid solution. Common accessory in basic igneous rocks.
Titanohematite	(Fe,Ti) ₂ O ₃	0–30	Term for optically homogeneous hematite–ilmenite. Common accessory in acid intrusive and anorthosite suites.

Composite Grains

In practice, composite grains can often be present in less weathered or more complex resources. Typical composite grains include

- Ilmenite plus altered ilmenite or pseudorutile, in any proportions
- Leucoxene plus ilmenite plus altered ilmenite or pseudorutile, in any proportions
- Ilmenite plus exsolved hematite or hematite plus exsolved ilmenite, plus the alteration products of ilmenite, i.e., altered ilmenite (plus pseudorutile) and leucoxene
- Magnetite plus exsolved ilmenite and their alteration products; i.e., the magnetite may be partly altered to hematite and ilmenite to the alteration products listed

Properties of Titanium-Bearing Minerals

Ilmenite

Ilmenite has a hexagonal crystal structure with thick tabular crystals and prominent basal planes, plus smaller rhombohedral truncations. The characteristics of this opaque crystal are close to those of hematite and similar to those of corundum, Al₂O₃. The ilmenite crystal structure has alternate octahedrally coordinated iron and titanium layers. A significant feature is the strength of the titanium-oxygen bond, represented as TiO₂. This bond is extremely difficult to break, so natural changes to ilmenite basically occur by the reordering or reaction of the iron layers, which affects magnetic susceptibility. Ilmenite typically has a hardness of 5.5 to 6.0 on the Mohs scale. Pure ilmenite has a melting point of 1,392°C.

Ilmenite from sedimentary sources occurs as homogeneous, subrounded to well-rounded, slightly elongated grains. These grains typically vary in size from 75 µm to 250 µm. In reflected light, and under oil, ilmenite is pinkish-brown and strongly anisotropic. The anisotropism colors are characteristically blue to green. The reflectance of ilmenite is close to that of magnetite and rutile, less than that of hematite, and greater than that of chromite.

Pseudorutile

Altered ilmenites are bluish-gray, compared to the pinkish-brown of ilmenite. The other optical properties of altered ilmenite are initially similar to those of ilmenite, but as alteration increases, anisotropism decreases. Eventually, ilmenite becomes isotropic pseudorutile.

Pseudorutile resembles rutile in color and reflectance (Table 2), although, unlike rutile, it is isotropic. The optical distinction of pseudorutile from altered ilmenite is complicated by the fact that altered ilmenite may also be isotropic. Pseudorutile is so fine grained that the properties of the hexagonal crystals cannot be discerned, making microscopic identification difficult. It can be clearly identified, however, by x-ray diffraction.

The upper TiO₂ content of pseudorutile is about 65%, and this value is often used as the cutoff between altered ilmenite and leucoxene compositions. Comparing the compositions of altered and unaltered ilmenites, it is clear that the titanium contents of the former are higher and that there is a corresponding decrease in iron with increasing TiO₂ levels.

Leucoxene

Leucoxene is easily recognized because it displays very bright, strong brown, yellow, fawn, and white internal reflections in both plane polarized and cross-polarized light. In reflected light, leucoxene is similar in color and reflectivity to rutile. The color and brightness of the internal reflections appear to be related to the TiO₂ content of the leucoxene, with brown indicating lower TiO₂ levels than yellow or white. As TiO₂ content increases, so too do the intensity and brightness of the internal reflections. Under cross-polarized light, leucoxene reveals a characteristic sugary texture.

Leucoxene grains are usually subrounded, often nonhomogeneous, and always pitted and porous to varying degrees.

Rutile

Rutile as found in most mineral sands deposits is characterized by its translucence and “foxy” red color. The prismatic crystal form

Table 3. Simple classification of titanium mineral deposits

Deposit Type	Typical Examples
Primary rock deposits	
Massif anorthosite	Lac Allard, Quebec Tellnes, Norway
Layered mafic type	Rooiwater, South Africa Stoffberg, South Africa
Sedimentary deposits	
Coastal environment	
Quaternary age	
Strand line	Capel, Western Australia Eneabba, Western Australia Trail Ridge, Florida Chavara, India
Aeolian	North Stradbroke Island, Queensland Richards Bay, South Africa Corridor Sands, Mozambique
Pre-Quaternary age	Murray Basin, Australia Camden, Tennessee Bothaville, South Africa
Alluvial environment	Gbangbama, Sierra Leone

that is evident in rutile in situ within igneous rocks is rarely preserved in rutile from mineral sands. Although more commonly translucent, rutile may be translucent to opaque. In the translucent phase, it exhibits parallel extinction and has a high refractive index with very high birefringence. The mineral may also be pleochroic. In reflected light, rutile is grayish white and anisotropic. The mineral is characterized by strong internal reflections and moderate reflectivity.

Other Minerals

Other minerals naturally occur with ilmenite, so, depending on methods of separation, they can be present in a commercial ilmenite product. Minerals that commonly occur with ilmenite are as follows:

- **Magnetite and titanomagnetite:** Magnetite and titanomagnetite are evident in ilmenite resources in Africa. When included in the magnetic fraction with ilmenite, the low TiO₂ contents of magnetite and titanomagnetite dilute the quality of the final ilmenite product.
- **Hematite and titanohematite:** Hematite generally occurs as discrete, homogeneous, occasionally porous, light-gray to white grains. Titanohematite is grayer than hematite, has a lower reflectance, is slightly less anisotropic, and does not display internal reflections. These minerals have to be removed because they dilute the quality of the ilmenite product.
- **Chromite:** Chromite is probably the most important particulate impurity occurring with ilmenite and has proved difficult to remove. Chromite has the composition FeCr₂O₄, or FeO•Cr₂O₃, and is a member of the complex spinel group of minerals to which magnetite also belongs.
- **Magnesia spinel:** The mineral spinel, MgAl₂O₄, can occur quite commonly and can lead to excessive MgO levels in some ilmenite products.
- **Other minerals:** Other minerals that may contaminate an ilmenite product include garnet, tourmaline, staurolite, and the aluminum silicates—sillimanite, andalusite, and kyanite.

Geology of Titanium Deposits

Titanium sources can be conveniently grouped into two simple classifications: (1) primary rock deposits and (2) sedimentary deposits (Table 3).

Sedimentary deposits are currently the world's major source of titanium, accounting for approximately 75% of the TiO₂ contained in total ilmenite production in 2003. The focus on titanium production from sedimentary deposits is primarily due to their easy accessibility and low mining costs. Because these deposits are mostly located on or close to existing coastlines, however, their exploitation can be environmentally sensitive and there are increasingly significant land-use conflicts. In the longer term, therefore, primary rock deposits may come to play a greater role in the sourcing of titanium.

Primary Rock Deposits

Ilmenite deposits occur in igneous rocks, particularly those related to massif-type anorthosites. Very large quantities of ilmenite also occur within layered mafic intrusions, which are also igneous in origin but are less commercially important because of extensive intergrowth of ilmenite with magnetite.

The two most important commercial deposits of the massif anorthosite type are the Lac Allard deposit in Quebec and the Tellnes deposit in southern Norway. In both these deposits, ilmenite occurs in close association with hematite and magnetite, resulting in ilmenite concentrates containing relatively low levels of TiO₂. Other deposits of the anorthosite type that have been mined in the past include those in the Sandford Lake District of New York State, the Roseland District of Virginia, and the Otanmäki deposit in Finland. Other anorthosite ilmenite deposits include the San Gabriel Range in California, the Duluth Complex in Minnesota, and the Laramie Range in Wyoming. Deposits of this nature are relatively common and, in the absence of the more economic sedimentary deposits, could potentially contribute a significant proportion of required ilmenite supplies in the future.

A characteristic of anorthosite-type deposits is that the host rocks are typically alkaline, which generally results in ilmenite concentrates having elevated levels of the alkaline oxides, CaO and MgO. Consequently, these deposits are generally not sources of chloride-grade ilmenite, although chemical processing to remove the alkali content (such as QIT's UGS process) can produce suitable quality chloride feedstock.

Perhaps the most noticeable occurrences of ilmenite in layered mafic-type deposits are those in the Bushveld Complex, South Africa. Examples include deposits that have been mined for their magnetite and vanadium content, the Rooiwater deposit, and the Stoffberg deposit. Sections of the Rooiwater deposit have been weathered to grains of free ilmenite, and it has been reported that ilmenite can be recovered by milling of the primary ore. In the other deposits, however, the close association of ilmenite and magnetite makes the recovery of free ilmenite difficult, so these deposits have not produced economic operations.

In China, high alkali content ilmenite is produced from a very large titaniferous magnetite deposit at Panzhihua in Sichuan Province. This deposit, which is also mined for iron ore, is China's principal source of ilmenite. A titaniferous magnetite deposit is also being investigated at Pipestone Lake, Manitoba, Canada.

Sedimentary Deposits

The weathering and erosion of titanium minerals from igneous and metamorphic rocks, followed by fluvial transportation and subsequent deposition and reworking, result in the formation of sedimentary deposits on coastal shorelines and in river beds and deltas. This weathering and transportation process results not only

in the formation of high-grade concentrations of titanium minerals as found on current and old shorelines but also in the chemical alteration of ilmenite grains caused by both oxidation and leaching by mildly acidic groundwaters.

When an area of titanium-bearing rocks is eroded, streams readily remove quartz and other light minerals and tend to sort the heavier minerals according to specific gravity, grain size, and shape. Deposition of fine, heavy minerals is most significant where streams enter the sea. Following deposition, these deposits are reworked by the combination of wind and wave action, with cyclonic storm events being the most significant mechanism of reworking to form high-grade strand line deposits on the shoreline. Today, such deposits can be observed on beaches as black layers, although often the quantity of mineral is relatively small and not sufficient to justify economic exploitation. When these strand lines accumulate over a long period of time during conditions of receding sea level, however, a series of strand lines can form that can constitute a major deposit of heavy minerals. Many such deposits have been found on ancient shorelines, which are now some tens of kilometers from the sea and may be covered with unmineralized sand.

Sedimentary Coastal Deposits

Most commercial sedimentary deposits of this type are found on shorelines of Quaternary age (0 to 2 million years). They include beach, or strand line, deposits and coastal aeolian dunes. The dunal deposits have been formed by wind transportation of sand from beach deposits, often resulting in the formation of very large deposits of lower-grade concentrations.

Typical Quaternary age sedimentary deposits, including both strand line and dunal concentrations, include the following:

- Deposits on the east coast of Australia, such as those on North Stradbroke Island
- The west coast of Australia, including deposits at Capel and Eneabba
- The east coast of southern Africa, including deposits around Richards Bay and those discovered more recently on the coastal plain of Mozambique
- Very recently formed deposits on the east and west coasts of India
- Deposits on the east and west coasts of Sri Lanka
- Deposits in Florida and Georgia in the United States

Pre-Quaternary deposits may be well above existing sea levels and often many hundreds of kilometers from the present coastline. In most instances, these deposits are highly altered, resulting in complex mineralogy, and typically include ilmenites with relatively high TiO₂ contents.

Examples of such deposits include the following:

- The Lakehurst deposit in New Jersey, which was mined in the past
- Deposits in the Murray Basin region of southeastern Australia, that are currently the subject of widespread exploration interest, with the announcement of two significant project developments in 2004—the Douglas and Pooncarie projects
- The McNairy sand deposits, Tennessee, which include the fine-grained Camden deposit that has been reinvestigated over recent years
- Upper Cretaceous deposits in the western United States

In some instances, natural weathering processes over long periods of time have resulted in the cementation of the mineral grains into consolidated sandstone, which may require crushing

and grinding to recover the heavy minerals. The Bothaville deposit in South Africa is one such example of a high-grade, significantly altered deposit of ilmenite that was once a series of coastal strand lines but today is observed as surface layers of iron-cemented sandstone.

Sedimentary Alluvial Deposits

Although most sedimentary mineral sands deposits have been formed in coastal environments, some have formed as alluvial deposits in river beds and deltas. Such deposits are often less well sorted than those in coastal environments, because they have not been subject to the high-energy environment associated with coastal storms. As a result, alluvial deposits may exhibit a greater range of particle sizes and may contain a broader range of minerals than is commonly found in coastal deposits.

Examples of such deposits include

- The rutile (and minor ilmenite) deposits at Gbangbama in Sierra Leone
- Alluvial tin deposits in Malaysia, from which ilmenite has been recovered as a by-product

Identified Resources

The major difficulty that arises in quantifying titanium mineral resources is the range of standards that individual countries and companies apply to the categorization of resources. The most significant aspect is the potential economic viability of reported ilmenite resources. In many classifications of mineral resources, such as that published by the Joint Ore Reserves Committee of the Australasian Institute of Mining and Metallurgy (the JORC Code), classification as a resource necessarily implies some potential for economic extraction. This standard, however, is not universally applied.

The U.S. Geological Survey (USGS) publishes titanium resources in its annual *Mineral Commodity Summaries*, using a consistently applied definition of resources and reserves. Table 4 shows the most recent USGS data on world ilmenite resources.

Analysis of global titanium resources by geographical region yields a significant difference in the geographical distribution of ilmenite resources associated with existing operations, compared with potential sources. Significantly, the undeveloped mining potential of Africa, including South Africa, Mozambique, Madagascar, and Sierra Leone, dominate global titanium resource potential. Of these, Mozambique accounts for more than half of Africa's total resources, all of which have been identified in the past two decades.

It is significant that in the estimation of TZ Minerals International (TZMI), approximately 50% of identified global titanium resources contain ilmenite of a quality that will necessitate beneficiation for use in TiO₂ pigment production. Most of these resources are of a quality that would probably be uneconomic for SR production under current technologies and cost structures unless iron wastes could be converted to saleable products. Consequently, the production of titanium slag will continue to play a significant role in the future supply of titaniferous feedstocks in the absence of improved SR technologies.

Brief Country Overview

Australia. Although Australia is the world's largest supplier of traded ilmenite, it accounts for only 14% of total identified ilmenite resources. The major portion of these resources is associated with existing operations in the Bunbury/Capel region, south of Perth, and in the Cooljarloo/Eneabba region, north of Perth in Western Australia. All deposits currently controlled by Iluka Resources in

Table 4. USGS summary of ilmenite and rutile resources (2003), in Mt of contained TiO₂*

Country	Reserves [†]	Reserve Base [‡]
Australia	141	183
Canada	11	13
India	21	26
Norway	18	18
South Africa	38	128
Ukraine	6	10
United States	4	37
Other countries	32	58
World total (rounded)	270	470

Source: USGS 2004.

* Reported by USGS in ton of ilmenite and rutile, converted by TZMI to contained TiO₂ using estimated TiO₂ contents as follows:

Australia:	ilmenite	60% TiO ₂ , rutile 96% TiO ₂
Canada:	ilmenite	35% TiO ₂
India:	ilmenite	50% TiO ₂ , rutile 95% TiO ₂
Norway:	ilmenite	45% TiO ₂
South Africa:	ilmenite	48% TiO ₂ , rutile 94% TiO ₂
Ukraine:	ilmenite	60% TiO ₂ , rutile 95% TiO ₂
United States:	ilmenite	60% TiO ₂ , rutile 95% TiO ₂
Other countries:	ilmenite	50% TiO ₂ , rutile 95% TiO ₂

† Reserves are "that part of the reserve base which could be economically extracted or produced at the time of determination" (USGS 2004, p. 194).

‡ The reserve base is the in-place demonstrated (measured plus indicated) resource from which reserves are estimated. It may encompass those parts of the resources that have a reasonable potential for becoming economically available within planning horizons beyond those that assume proven technology and current economics. The reserve base includes those resources that are currently economic (reserves), marginally economic (marginal reserves), and some of those that are currently subeconomic (subeconomic resources).

Western Australia are included as resources associated with existing operations.

Potential deposits include low-grade resources on the central coast of Queensland, of which the Bayfield deposit is the largest; the Goondicum weathered-rock ilmenite deposit, also in Queensland; and more recent discoveries of heavy mineral in the Murray Basin region of southeastern Australia. Although this region is currently attracting significant exploration activity, the identified resources of ilmenite to date are relatively small, amounting to about 15 Mt of ilmenite. Given the relatively early stage of exploration work, though, significant additional resources could be located. The very large fine-grained ilmenite deposits investigated by the former CRA Limited, known as the WIM deposits, have not been included in the identified ilmenite resources because of the significant uncertainties associated with their potential economic viability.

Brazil. Identified ilmenite resources in Brazil are relatively small, basically the one existing ilmenite-producing operation at Mataraca on the north coast and a deposit known as Bujuru on the south coast of Brazil. Brazil also hosts very large resources of anatase that are not included in the tabulation of identified ilmenite resources.

Canada. Canada's major ilmenite resource is the Lac Allard deposit currently being mined by QIT. Additional deposits of titaniferous magnetite in northern Manitoba may ultimately prove to be potential sources of ilmenite suitable for titanium slag production.

China. The major source of ilmenite in China is the Panzhihua titaniferous magnetite deposit in Sichuan Province, which has

been the major source of ilmenite for TiO₂ pigment production in China for many years. Coastal-type sedimentary deposits occur on Hainan Island and on the southern coast in Guangdong and Guangxi provinces, but these are relatively small. There are a number of other reported deposits of ilmenite in both inland alluvial locations and other primary rock deposits; data on these potential resources, however, are very limited.

India. There are significant resources of 60% TiO₂ ilmenite on the western coast of India in Kerala State, although the population density in the region hinders exploitation of these deposits. Large deposits of 50% to 53% TiO₂ ilmenite have been identified in the western portion of Tamil Nadu State in the south of the country.

The eastern coast of India, encompassing the coastlines of Andhra Pradesh and Orissa states, contains very large deposits of 47% to 50% TiO₂ ilmenite. Currently, one of these deposits in Orissa State is being mined, and a number of others are being considered for possible development. Most of the ilmenite from this region, however, requires beneficiation before being suitable as feedstock for production of TiO₂ pigment.

Kenya. The exploration for mineral sands deposits along the coast of Kenya has been relatively recent, resulting in a number of deposits being located, one of which, at Kwale, is currently the subject of a final feasibility study.

Madagascar. Large deposits of 60% TiO₂ ilmenite in the southeast of the country have been investigated by Rio Tinto for many years, with a decision expected to be made on the development of the project in 2005. There are additional ilmenite resources on both the eastern and southwestern coasts of Madagascar. Ticom Limited is investigating the deposits located near Morombe on the western coast of the island.

Mozambique. Exploration of Mozambique's long coastline for heavy mineral sands has occurred in the last 15 years, and three large deposits have been located. The most significant is the Corridor Sands deposit in the south of the country, which is by far the largest undeveloped source of ilmenite. Although only three areas have been explored in any detail, there are known occurrences of heavy minerals along much of the coastline, one of which is the Moma deposit, which is being developed by Kenmare Resources.

Norway. Norway's ilmenite resources are contained in primary rock deposits, the most significant being the Tellnes ore body in the south, which is currently being mined to produce sulfate-grade ilmenite.

South Africa. South Africa's resources are widespread. The most important occur on the east coast, both north and south of Richards Bay in KwaZulu-Natal. Deposits have also been identified on the southeastern coast. There are reported heavy mineral occurrences along large sections of the western coast, and Namakwa Sands is now mining one such deposit. It is likely that additional occurrences along the western coast could increase the identified resources.

South Africa also contains large deposits of titaniferous magnetite in the Bushveld Complex, some of which are included in the estimate of ilmenite resources. A moderately large deposit of cemented, highly altered ilmenite at Bothaville has also been the subject of preliminary technical investigations.

Sri Lanka. Sri Lanka's ilmenite resources include high-grade beach deposits on the northeastern coast that are currently being mined, although the operation is severely affected by the civil war in Sri Lanka, and newly discovered large deposits of 48% to 50% TiO₂ ilmenite on the northwestern coast, which are being explored by Iluka Resources Limited and Consolidated Rutile Limited.

Ukraine. Large deposits of ilmenite in Ukraine have been mined for many years, primarily to provide titanium feedstocks for

pigment production in Ukraine and titanium metal production in both Ukraine and Russia. Since the mid-1990s, some ilmenite has been exported from Ukraine for SR production in the United States and, more recently, for sulfate pigment production in Eastern Europe and chloride pigment production in the United States. The resources are in two general areas known as Irshansk, containing ilmenite predominantly of 55% to 59% TiO_2 content suitable for sulfate pigment production, and Vilnohirsk with ilmenite containing 64% TiO_2 , but with high Cr_2O_3 content.

United States. Identified ilmenite resources in the United States are predominantly coastal-type sedimentary deposits in Florida, Georgia, and Virginia. Although rock ilmenite deposits have been mined in the past, none of these are currently included in identified ilmenite resources.

TECHNOLOGY

Mining and Concentration of Heavy Mineral Sands

Apart from two rock ilmenite operations, all titanium production is sourced from heavy mineral sands mining operations using dredging or dry mining techniques. The choice of method depends primarily on the physical nature of the deposit and the scale of operation. Dredging is the preferred and more economical choice for large-scale operations. Dry mining methods are used for smaller scale operations in situations where there is inadequate water, where the deposit contains hard, rocky material, or where there is a high clay content.

Dredging

Large-scale dredging operations typically use high-volume suction cutter or bucketwheel dredges operating at between 500 tph (7 Mtpy) and more than 3,500 tph (26 Mtpy), allowing for 85% availability. The excavated slurried sand is pumped directly to a wet concentration plant. Both the dredge and concentrator float in a pond of water and move forward as the mining operation progresses. The capital cost of a high-volume dredge and wet concentration plant is generally higher than the capital cost of the plant and equipment associated with a dry mining operation; the unit operating cost, however, is much lower. A principal cost component in pumping high volumes of high-density slurry is electricity, particularly if tailings have to be stacked at high levels. Hence, power costs are a major factor in the economics of the dredging operations.

Dry Mining

Dry mining operations typically involve using conventional earth-moving equipment (i.e., scrapers, excavators, and trucks or front-end loaders) to excavate the ore and transport it to a stationary wet concentration plant. Some mineral sands companies prefer to conduct their mining operations on a contract basis, thus avoiding the capital costs associated with purchasing mining equipment. Irrespective, the capital cost of these dry mining operations is typically lower than that for dredging, but the operating cost is considerably higher, unless heavy mineral grades are extremely high.

The economics of mining operations are further affected by the cost of transport of the ore from the mine to the concentration plant. If the concentration plant is fixed in one place, the distance between the mine and the plant can become substantial and the transport cost component significant. That is why it is typical for the concentration plant to be moved regularly (i.e., every 6 to 24 months) to reduce transport costs.

Mining of Rock Resources

There are only two operating rock ilmenite mines at the present time, in Canada and Norway, although possible further mines are

being investigated in Australia and Finland. There was a third operation at Otanmäki in Finland, which provided feedstock for Kemira's ilmenite-based TiO_2 pigment plant until the operation closed in 1984.

Lac Allard, Quebec, Canada

QIT's ilmenite deposit located 43 km inland from Havre St-Pierre on the St. Lawrence Seaway, 960 km from Montreal, was discovered in 1946. The ore body consists primarily of coarse-grained ilmenite with disseminated fine lenses of hematite. Associated with the ilmenite is the basic feldspar anorthosite. The ore being mined typically contains 32% to 36% TiO_2 . Mining in this operation is carried out using conventional open-pit methods in a horseshoe-shaped mine. Production exceeds 3 Mtpy.

Primary blasting is performed weekly during the months when the mine can be accessed, and the ore is trucked to a crushing station, where it is initially processed by a jaw crusher and then by a secondary cone crusher. The 75-cm ilmenite product is loaded in hopper cars for transport to Havre St-Pierre for shipment from April to December.

In all respects, this would be considered a relatively simple mining operation.

Tellnes, Norway

The other rock mining operation, owned by Titania (a subsidiary of NL Industries), is at Tellnes about 150 km northeast of Stavanger, Norway. The deposit was discovered in 1954 and, since 1960, has operated as a replacement operation for the Sandbekk deposit 2 km to the south, which was originally opened in 1916 to provide feedstock for the world's first sulfate process TiO_2 pigment plant.

In contrast to the Lac Allard operation, the Tellnes mining operation is somewhat more complex because of the nature of the anorthosite ore resource. The titanium ore exists as intrusives in the anorthosite massif, but in this instance it is associated with far greater quantities of magnetite and sulfide minerals. Annual production from the open-pit mine is about 2 Mt of ore and 1.6 Mt of waste rock. After blasting, the ore is transported to a primary crusher, where its size is reduced to 200 to 250 mm.

To remove some of the unwanted constituents, it is first necessary to grind the ore. Gravity and magnetic separation stages are then used to remove magnetite, and finally flotation removes the sulfide minerals.

Processing of Mineral Sands

Wet Concentration

Mineral sand deposits contain from less than 1% to more than 10% heavy mineral in some Australian operations, to more than 20% in some Indian operations. Wet concentration plants separate the heavy minerals from the silica sand to make a heavy mineral concentrate (HMC) containing 90% to 97% total heavy mineral. This process involves, first, separating the sand from rocks and pebbles by screening, followed by separating the fine clay particles (slimes) from the sand, typically using hydrocyclones. Where the clay content of the ore is low, this slime separation stage is not necessary. Many current deposits, however, have a relatively high clay content, and slime separation is becoming an increasingly important aspect of mineral sands operations. The slimes, and most of the water, are then either pumped directly into slime-settling ponds or passed to a mechanical thickener where the solids content of the slimes is increased and a large portion of the water is recovered. The thickened slimes and sand tailings are then pumped back into the mined-out area.

Table 5. Physical characteristics of minerals used for mineral separation

Mineral	Specific Gravity	Magnetic Susceptibility	Conductivity
Ilmenite	4.6–4.8	High	High
Pseudorutile	4.2	High	High
Rutile	4.2	None	High
Leucoxene	3.5–4.2	Weak	High
Sphene	3.5	Weak	Weak
Magnetite	5.2	Very high	Very high
Hematite	5.3	Moderate	Moderate
Chromite	4.5–4.8	High	Moderate
Zircon	4.7	None	None
Monazite	4.6–5.4	Moderate	None
Garnet	3.5–4.3	Moderate	Weak
Kyanite	3.6	None	None
Staurolite	3.7	Weak	None
Quartz	2.7	None	Weak

After the removal of oversize and slimes, the heavy mineral particles are separated from the lighter silica sand using either spiral separators or cone concentrators. The sand slurry is repeatedly passed over sequential stages of the separating equipment, so that more than 90% of the heavy minerals are recovered from the sand. The resultant HMC is then transported to the dry separation plant. For some operations, a separate ilmenite-rich concentrate is also extracted using wet high-intensity magnetic separators (WHIMSs).

Ilmenite Separation

Separating ilmenite as a final mineral product from heavy mineral sands deposits is achieved by using the different magnetic and conductive properties of the various minerals present. Further separations are based on either grain size or specific gravity. Table 5 lists the key physical characteristics of those minerals that can be present with ilmenite.

Ilmenite is typically extracted first because of its preponderance in the mineral suite. Where there are minerals present that make recovery difficult, these are extracted first. In all cases, pseudorutile and ilmenite constitute the majority of the final ilmenite product.

Ilmenite Recovery

Potential losses of heavy mineral occur at each stage of ilmenite production: mining, wet concentration, and dry processing.

Some of the heavy mineral present in the resource may not be recovered because of difficult mining conditions or mine planning decisions about the minimum economic grade to be mined. Mineral recovery usually refers to the percentage of heavy minerals recovered from the ore mined. Losses in the mining operation are generally not included in this calculation, although they are taken into account when expressing recovery from the original mineral reserves.

Heavy mineral is lost in the gravity separation processes in the wet concentrator and at numerous points in the dry separation process. Typical average heavy mineral recoveries in the wet concentration process are approximately 85% to 95%, with the minerals of highest specific gravity exhibiting highest recovery. Normal recovery rates for ilmenite are 90% to 95%.

Dry mill recovery of ilmenite is also typically in the range 92% to 95%, making the overall mining and processing recovery in the range 82% to 90%.

Beneficiation

Overview of Upgrading Processes

Because of the limited resources of naturally occurring, high TiO₂ minerals suitable for processing to TiO₂ pigment, the titanium feedstock industry has made a concerted effort since the early 1960s to develop upgraded products from ilmenite that can be used as substitutes for, or with, ilmenite or rutile. All upgrading essentially involves removing iron and, in some instances, minor impurities. Two types of intermediate products have been developed: SR and high-titania slag, generally termed *slag*.

The oldest form of upgraded product is Sorel slag (originally 72% TiO₂ and now 75% to 80% TiO₂) produced since 1951 by QIT in Quebec from the Lac Allard rock ilmenite deposits. The same technology has been applied to the upgrading of 47% TiO₂ ilmenite mined by Richards Bay Minerals in South Africa to produce an 85% TiO₂ slag. Similar technology is used at the Tinfos smelter in Norway, but with different processing before smelting.

Recently developed, direct current (dc) or plasma arc smelting technology is used by Namakwa Sands for its slag operation on the west coast of South Africa and by Ticon South Africa at Empanjeni, near Richards Bay.

In 1995, after many years of research, QIT announced the development of a chemical leaching process for upgrading its standard sulfate grade Sorel slag by removing MgO and CaO and some iron, resulting in an increase in TiO₂ content to approximately 95%. The product from this process is referred to as UGS, with an intermediate 83% TiO₂ product, heat-treated slag (HTS), also being produced that has achieved technical acceptance as an alternative to rutile.

A number of processes have been developed to upgrade ilmenite to 90% to 95% TiO₂ products, generically known as SR. These processes vary in the extent to which the ilmenite grains are reduced, in the precise nature of the reduction reaction, and in the conditions used in the subsequent leaching process to remove iron. All the existing commercial processes are based on the reduction of ilmenite in a rotary kiln, followed by leaching to remove the iron from the reduced ilmenite grains.

The Becher process for SR production has been used exclusively in Western Australia, where five kilns have about 700,000 t of SR capacity. The other SR plants, located in India and Malaysia, use partial reduction and HCl leaching techniques based on the Benilite process.

As the direct use of ilmenite for the production of TiO₂ pigment has declined, slag has become the most important titanium feedstock for the TiO₂ pigment industry. The production of slag is favored in situations where large quantities of moderately low TiO₂ ilmenite, relatively free of impurities, are available along with plentiful supplies of inexpensive electric power. This situation exists in Quebec, Norway, and South Africa. One of the economic advantages in slag production, compared to SR production, is that iron is recovered as a coproduct and provides a significant contribution to the revenue of slag producers. In SR production, iron is discarded as a waste product and therefore is a cost rather than a revenue source. Iluka Resources, however, the world's largest SR producer, is continuing research to make a marketable product by smelting the iron waste.

One of the disadvantages in the slag production process is that it provides no opportunity for removing most minor impurities that may be present in the original ilmenite and which become concentrated in the slag product. Consequently, the long-term production of slag is dependent on supplies of ilmenite with low impurity levels, unless further chemical processing (such as QIT's new UGS

process) is used to remove such unwanted impurities. Another disadvantage of slag is the retention in the product of about 10% FeO, which generally limits the TiO₂ content to an upper level of around 86% and, more important, requires the use of extra reagents and waste treatment facilities at TiO₂ pigment plants.

The Becher process for SR production suffers a similar disadvantage in relation to impurity removal, although it can remove approximately half the manganese content in the ilmenite if sulfur is added in the process. Acid leach SR processes are more flexible in their ability to remove unwanted minor impurities present in the ilmenite, and, in the longer term, as naturally available high-purity ilmenite supplies decline, such processes may gain added favor in the feedstock production industry, subject to satisfactory economics.

Slag Production

Smelting of ilmenite to produce titanium slag is conducted at five major Western world operations:

1. QIT at Sorel, Quebec, Canada: capacity 1.2 Mtpy
2. Richards Bay Minerals, Richards Bay, South Africa: capacity 1.0 Mtpy
3. Tisor South Africa, Empangeni, South Africa: capacity 250,000 tpy
4. Tinfos Titanium and Iron KS, Tysseidal, Norway (Tinfos): capacity 200,000 tpy
5. Namakwa Sands Limited, Saldanha Bay, South Africa: capacity to 205,000 tpy

In addition, titanium slag is produced at Panzhihua in China, Berezniiki in Russia, and Ust-Kamenogorsk in Kazakhstan.

The most important factor for the location of an ilmenite smelter is the availability of cheap electric power, because the electric arc furnaces used to smelt the ilmenite are high power consumers. The ilmenite treated by the smelters above typically contains 36% to 50% TiO₂. These lower TiO₂ ilmenites are the preferred feedstock for smelting, because the high iron content provides suitable thermodynamic conditions for smelting and high-grade pig iron is produced as a valuable coproduct.

The quality of the slag produced is directly related to the level of impurities in the ilmenite, many of which pass directly to the slag rather than the pig iron. Among these are the alkali oxides, calcium and magnesium, which are the most important impurities generally associated with the lower TiO₂ ilmenites. The radionuclides thorium and uranium, which would report to the slag if present in the ilmenite, are generally in very low concentrations in the lower TiO₂ ilmenites used as feedstock and therefore present no problems.

Two grades of slag are produced that are readily identified by their alkali (MgO and CaO) content and the difference in TiO₂ levels, which is a consequence of the impurity content. Both South African slag products have relatively low MgO levels, with the maximum being 1.1%, and relatively high TiO₂ levels at 85% to 86%. These slags are suitable for production of TiO₂ pigment by the chloride process because the upper limit of combined MgO and CaO content for that process is 1.6%, with a preferred limit of 1.0%. Chlorinatable slag is a preferred product because of its greater market potential and higher value.

Sorel slag and the slag produced by Tinfos from Tellnes ilmenite have high MgO contents, 5.0% and 7.9%, resulting from ilmenite MgO impurity levels of 2.9% and 4.6%, respectively. The TiO₂ contents are lower, in the range of 75% to 80%, and these slags are suitable only for the sulfate process.

Sulfate-grade slag has a wide particle size range to tolerance because it has to be ground before being digested with sulfuric acid.

In contrast, chloride-grade slag has a tighter particle size specification range because of the "blow-over" of fine particles in the chlorination process. As a consequence, chloride-grade slags with particles less than 100 µm are used in some sulfate process plants, even though the presence of more rutile phase in the slag product means that recovery of TiO₂ units is slightly lower.

Controlling the particle size of chloride slag is therefore critical. Technology is progressively evolving so that now only 10% to 20% of this slag product has to be used in the sulfate process.

In July 1997, Tinfos began smelting ilmenite from BHP's Beenup project in Western Australia, which was low in CaO and MgO and therefore allowed production of mainly chlorinatable slag. With the closure of the Beenup project in 1999, Tinfos returned to making sulfate slag from Tellnes ilmenite.

The Cr₂O₃ level in ilmenite feedstock has to be controlled because it affects the quality of coproduct iron. Ilmenite roasting is used at Richards Bay Minerals for this purpose and is planned to be installed in the smelter stage of the operation proposed by Iscor Heavy Minerals Limited, for development of its deposits near Richards Bay.

Key Operations in Slag Making

A temperature in the range of 1,650°C to 1,700°C is required to ensure that the thermodynamics of the process work correctly.

It is also important that excessive amounts of a rutile phase are not formed, particularly for slag used in the sulfate process. For the sulfate process, it is also important that M₃O₅ phase forms correctly, because this phase is soluble in sulfuric acid. (M₃O₅ is a general term describing a range of metal oxides.)

It has to be recognized that one of the limiting factors in ilmenite smelting is the inability to reduce the FeO beyond a given level. In essence, two main reactions are occurring in parallel:

1. $\text{FeO} + \text{C} = \text{Fe} + \text{CO}$
2. $\text{TiO}_2 + \text{C} = \text{Ti}_2\text{O}_3 + \text{CO}$

As the FeO levels decline, the TiO₂ level increases, which requires higher operating temperatures because of the fluxing role that FeO provides. This clearly places a limit on the effective level of FeO that can be produced in a typical slag, which is generally considered to be in the range of 8% to 10%.

This requirement for high temperature also places a restriction on the refractories in the furnace, which have to be water-cooled to ensure that a layer of slag is built up on the inside of the steel lining to prevent melting of the furnace wall, which has occurred by accident on several occasions.

The impurity oxides of chromium, silicon, vanadium, and manganese are also partly reduced to the metal and oxygen. The following partition ratios between slag and iron, expressed as percentages reporting to the slag, apply:

- V₂O₅, 20%
- MnO, 80%
- Cr₂O₃, 20%
- SiO₂, 40%

All other impurities report entirely to the slag.

Upgraded Slag

For many years, QIT actively sought ways to improve the quality of its Sorel slag product by reducing iron and MgO levels to produce a new high-grade feedstock product suitable for the chloride process.

In February 1995, QIT announced plans to build a new plant at Sorel to manufacture a 95% TiO₂ product to be known as UGS. The plant began operating in late 1997, and the product has

achieved technical acceptance to the extent that the plant is now being expanded to 325,000-tpy capacity.

The UGS process has three stages:

1. Sizing of the slag, which helps to partly reduce the M_3O_5 phase in the feed
2. Heat treatment to facilitate the leaching of FeO, MgO, and CaO
3. Hydrochloric acid leach

The final process steps are similar to those for acid leach SR.

Synthetic Rutile

SR is manufactured commercially using two main technologies: the Becher process and the Benilite process. The end product of both processes is a high TiO_2 (90% to 93%) feedstock designed for the chloride process, with slightly lower equivalent titanium content and a slightly finer particle-size distribution than rutile. Both technologies remove iron through ilmenite reduction and the subsequent leaching of iron, but there are minor differences.

Becher SR Process

Development. The Becher process was developed in Western Australia in the late 1960s to process ilmenite with TiO_2 levels that lay outside the relatively narrow specifications dictated by sulfate pigment plants. Western Australian feedstock producers had quantities of ilmenite typically about 55% TiO_2 that could not be sold directly to the pigment industry and therefore sought new markets for the material. Upgrading the TiO_2 content of ilmenite to about 90% produced a suitable feedstock for chloride process pigment manufacture.

With access to a low-impurity ilmenite source and a suitable reducing agent—subbituminous coal—a process was developed whereby the iron oxide content of the ilmenite is converted to metallic iron in a rotary reduction kiln at 1,050°C to 1,150°C and then removed by accelerated corrosion rather than acid leaching. To treat 55% TiO_2 ilmenite, a preoxidation step was required to convert FeO to Fe_2O_3 , to reduce kiln retention time. The preoxidation stage was eliminated in the late 1970s when 60% TiO_2 Eneabba ilmenite started to be used, resulting in a significant cost saving. The process is currently used only to treat ilmenites with 58% to 63% TiO_2 content derived from a number of producers in Western Australia.

An improvement made in 1975 removed approximately 50% of the manganese from the ilmenite, whilst simultaneously further reducing the iron content from 3.5% to 2.5% and improving the TiO_2 content from 90% to 93%. This improvement was achieved by adding sulfur or sulfates to the kiln and then adding a final acid-leaching step. The process with sulfur doping and acid leaching is known in some quarters as the improved Becher process, whereas the initial process, without the improvements, produces a standard-grade 90% TiO_2 SR.

Process Details. The improved Becher process, which operates most effectively with a 60% to 63% TiO_2 ilmenite feedstock containing a majority of pseudorutile, has three main processing steps:

1. The first step in the process is to reduce the iron content of the ilmenite to its metallic state. Iron, coal, and sulfur are fed into a rotary kiln with an exit temperature of 1,050°C to 1,150°C. The iron content of the ilmenite is reduced to metallic iron, and there is a partial reduction of the TiO_2 to Ti_2O_3 . The sulfur reacts with the iron and manganese content to form a complex sulfide phase that is subsequently removed with sulfuric acid. Oversize particles are removed together with waste char, before the reduced ilmenite passes on to the aeration stage.
2. Reduced ilmenite is mixed with aerated water and ammonium chloride catalyst in batches. The metallic iron within the

ilmenite particles is dissolved in the solution and diffuses in the form of complex ions to the grain surface. Here it is oxidized in the presence of oxygen-rich water to iron oxides and hydroxides, which are insoluble and so precipitate out of solution and are removed as waste.

3. The resultant iron-depleted ilmenite is leached in a weak sulfuric acid solution to remove the manganese sulfides and any residual metallic iron. The SR is then washed, dewatered, and dried ready for dispatch.

The SR product of the Becher process typically contains 90% to 93% TiO_2 , depending on the initial ilmenite quality. The product can be quite friable because of the dissolution of iron from the ilmenite lattice.

The typical reduction products contained in reduced ilmenite from the Becher kiln are rutile, reduced rutile, iron, and ferrous pseudobrookite. The ferrous pseudobrookite, also known as M_3O_5 phase, is a minor phase that contains a small proportion of the original iron in the ilmenite. It is stabilized at kiln temperatures above 1,050°C by impurity elements contained in the ilmenite such as manganese, magnesium, aluminum, uranium, and thorium. These impurities are held in this M_3O_5 phase, which is insoluble in dilute acid. Apart from manganese, which can be partially removed by sulfidization, all impurity elements are therefore retained in the SR.

At lower reduction temperature the impurity elements enter a metatitanate or rhombohedral phase M_2O_3 . This phase is soluble in hydrochloric acid and explains the greater success of the Benilite process in removing impurities.

The Becher process requires the higher reduction temperature to cause formation of metallic iron, which can be leached by the corrosion process at far lower cost. The synthetic rutile enhancement process (SREP) variation is an innovation, described later, that seeks to retain the advantage of metallic iron formation while allowing removal of some impurity elements, albeit at some cost.

The time required in the rotary kiln to achieve complete reduction of iron controls the rate of output, and thereby the efficiency, of the whole process. The retention time is a function of the weathered state of the ilmenite, although the FeO content is often used as a rough guide. In the weathering process, iron is leached out of ilmenite, leaving cracks and cavities in the grains that make them more permeable. In the reduction process, the carbon monoxide is then able to react with iron more quickly because of the changed physical properties of the grain.

Though unweathered/higher FeO ilmenites require longer kiln retention, it is also important to assess the homogeneity of the ilmenite feed. As all ilmenite feedstocks will contain particles with a range of chemical compositions and iron contents, 60% TiO_2 ilmenite may contain particles with as little as 2.0% FeO, and some with as much as 7.0% FeO. This distribution of FeO values in the individual particles that constitute the ilmenite feedstock determines the kiln retention time, with the process only as efficient as the least weathered component (i.e., the highest FeO levels).

RGC Mineral Sands Limited developed an SREP in the mid-1990s to reduce the U+Th levels of the SR produced from its Eneabba ilmenites to salable levels. The process is technically successful but expensive to operate.

The process depends on the phenomenon that at high enough temperatures (above 1,200°C) an impurity-rich phase appears on the surface of the mineral grains. Adding a flux lowers the reaction temperature, and the impurity-rich phase can be rendered soluble in a series of leaching steps.

At the Narngulu plant, the SREP process operated by Iluka is fully integrated with the existing Becher process. A borate-based

flux is added to the kiln and forms a glassy phase that provides a soluble sink for the manganese, magnesium, thorium, and uranium.

The Becher process is generally the most cost-effective method of SR production because iron is removed by corrosion rather than acid leaching. It is most effective with ilmenites containing about 62% TiO_2 and low FeO levels. There are limitations to the process, however: impurities other than iron and manganese cannot be removed unless a process such as SREP is used, which requires additional costly acid-leaching steps, and it is unsuitable for use with highly weathered ilmenites containing leucoxene. There are also costs associated with disposal of iron oxide and neutralized acid effluent.

Future Developments. With declining availability of 60% TiO_2 ilmenites, increased attention is now being focused on applying the Becher process to lower TiO_2 ilmenites. Possible modifications are

- Reinstating the preoxidation stage, which has the effect of artificially weathering ilmenite
- Accelerating the kiln reduction process by preheating the coal to 700°C to 800°C
- Using a combination of preoxidation of ilmenite and pre-drying coal

Using lower TiO_2 ilmenites would require higher input volumes of both ilmenite (because of the lower quality) and coal (to maximize kiln reduction). It is estimated that the combined effect would be to reduce kiln capacity by about 5% to 10% if a 55% TiO_2 ilmenite were used in place of a 60% ilmenite and preoxidation was reinstated.

Work carried out by Lurgi Metallurgie (now Outokumpu) on iron ores has potential application to ilmenite upgrading. The principal difference in the iron reduction processes is that a circulating fluidized bed (CFB) replaces the rotary kiln used for reduction in the Becher process. The advantages of the CFB largely apply to the coal requirement. Because it operates at lower temperatures, coal consumption is reduced and there is a greater flexibility in the coal type that can be used. The process is also believed to widen the range of acceptable ilmenite feedstocks. Overall, capital and operating costs are also said to be lower, but no commercial plant has yet been installed.

Some work has also been carried out on a possible hydrochloric acid leach stage of the reduced ilmenite in order to remove some of the impurities, such as Cr_2O_3 , MnO, MgO, and CaO, which are not normally reactive in the Becher kiln.

MARKETS

Uses for Titanium

TiO_2 Pigment

More than 93% of the world's titanium is used as TiO_2 pigment. Titanium metal consumption accounts for only 2.5% of total titanium usage; other end uses include metallurgical flux, welding-rod coatings, titanium carbide, titanates, and other titanium chemicals. Trends in the TiO_2 pigment industry, then, drive the exploitation of titanium mineral deposits.

In this respect, titanium is different from most of the other metallic elements. Ores containing aluminum, iron, copper, zinc, or nickel are mined primarily to satisfy demand for the metal, either unalloyed or in combination with additives to create alloys with enhanced properties. Thus, trends in demand for aluminum metal drive the search for and exploitation of bauxite deposits. By contrast, ore containing titanium is mined primarily to satisfy demand for a chemical product— TiO_2 pigment.

Nonrecyclability of TiO_2

The issue of recycling is one of fundamental importance in the iron and steel industry and in most nonferrous metal industries. In recent years, governments around the world have been keen to encourage the recycling of metals, partly on the grounds of minimizing the amount of consumer waste that has to be disposed of and partly on the grounds of conserving valuable nonrenewable resources. For a number of countries, increased recycling of metal can also help reduce the total import bill and therefore benefits the balance of payments.

For the mining and smelting sectors, trends toward increased recycling have an important effect insofar as recycled metal competes against metal derived from virgin ore. As recycling becomes more widespread, the demand for virgin ore is damped down. Moreover, if refiners are mandated to use recycled metal feedstock, or if they find it cheaper to do so, it places a ceiling on prices for the virgin metal ore. This can already be seen with lead, where recycled metal now accounts for about 50% of the world's total consumption.

Recycling also has a net effect on certain chemicals such as chlorine and sulfuric acid, both of which are used and can be recycled during the manufacture of TiO_2 . In terms of the world's total consumption of chlorine and sulfuric acid, however, recycled material plays a fairly minor role. For most chemical products, recycling plays no role at all.

Such is the case with titanium dioxide, which is mainly used as a pigment in paint, paper, plastics, inks, and rubber. The TiO_2 becomes so intimately incorporated into the end product that in most cases it is beyond the bounds of current technology to recover the TiO_2 values from consumer waste. Indeed, TiO_2 cannot even be economically recovered from scrap paint, paper, or pigmented plastics that have not yet left the factory.

The issue of recycling will continue to have little impact on trends in consumption and pricing in the titanium minerals and TiO_2 pigment industries.

Forms of TiO_2

Titanium dioxide occurs naturally in three crystalline forms: primarily anatase and rutile, with brookite a rare occurrence. Commercially manufactured TiO_2 is available as either anatase-type or rutile-type, categorized according to the crystalline form. Anatase pigment is currently made by sulfate process producers only; rutile pigment is made by both chloride and sulfate process producers.

Rutile-type is the thermodynamically more stable form. Anatase-type TiO_2 undergoes irreversible transformation to rutile-type TiO_2 above 700°C. The rate of transformation is affected by the presence of various other substances, which either catalyze or inhibit the reaction. Rutile has a more compact crystal structure, and this explains why it has a higher specific gravity and is harder and more abrasive than anatase. For some applications, particularly in the textile, rubber, and ceramics industries where abrasiveness is an issue, anatase is the preferred form of TiO_2 . In all other applications, either the anatase or rutile form can be used. Rutile grades are often favored because of their better hiding power and photochemical inertness. In the European inks and paper sectors, anatase tends to be more popular.

Other Uses

The other main consuming industries for titanium raw materials are

- Titanium metal (chloride slag, rutile, and SR)
- Fluxes for coating welding electrodes (rutile and ilmenite)

- Metallurgical fluxes in the iron and steel industry (ilmenite)
- Sandblasting and drilling muds (ilmenite)

These industries consume less than 10% of the total TiO_2 contained in the various grades of titanium raw materials. They can have a moderately important influence, however, on the demand for specific grades of raw material.

Titanium Metal

Titanium is a low-density, high-strength metal that is extremely resistant to corrosion. The metal's high strength-to-weight ratio makes it ideal for aerospace applications, which are its major markets. Use of titanium metal is gradually being extended into other transport areas as weight reduction and fuel economy become more important.

Because of titanium's corrosion-resistant properties, the metal is being used in specialized, corrosive environments in chemical process plants such as desalination plants.

The first stage in the production of titanium metal is the production of titanium sponge, a tradeable commodity. Only nine companies worldwide produce titanium sponge. Japan, Russia, and Kazakhstan are the largest producers, with smaller production from Ukraine, the United States, and China.

Commercial production of titanium metal dates back to the early 1950s. The most widely used manufacturing process is the Kroll process, which involves the reduction of titanium tetrachloride with molten magnesium to form titanium sponge.

Titanium sponge produced by metallic reduction processes contains significant quantities of impurities that are subsequently removed by leaching, vacuum arc remelting, and cold-hearth techniques. Several stages of remelting may be required to produce progressively purer titanium metal. The ultimate product from this purification process is known as titanium ingot.

Titanium ingot is fabricated into mill products (i.e., bar, sheet, plate, tubes, etc.) that are used for metal casting, the production of fabricated products, or as feed stock in the production of titanium alloys. The fabricating and machining stage of titanium metal generates significant quantities of scrap metal. Approximately 80% of new metal output is scrap that is recycled and contributes significantly to the total economics of the titanium metal business.

Titanium tetrachloride (TiCl_4), known as "tickle" in the industry, is produced through the chlorination of titanium raw materials and is an intermediate product in the chloride route process for pigment production. Titanium sponge producers either purchase titanium tetrachloride from pigment producers, a practice in the United States, or purchase titanium raw materials for chlorination.

The quality of titanium raw materials required for titanium sponge production is similar to that required for chloride route process pigment production. One distinction is that raw materials for titanium metal production generally require low levels of tin. Titanium sponge producers use chloride slag, rutile, and SR as raw materials.

Welding Electrode Flux

Titanium minerals are used as a component of fluxes for coating welding electrodes. The wide variety of flux compositions depend on the nature of the welding process, the materials to be welded, and the desired characteristics of the weld.

Titanium dioxide is most commonly added to welding electrode flux in the form of rutile. Leucoxene is also widely used, although some electrode producers prefer not to use it because of possible variations in its composition. Ilmenite has also been used as a low-cost substitute for rutile.

The most important requirement in flux raw materials is consistency of both particle size distribution and chemical composition. Phosphorus and sulfur are particularly deleterious impurities. Heavy minerals can also affect the quality of the weld. In general, silica, alumina, and alkaline earth oxides are not critical because they are a necessary component of the flux. It is important, however, that the content of these oxides be consistent.

Consumption of titanium minerals for welding electrode fluxes is estimated to have been about 100,000 tpy of TiO_2 units in the late 1980s, declining in the early 1990s because of the worldwide economic recession. The consumption of electrodes is influenced particularly by the construction industry and overall manufacturing activity. Demand for raw materials has since increased to an estimated 110,000 TiO_2 units. It is reported, however, that new continuous welding processes require lower TiO_2 content in the flux, which may limit the future growth in demand in this industry.

Metallurgical Flux

Lower quality titanium raw materials are used as a metallurgical flux in smelting operations, particularly in iron and steel production. Low TiO_2 ilmenite from Lac Allard in Canada and ilmenites from Southeast Asia and the east coast of Australia are used for this purpose in Europe, Japan, South Korea, and Brazil.

Drilling Muds

Because of its high density, ilmenite has at times been used as a component of drilling muds, particularly in North Sea oil drilling operations.

Product Pricing

Of the 110 elements in the periodic table, titanium ranks seventeenth in terms of global consumption by tonnage. TiO_2 is now the third top inorganic chemical behind ammonia and phosphoric acid in terms of consumption.

To establish a basis for forecasting future prices for titanium feedstocks, it is necessary to briefly examine the long-term historical trends in prices.

Rutile

Figure 3 shows prices for Australian exports of bulk rutile during the period from 1970 to 2003, in real 2003 terms and in nominal values. The prices come from the ABS export data in Australian dollar values (AUS\$) and have been converted to U.S. dollar values (US\$) using the annual average AUS\$–US\$ exchange rate.

During this period, US\$ prices for rutile have moved within a real price band of US\$400 to US\$800/t f.o.b., but show an overall declining trend of approximately 0.8%/yr in real terms. The cyclical nature of the rutile price broadly reflects the cycles in the TiO_2 pigment industry, with troughs in 1978, 1983, 1993, and 2000. Prices declined sharply from 1990 to 1993, in tandem with the global economic slowdown, reaching levels close to their historical low real values before beginning a slight uptrend. This was accelerated by market tightness triggered by the cessation of production at Sierra Rutile Limited (SRL) in early 1995. Prices have subsequently softened to more sustainable levels, in view of the fact that following the SRL closure, rutile is now regarded as a niche product relative to the dominant feedstock types.

Although it is not possible to obtain accurate prices for all ilmenite products (some of which are sold under long-term contracts negotiated some years ago), TZMI analyzed the prices of ilmenite exported from Australia for both sulfate and chloride use. Because Australian ilmenite accounts for the bulk of global trade,

this is a reasonable parameter to use in the analysis of price trends. The base data came from the Australian Bureau of Statistics.

Figures 4 and 5 show the trends in both nominal and real 2003 US\$ terms for Australian chloride and sulfate ilmenite prices, respectively, from 1975 until 2003.

The US\$ real price for 60% TiO₂ chloride-grade ilmenite shows a slightly declining trend line over the period to 1986, after which there was a 2-year transition period during which ilmenite was related to a much higher nominal level. Since 1988 there has been a trend-line growth in real US\$ prices of 1.3%. The fluctuations in recent years basically reflect a changing mix of ilmenite contracts.

Similarly, the long-term trend line for Australian 54%- to 57%-TiO₂ ilmenite for the sulfate process declined by 1.2%/yr during the period from 1970 to 1986, followed by a 2-year transition zone after which the trend-line rate has been -0.8%/yr.

It is noticeable that prices for sulfate ilmenite have historically been higher than prices for chloride ilmenite, although the TiO₂ content of sulfate ilmenites is lower than that of chloride ilmenite products. There are a number of reasons for this apparent anomaly:

- The market for chloride ilmenite is relatively narrow, with only one pigment producer (E.I. DuPont de Nemours and Co.) able to use ilmenite directly for chloride pigment production.
- The only other application for chloride ilmenite is as feedstock for SR production, but most ilmenite for this purpose is produced internally by the SR producer. The major exception is Kerr-McGee, which has for many years purchased 51% TiO₂ ilmenite from Consolidate Rutile Limited (CRL) and other sources.
- Consequently, DuPont has been able to use its considerable purchasing power to negotiate very favorable prices for chloride ilmenite.
- Average prices for chloride ilmenite have been influenced significantly by lower priced long-term supply contracts with DuPont. In particular, this applied to sales made in A US\$ terms of Eneabba ilmenite, which has relatively high U+Th content and for which DuPont is effectively the only buyer.

Recent contract prices negotiated for high-quality 60%-TiO₂ ilmenite, however, are at levels above current prices for 56%-TiO₂ sulfate ilmenite.

The rerating in the price of ilmenite, which clearly had been undervalued in comparison with other feedstocks before this date, arose for several reasons, including:

- The RGC takeover of Allied Eneabba, with a consequent increase in concentration of chloride-grade ilmenite supply
- The decision to build several SR plants in Australia, which moved some ilmenite from the traded category to the captive category
- Increased scarcity of quality ilmenite

In addition, later new operations such as Tiwest's Cooljarloo mine and Cable Sands' Jangardup mine resulted in the emergence of a wider spread of ilmenite supply. Another contributing factor was the policy decision of WSL from 1990 to purchase 60%-TiO₂ ilmenite for its Becher SR plant operations and so help prolong the life of its own resources.

As a result of these developments, the market began to play a greater role, particularly in the supply of chloride ilmenite, and prices rose accordingly.

Synthetic Rutile

The SR prices shown in Figure 6 are based on the reported value of Australian exports in AUS\$ and converted to US\$ as the source of

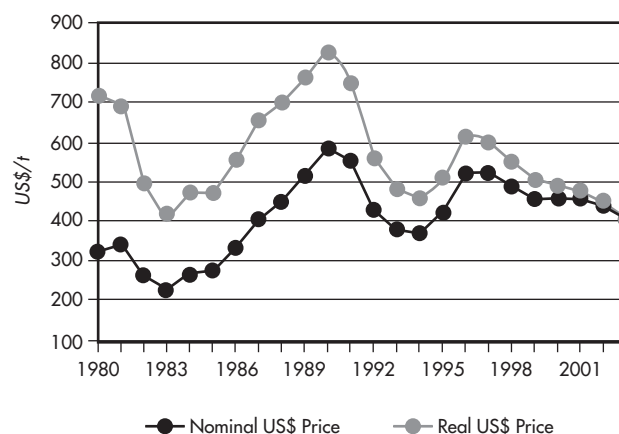


Figure 3. Rutile prices in real and nominal terms (1980–2003), US\$/t

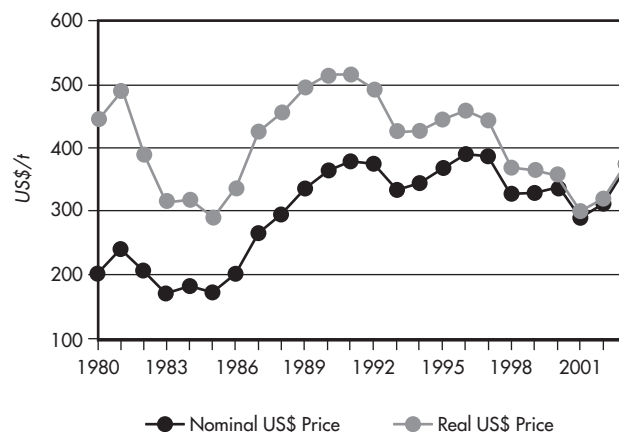


Figure 4. Australian chloride ilmenite prices, nominal versus real (1980–2003), US\$/t

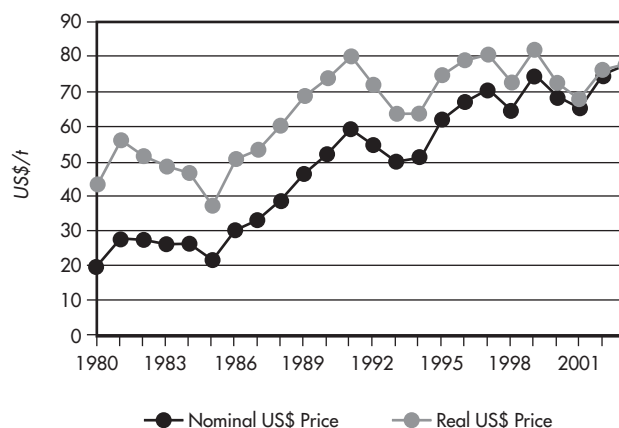


Figure 5. Australian sulfate ilmenite prices, nominal versus real (1980–2003), US\$/t

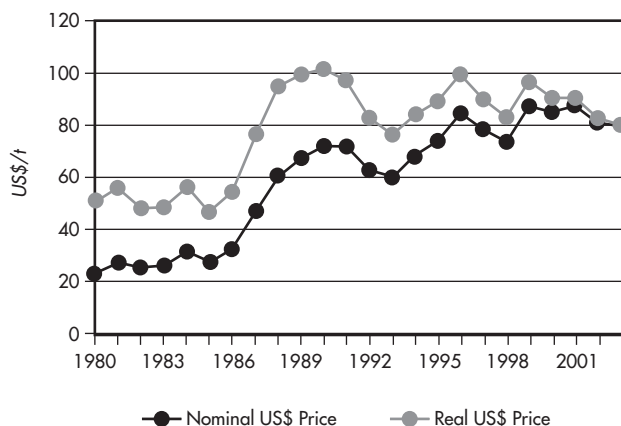


Figure 6. SR prices nominal versus real (1980–2003), US\$/t

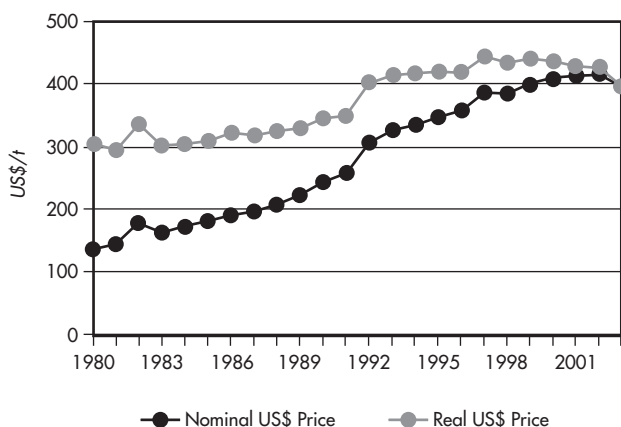


Figure 7. Chloride slag prices nominal versus real (1980–2003), US\$/t

price data represents the highest proportion of total SR purchases. The chart clearly shows that since the late 1980s, real US\$ prices have fallen. This reflects the impact of currency exchange variations. SR is the only high-TiO₂ feedstock that has been sold extensively in AUS\$, mainly because Australia has dominated supply. The result of this practice, which continues today, is that although both real and nominal prices in AUS\$ terms have risen since the mid-1980s, in US\$ terms, SR prices declined as the AUS\$ devalued against the US\$. The situation developed whereby in US\$ terms, SR was considerably cheaper than would be expected for its TiO₂ content. Its price was low relative to the other TiO₂ feedstocks that are sold in US\$. In the last few years, however, as the AUS\$ strengthened considerably against the US\$, that trend reversed. As a result, the US\$ price of SR is now closer to its relative economic value.

Chloride Slag

Figure 7 shows historical chloride slag price data from U.S. import statistics. In real terms, chloride slag prices have shown very little fluctuation in price during the period from 1980 to 2003, consistently increasing at an average 2%/yr over this period, although they were basically flat for the period from 1997 to 2003. The upward price trend was the result of most slag sales being contracted on a long-term basis with escalating price provisions, as

well as the fact that RBM was the only producer of chloride slag until 1995 and so faced no direct price competition. The reduction in slag prices in 2003 is clearly evident.

Upgraded Slag

Because UGS was first produced commercially only in late 1997, comparable long-term trend lines cannot be calculated. In fact, most UGS prices in real terms did not change in the period to 2002 because of QIT's tight contract provisions.

It is highly relevant to note that several initial contracts for 95% TiO₂ UGS were originally priced in early 1996 terms at US\$480/t. The application of an escalation rate based on the U.S. Consumer Price Index (CPI) meant that the price of UGS has increased in nominal terms but remained constant in real terms.

Because of market resistance to these escalated prices, which has inhibited some sales, QIT recently prepared to reduce prices to remain competitive relative to other high TiO₂ feedstocks.

Recent Price History

To put any price projections into perspective, it is important that the recent price history for key products be noted. Tables 6 and 7 show these in nominal and real US\$ 2002 terms, respectively.

For 2003, the general pricing direction was downward, with the prices of several feedstocks coming under pressure because of persistent oversupply and more competitive market conditions, influenced by the entry of new suppliers. Other feedstocks simply continued existing downward trends. Exchange rate moves again played an important role in influencing price moves, particularly the strengthening AU\$ and its influence on SR pricing in the U.S. market. Confusing the overall trend was the coexistence of older, long-term contracts and recently negotiated new contracts, which led to tiered pricing levels for some products, particularly slag. Average prices for sulfate ilmenite fell slightly, under pressure from increasing supply, whereas average chloride ilmenite prices improved, although the higher prices reflected more widespread trade in better-quality products rather than the overall market direction. Chloride slag prices declined in 2003, with some price increases (which resulted from price-escalating clauses in existing contracts) being offset by lower prices for more recent contracts. Average bulk rutile prices fell in 2003, further extending the general decline in rutile prices since the brief surge in 1995 after SRL closed. Rutile supply progressively tightened during 2003, however, because of lower output from several major producers, and this has led to strengthening rutile prices in recent months. Higher prices are particularly evident for bagged material used in welding electrode markets.

The pricing events of 2002 and 2003 are highly relevant in TZMI's view because they herald a significant new era during which TiO₂ pigment producers will clearly exercise considerably greater influence on pricing than has been the case in the past, particularly with the Rio Tinto group.

ECONOMIC FACTORS

By-products and Coproducts

Zircon

Zircon is by far the most significant coproduct (and in some instances a by-product) of titanium mineral production and is an important contribution to the revenue of these producers. Zircon concentrations can range from as low as 0.1% in low-grade dunal occurrences to as high as 3.0% in high-grade strandline deposits. More than 70% of titanium feedstock production also generates zircon revenue, which typically accounts for between 15% and 35% of

Table 6. Annual nominal free on board (f.o.b.) prices of selected titanium products (1998–2003), US\$

Titanium Product	1998	1999	2000	2001	2002	2003
Sulfate ilmenite	74	87	85	87	81	80
Chloride ilmenite	65	75	69	66	75	78
Rutile	490	458	463	462	442	409
Synthetic rutile	329	330	336	293	313	375
Sulfate slag	307	307	320	325	335	337
Chloride slag	387	400	410	415	420	397

Table 7. Annual real f.o.b. prices of selected titanium products (1998–2003), US\$

Titanium Product	1998	1999	2000	2001	2002	2003
Sulfate ilmenite	83	96	90	90	83	80
Chloride ilmenite	73	83	73	68	76	78
Rutile	552	506	494	479	452	409
Synthetic rutile	371	365	359	304	320	375
Sulfate slag	346	339	342	337	342	337
Chloride slag	436	442	438	431	429	397

total mineral production revenue and in some operations is as high as 50%. Zircon is therefore fundamental to the economic success of many titanium mineral producing operations. This coproduct is covered in a separate chapter within this volume.

Garnet

Garnet can be an important coproduct for mineral sands operations. Several mineral sands operations on the east coast of India are in fact mining garnet, and the titanium-bearing minerals are considered to be a by-product. Recent expansion and upgrading work at some of these operations has improved the separation of ilmenite from the waste stream, leading to its sale as a commercial product. Garnet from mineral sands mining is used in water-jet cutting, filtration, and abrasives applications.

Sillimanite

Sillimanite is a by-product of mineral sands mining in regions where the mineral sands were derived from the erosion of metamorphic basement rocks—the west coast of India, in particular. Sillimanite and its polymorphs—andalusite and kyanite—are used principally in the refractories market. When calcined, sillimanite and its polymorphs convert to a mixture of the very high temperature refractory mineral mullite and free silica. Mullite is particularly valuable in the refractory industry because it forms interlocking crystals that are stable up to 1,800°C, making it an excellent material for lining furnaces.

Monazite

Monazite is a rare-earth phosphate mineral that accumulates in mineral sands deposits owing to its high specific gravity. Its high content of the element thorium gives this mineral substantial natural radiation, which has limited its use since the 1990s. In the past, monazite was a sought-after mineral because of that high content of thorium (approximately 3% to 9% ThO₂). Thorium's main use was in gas light mantles, where the presence of thorium compounds produced a high incandescence at extremely high temperatures without melting, which made thorium gas lamps much brighter than ordinary gas lamps. The expansion of modern electric light has caused a decline in this application, which has been restricted in

developed economies to use in camping equipment. Even this application has fallen away in recent years, however, from the perceived danger from radiation. Most gas mantles produced today are made with yttrium.

Monazite is now most commonly used as a source of rare earths. The rare earths have found a niche market in high-technology applications such as permanent magnets, nuclear magnetic resonance, and catalysts for the automotive industry, among others.

Pig Iron

High-purity pig iron (HPPI) is an increasingly important coproduct to the titanium minerals industry, particularly as the production of titanium slag increases in line with industry demand for higher TiO₂ feedstocks. HPPI is typically sold at a much lower price than titanium slag; however, revenue from iron can represent 20% to 25% of the revenue from titanium feedstocks. HPPI is used within the steel industry as a high-quality source of iron, where it commands higher prices than conventional iron products. The market for HPPI in recent times has been strong, with high prices owing to an increase in demand for steel from China.

OUTLOOK AND FUTURE TRENDS

Supply/Demand Fundamentals

The TiO₂ pigment industry has generally been cyclical in nature, and the status of the market for titanium feedstocks at any point in time depends on these cycles. The trends in demand for feedstocks, however, do not mirror exactly the trends in pigment consumption, despite the pigment production industry consuming 93% of annual off-take in 2003. This arises because of the long distribution chain between pigment producers and the final consumption of pigment. The accumulation of stocks in this chain causes the market impact on demand for feedstock to lag behind the market trends for pigment consumption.

Forecast titanium feedstock demand is built up as follows. Short-term pigment consumption growth is estimated from an analysis of forecast economic growth on a regional basis. The historical correlation between gross domestic product (GDP) growth and pigment consumption is used to give a broad estimate of future pigment consumption growth. Available industry forecasts of TiO₂

Table 8. Global titanium feedstock supply/demand balance (2001–2005), thousand TiO₂ units*

Consumption/Production	2001 [†]	2002 [†]	2003 [†]	2004 [‡]	Year-on-Year, %	2005 [§]	Year-on-Year, %
Estimated titanium feedstock consumption							
TiO ₂ pigment	4,408	4,625	4,790	5,053	5	5,139	2
Ti metal	145	152	143	167	17	204	23
Other uses	150	154	157	165	5	168	2
Total demand	4,702	4,931	5,089	5,384	6	5,511	2
Estimated chloride-grade feedstock production							
Chloride ilmenite and leucoxene	637	651	709	718	1	749	4
Rutile	414	423	364	358	-2	385	7
Upgraded slag	190	185	223	247	11	266	8
Chloride grade slag	781	738	692	770	11	924	20
Synthetic rutile	860	842	798	740	-7	732	-1
Subtotal	2,882	2,839	2,788	2,834	2	3,056	8
Chloride-grade supply/demand balance	217	-37	-130	-115	-11	10	
Estimated sulfate feedstock production							
Sulfate ilmenite	1,267	1,362	1,529	1,510	-1	1,585	5
Chloride fines**	117	118	128	129	1	149	15
Sulfate-grade slag	673	579	597	631	6	614	-3
Subtotal	2,058	2,058	2,253	2,270	1	2,348	3
Sulfate-grade supply/demand balance	24	2	76	24		-16	
Feedstock supply/demand balance							
Total demand	4,702	4,931	5,089	5,384		5,511	
Total supply	4,940	4,897	5,041	5,104		5,404	
Supply/demand balance	236	-34	-49	-281		-108	

* TiO₂ units are calculated as tons of feedstock multiplied by the proportion of TiO₂ contained.

† Data based on full-year production figures.

‡ Data based on estimated production figures.

§ Forecasts.

** Chloride fines are that portion of chloride slag production for which the particle size is too small to be successfully used in the chloride process. It is usually used as a supplementary feedstock for sulfate process plants.

pigment consumption in the major market segments of coatings, plastics, and paper supplement this analysis.

For 2003, pigment consumption was estimated using complete data for virtually all the major consuming countries. Individual pigment plant capacities come from reported capacity at the end of 2003, with adjustments for announced changes in capacity and additional forecast changes estimated by TZMI.

The annual estimates of global pigment production from 2004 onward were allocated plant by plant, based on assessed production levels for 2003, expected changes in production, and adjusted for forecast changes in capacity.

Feedstock demand is estimated for each product, based on the assessment of consumption of individual products by each individual pigment plant in 2003. To calculate future feedstock consumption, adjustments were made to the product mix in those cases where the 2003 data were considered to be abnormal or known changes were foreshadowed. This adjusted feedstock consumption mix then was prorated by the individual pigment plant's forecast production to determine forecast consumption for each feedstock product on an individual plant basis. These individual plant forecasts are totaled for each major consumer or groups of minor consumers.

- Future titanium sponge production was forecast on a global basis using industry forecasts (from both producers and industry associations such as the Japan Titanium Society) for future

titanium metal demand. This global production was allocated to individual titanium sponge producers based on historical performance and expected changes in production capabilities.

- Forecast demand for feedstocks for titanium sponge production was estimated in a similar manner to the demand for feedstocks for pigment production, plant by plant.
- The growth in demand for feedstocks for welding electrodes and other applications was estimated using general economic trends and industry data. These trends were applied in calculating forecast feedstock consumption by product.

Table 8 gives the estimated supply/demand balances for 2001 through 2005. Although every effort is made to provide the most accurate information possible, the margin of error on this analysis is estimated at about 50,000 TiO₂ units, and the supply forecasts do not include any adjustments to inventory levels.

Higher production is forecast for 2005 for feedstock products with the exception of SR and sulfate slag. For SR, all plants are already operating at capacity. For sulfate slag, there is significant oversupply at present. The oversupply is reflected in the decision of one major producer of titanium slag to schedule a prolonged shutdown of its smelter in 2005, resulting in overall lower levels of supply.

TZMI forecasts indicate that supply and demand for titanium feedstocks will be closely balanced in 2005. After 1 year of strong

pigment consumption growth in 2004 and further growth of about 3.0% to 3.5% in 2005, a need for higher levels of slag production is expected, with some suppliers that have been operating at reduced capacity in the past few years progressively returning to full capacity by 2006. Although overall demand is expected to continue to grow at average rates of just under 3.0%/yr, the additional slag production and new supplies of rutile and ilmenite from new projects in 2006 should return both chloride- and sulfate-grade feedstocks to an oversupplied position from 2006.

The Longer-Term Market Outlook

Figure 8 shows TZMI's assessment of the likely supply/demand scenario through to 2008. The analysis indicates the possibility for the titanium feedstock market to be oversupplied through to 2010, based on additional supply from both approved new projects and selected likely feedstock projects. These projections are based on the assumption that demand for titanium feedstocks continues to grow at approximately 2.9%/yr during this period, while supply from existing operations remains static and, in some instances, declines because of resource depletion or lower grades. The approvals in 2004 for new projects such as Kenmare Resources' Moma project, Iluka Resource's Douglas project, and Bemax Resources' Poona project, however, will add considerably to future supply, and greatly reduce the size of the potential supply gap.

A considerable number of new projects are being evaluated. Clearly, there is not room in the market for all of them to proceed to development in the time frame indicated, and only a select few will ever reach production stage. In Figure 8, TZMI therefore estimated total supply from "likely" new projects (without naming individual projects), and this is depicted as the shaded area in Figure 8, representing approximately 350,000 T iO₂ units of new supply at its peak. Of considerable strategic importance is which project or projects are developed first, because this will influence the availability of individual feedstock products and affect the subsequent development of other new projects by further altering the dynamics of the potential supply gap.

Strategic Issues

The titanium feedstock industry is highly concentrated and therefore dominated by relatively few companies at both ends of the supply chain. Just two companies are responsible for almost 50% of global titanium feedstock supply, and just three companies possess more than 50% of installed T iO₂ pigment production capacity. Clearly the relationships that develop between these large suppliers and consumers of T iO₂ feedstocks can have a significant effect on the titanium feedstock industry as a whole. In particular, the actions that the industry leaders take to maintain or exchange their respective positions have implications for the entire industry.

It is in the interests of the major feedstock consumers that new titanium feedstock projects receive approval, because the increased supply will flow on to more competitive pricing of titanium feedstocks. In turn, feedstock producers must rely in part on off-take agreements to gain approval for developing new projects through to commercialization. The titanium feedstock industry is therefore in the difficult position of effectively handing control of future pricing of their products to their consumers, which could have implications for future profitability of the titanium feedstock industry.

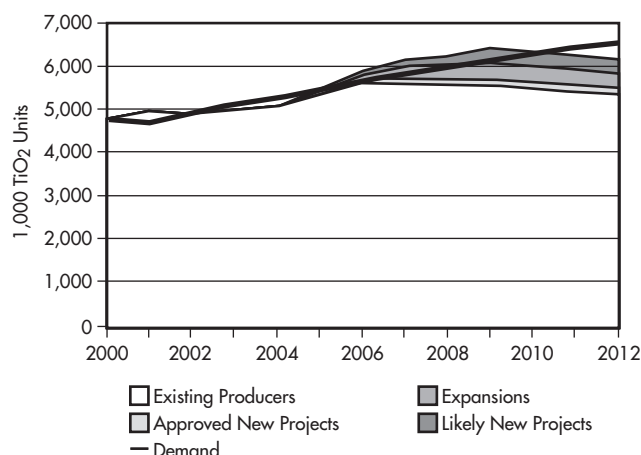


Figure 8. Global titanium feedstock supply/demand balance (2001–2005)

The influence of China is another important strategic issue for the industry. China recently emerged as a significant force in the titanium industry. In 2003, for the first time, China surpassed the United States as the world's largest titanium pigment importer, importing more than 250,000 t of T iO₂ pigment compared with just 100,000 t in 1999. Since 1999, consumption and production of T iO₂ pigment in China have both more than doubled. China does not yet have access to the chloride process of T iO₂ pigment production, the technology for which is tightly controlled by existing producers. Nevertheless, it is simply a matter of time before the technology is introduced there. This is particularly relevant given the current push for tighter environmental standards for industry in China. Many of the existing sulfate plants do not operate within existing environmental standards. Tighter regulations might embargo further expansion of sulfate route pigment production capacity. Western sulfate pigment producers have developed efficient waste management and coproduct streams to comply with tightened environmental regulations while remaining cost-effective. If China seeks to further increase its pigment production capacity without chloride route technology, there may be an increased focus on the use of high-T iO₂ feedstocks. This has the potential to dramatically alter the dynamics of the global titanium feedstock industry.

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Tripoli (Microcrystalline Silica)

William A. Bratney

Tripoli is an industrial mineral commodity important to many market sectors, including the paint industry, in which it performs as a chemically inert, very fine-grained extender. In the plastics, rubber, adhesives, and sealants industries, it serves as a functional filler imparting strength, opacity, and other beneficial properties. Because of its uniform size, mineral hardness, and orientation of the crystal faces, the abrasives industry uses tripoli as a buffing and polishing compound.

Microcrystalline silica is a better name than tripoli for this soft, porous, siliceous material, because it describes the physical and chemical characteristics of the material. In this chapter, microcrystalline silica is used in preference to tripoli for most of the discussion. The term *tripoli* is still the appropriate term for microcrystalline silica that is used principally as an abrasive.

Microcrystalline silica consists almost entirely of extremely small quartz crystals, many of which are less than 1 μm long. Three companies produce microcrystalline silica in the United States, all from open-pit mines. The ore is beneficiated by crushing, grinding (often to a micronized particle size), and sizing. All the active operations are located in the central part of the United States. Important prospects exist in other countries, and it is reportedly produced for export in China (C.T. Steuart, personal communication). Physical and chemical differences among the active deposits exert a strong bearing on the markets served, especially natural grain size, color and brightness, impurities, ease of disaggregation, and product porosity.

DEFINITIONS

Tripoli

Tripoli is the historical term for microcrystalline silica used principally in abrasives applications. It is an extremely fine-grained, generally friable, and porous rock that consists almost entirely of submicroscopic quartz crystals, most of which are less than 2 μm long. Some deposits of this microcrystalline quartz may form as a result of the hydrothermal alteration of a chert-bearing limestone, while others may originate through deep weathering of an originally siliceous limestone with solution and removal of calcite and the introduction of and recrystallization of quartz. The term tripoli has been used and, in some instances, continues to be used interchangeably with microcrystalline quartz. Both the rock and the commercial material derived from it are best described as microcrystalline silica. Historically, in the United States the term tripoli was first used to describe the fine-grained, easily disaggregated

material from Seneca, Missouri, because of its similarity to a rock from the Tripoli region of North Africa (Hovey 1894). Missouri and Oklahoma material is also sometimes called tripolite (Quirk and Bates 1978). Other deposits of microcrystalline silica, such as those in southernmost Illinois, later came to be known as tripoli. The North African tripoli rock, however, is actually diatomaceous earth, or diatomite, a material that is similar in macroscopic appearance to the rock from Seneca, Missouri, but is of entirely different origin, having formed by the accumulation of the siliceous remains of microscopic marine or freshwater golden algae, or diatoms. The essential difference between diatomaceous earth and microcrystalline silica is that diatomite is composed of opaline (and therefore amorphous) silica rather than crystalline silica. Microscopically, the shape of the diatoms and their open internal structure are distinctive and important criteria in the use of diatomite as filtration media, a market area for which microcrystalline silica is unsuitable.

Microcrystalline Silica

The distinction between the use of the terms microcrystalline silica and tripoli is dictated largely by convention and markets. Material produced from the southern Illinois deposits is used widely in filler and extender applications, and it is generally referred to as microcrystalline silica. That material used as an abrasive buffing or polishing material, both from the Illinois district and from other states, is commonly called tripoli.

Novaculite

Although originally used to describe a rock suitable for the manufacture of whetstones, novaculite is now defined more generally as a homogeneous, mostly white or light-colored rock, translucent on the thin edges, with a waxy or dull luster, and composed of almost entirely microcrystalline quartz (Steuart, Holbrook, and Stone 1983). The more compact rock mined in central Arkansas from the Arkansas Novaculite is referred to as novaculite, whereas the more porous and friable rock is referred to as tripoli or tripolitic novaculite.

Amorphous Silica

Amorphous silica, as an industrial term, was once used to describe the material produced from the deposits in southern Illinois. It has been replaced by the term microcrystalline silica. The term amorphous silica came into use at a time when optical methods for the identification of very fine-grained quartz were not widely available,

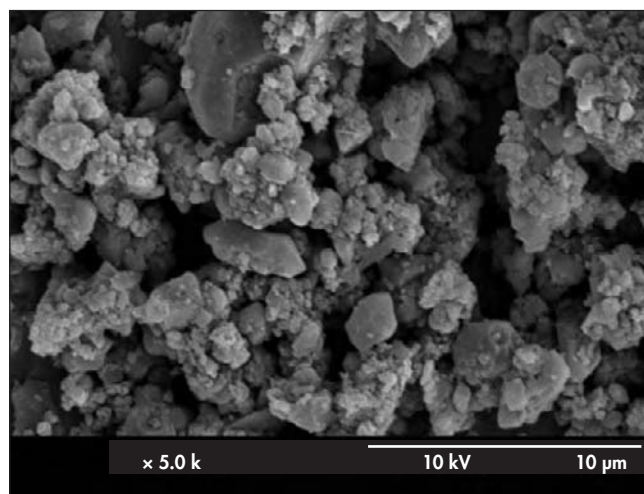


Figure 1. SEM photograph of material from American Tripoli, Inc. It is known as Seneca Standard tripoli.

Table 1. Tripoli production and value data

	1998	1999	2000	2001	2002
Production, t	79,600	84,900	72,000	60,500	66,600
\$ Value (× 1,000)	16,900	20,200	15,900	15,000	16,600
\$ Value/t	212	238	221	248	249

and the Illinois product, composed of quartz grains too small to be seen with the unaided eye, was thought to consist of amorphous silica. The material mined in the midcontinent region of the United States is clearly crystalline quartz, as shown by x-ray diffraction (XRD) analysis and scanning electron microscopy (SEM; Figure 1).

Opal

Opal exists in three forms: opal-A, opal-C, and opal-CT. It precipitates from sea water or fresh water as an amorphous gel (opal-A) with its composition being between 3% and 10% or more of water. Over time, through diagenesis it can transform into opal-CT (an opal showing the beginning of formation of domains of short-range ordering similar to the arrangement of atoms in extremely fine grained cristobalite and tridymite) or into opal-C, then to chalcedony (fibrous microcrystalline quartz), and then to macrocrystalline α -quartz. Morganite, a microcrystalline monoclinic polymorph of quartz, first described by Flörke, Jones, and Schmincke in 1976 and named in 1984, is widespread in microcrystalline quartz varieties and is being identified more frequently in this transitional sequence from amorphous silica to quartz. The process is marked by progressive reductions in the porosity of the deposited silica and its water content, and a consequent increase in its density. The instability of the attached water molecules gives opal its tendency to crack or decrepitate at high temperatures. Opaline silica makes up the bulk of the silica in economically important diatomaceous earth deposits and also forms in hot springs environments, in association with crystalline silica, as geyserite or siliceous sinter.

Related Terms

Other common varieties of microcrystalline silica are chert, chalcedony, jasper, and flint. The crystalline structure of chalcedony is unique in that the quartz can be fibrous or porous, but still the mate-

rial is considered to be crystalline, and quartz can be recognized by XRD analysis.

Chert, chalcedony, jasper, and flint are interchangeable terms for hard, very fine-grained microcrystalline silica. This material is extremely dense, breaks with a conchoidal fracture, and has been used throughout history for edged weapons such as knives, spear points, war clubs, and arrowheads. Close inspection reveals this form of silica to be composed of tightly interlocking quartz crystals of less than about 30 μm in diameter. It may also contain amorphous silica.

Ganister is a term for a high-silica, friable rock that is marketed in irregularly sized pieces, and that is an inch or less in size; it is used in the manufacture of silica brick (Lamar 1953). The color of this material is usually white or cream, but it may be stained to red, orange, or yellow by iron oxides without adversely affecting its industrial application.

The commodity known as *rottenstone* is sometimes included within the general mineral commodity category of tripoli. Rottenstone is mined in Northumberland County in eastern Pennsylvania, and it is formed by the weathering of siliceous shale of Devonian age (Faill 1979). This material is used as a filler and extender in certain applications, but it is unlike tripoli both in origin and physical properties.

Spiculite is a rock consisting of siliceous sponge spicules that formed by the removal by solution of the carbonate matrix of a spicule-bearing limestone. Spiculite has been mined in Texas and, because it resembles tripoli in several aspects, it is included in the discussion of deposits.

PRODUCTION AND TRADE, RESOURCES AND RESERVES

Sales and Exports

Information compiled by the U.S. Geological Survey (USGS) *Minerals Yearbook* staff (Dolley 2002) shows that sales of tripoli and silica-rich rottenstone from Pennsylvania amounted to 66,600 t in 2002. This represents an increase of approximately 10% over the 60,500 t processed in 2001. Table 1 gives tripoli production and value data between 1998 and 2002 (Dolley 2002).

A USGS annual survey of producers (Dolley 2002) indicated that the output of crude tripoli produced domestically in 1995 was 79,700 t with an estimated value of \$3 million. In the United States, four firms are known to produce or process tripoli. Malvern Minerals Company, in Garland County, Arkansas, produces crude and finished material. Malvern also produces a black material from novaculite. American Tripoli Company produces crude material in Ottawa County, Oklahoma, and finished material in Newton County, Missouri. Unimin Specialty Minerals Inc. in Alexander County, Illinois, produces crude and finished material. Keystone Filler and Manufacturing Company in Northumberland County, Pennsylvania, processes rottenstone. This company has been in operation for 60 years. It purchases the mined rottenstone and processes it by grinding into a product that is 99% –325 mesh for the brake-liner industry.

In prior years, the production and consumption of microcrystalline silica (including tripoli) products ranged from an average of 35,864 t for the years 1951–1955 (Chandler and Tucker 1961) to 105,220 t in 1979, the year of maximum sales (Anon. 1981). In 1979, the sale of microcrystalline silica for use in the filler and extender markets exceeded the sale of tripoli for the abrasives industries.

Tripoli has unique applications as an abrasive because of its hardness and because its grain structure lacks distinct edges and corners. It is a mild abrasive, making it suitable for use in toothpaste and tooth-polishing compounds, industrial soaps, and metal/

jewelry polishing compounds. The automobile industry uses it in buffing and polishing compounds for lacquer finishing. The end-use pattern for tripoli has changed significantly in the past 25 years. In 1970, nearly 70% of the processed microcrystalline silica was used as an abrasive in various tripoli products. Kelley, Dolley, and Olson (2004) charted tripoli production and sales statistics for use in the abrasives industry through 2002. In 1989, almost 2.5 times as much of this commodity was used in filler and extender applications than in abrasives (Austin 1992). In 1995, more than 75% of microcrystalline silica output was used as a filler and extender in paint, plastic, rubber, caulking compounds, and enamel. The best grades of microcrystalline silica are used as fillers and extenders in paints. These applications may account for as much as 85% of the microcrystalline silica used as a filler and extender. The average reported value of all microcrystalline silica sold or used in the United States was \$131/t in 1995, slightly less than its value the previous year. The average reported value of abrasive tripoli sold or used in the United States in 1995 was \$151/t (Balazik 1995).

Foreign competition has not been a significant factor in these markets because significant production is largely confined to the United States (Harben 1983). The United States is an exporter of Tripoli; export from the Missouri–Oklahoma District was reported as early as 1894 (Fellows 1967). Foreign markets for microcrystalline silica continue to be important. For instance, Arkansas tripoli, in addition to supplying domestic customers, is exported to Canada, Taiwan, most of Europe, Israel, Turkey, Australia, New Zealand, the Republic of South Africa, Saudi Arabia, and South America.

TRIPOLI DISTRICTS

All the commercial deposits of microcrystalline silica in North America occur in three districts in the central and southern United States. They include the deposits in southernmost Illinois, the tripolitic novaculite mines of central Arkansas, and the Missouri–Oklahoma tripoli district. Textural differences exist between these deposits, but there are many similarities in geologic setting. Deposits of tripoli also have been described in Alabama, Georgia, Mississippi, and Tennessee. These occurrences are currently undeveloped and were mined originally as local sources of abrasives and polishing compounds. Siliceous sponge spicule accumulations were mined in the past in Texas for use in special drilling muds.

Southern Illinois District

Illinois has been the site of major microcrystalline silica production since the early 1900s. The first reported shipments were before 1906, and Bain (1907) reported three mills in operation at that time. At least nine companies have produced microcrystalline silica from the many small deposits in Union and Alexander counties in southernmost Illinois (Berg and Masters 1994). Unimin Corporation purchased Tammsco in 1987, and then acquired Illinois Minerals from Georgia Kaolin 2 years later. Unimin Specialty Minerals Inc. operates the McCrite-Birk open-pit mine in Alexander County, which supplies tripoli to the processing plant in Elco. The Tamms plant is now used as a grinding facility for other Unimin Corporation mineral products. Other occasional production in the district comes from Lone Star Industries' mine, where off-color microcrystalline silica and chert are produced for use in its portland cement plant at Cape Girardeau, Missouri. Unimin Specialty Minerals Inc. regularly supplies iron-stained microcrystalline silica and chert from its overburden stripping and from off-color interbeds within the mine to several cement producers in the midcontinent region.

The southern Illinois tripoli district lies a few kilometers west of the small town of Elco. The silica-rich rocks encompass approximately 150 km² in Alexander and Union counties. This area con-

tains well over 100 inactive underground mines and prospect pits. There are also several inactive mines in the Wolf Lake Area, about 17 km northwest of Elco.

Microcrystalline silica deposits are located within a Devonian stratigraphic sequence exposed along a north-south trending belt on the southwestern margin of the Illinois Basin. Mississippian-aged sedimentary rocks are exposed east and northeast of the district, and Ordovician and Silurian units crop out to the southwest along the Mississippi River. The Lower Devonian Clear Creek Chert hosts the active mines. Outside of the tripoli mining area, the Clear Creek Chert is a dolomitic limestone containing chert interbeds; but within the district, carbonates are not found within this formation and silica has been introduced. The Clear Creek Chert is a 60- to 90-m-thick mixture of chert beds, decomposed, friable, variably colored to white microcrystalline silica beds, and fossiliferous thinly bedded chert layers. The Backbone Limestone, the unit lying immediately beneath the Clear Creek Chert in other parts of the southern Illinois region, is not found in the tripoli district, presumably because it has been removed by solution. The Grassy Knob Chert directly underlies the Clear Creek Chert, and it consists of massive chert beds near the mines, becoming less cherty with depth near the contact with the Lower Devonian Bailey Limestone. The Clear Creek Chert is overlain unconformably by the Dutch Creek Sandstone Member of the Grand Tower Limestone. This unit is a tan to off-white, silica cemented, medium- to coarse-grained, massively bedded sandstone, 0 to 3.0 m thick in this area.

In the Elco District, the uppermost 20 to 30 m of the Clear Creek Chert consists of massive chert beds that cap narrow, flat-topped ridges between deep hollows (Levine 1973). Beneath these chert beds, thinly bedded (less than 30 cm thick), prominent, hard chert beds are interbedded with softer chert and friable microcrystalline silica. Commercial beds of microcrystalline silica range from 2.4 to 12.2 m thick (Berg and Masters 1994). The best material is strikingly white, but cream to buff lenses are also mined. Sunglasses are strongly advised when visiting the open-pit mines. Poor-quality material occurring within the mining horizon is carefully stripped during development and is stockpiled for use as cement kiln feedstock throughout the region. The McCrite-Birk mine occupies more than 10 ha, and it is by far the largest tripoli mine developed to date. Bedding in the mine is typically close to horizontal, but it is impossible to follow the individual layers more than a few tens of meters. This is due to the abundant near-vertical joints and also to the many high-angle faults with offsets of only a few centimeters to more than 5 m. These structures are often filled with gray kaolinite clay and are typically bounded by strongly iron-stained material. Shrinkage resulting from volume reduction—caused by the removal of the original carbonates—is believed to be responsible for the numerous structures in the deposits.

The origin of the southern Illinois tripoli deposits is complex. The presence of brachiopods, trilobites, and other marine fossils preserved in many of the hard chert layers and associated with the bright white microcrystalline silica zones, coupled with the existence of carbonates in adjacent parts of the Illinois Basin, requires a mechanism to not only remove essentially all of the original carbonate material but also introduce abundant silica to the formation while aggressively bleaching the rock to its current whiteness. Berg and Masters (1994) and other geologists believe that deep in-place dissolution of the carbonates may have been caused by circulating convective hydrothermal systems driven by heat from mafic plutons emplaced within the Precambrian basement. A distinct magnetic anomaly exists west of Tamms and Elco, and another one has been mapped below the Wolf Lake deposits (Heigold 1976). The hot waters bleached the rock, and they carried dissolved silica, which

was precipitated as euhedral, microscopic quartz crystals, in the voids created by the solution of the carbonate beds.

Missouri–Oklahoma Border District

Seneca, Missouri, has been an important center of tripoli production for more than 100 years (Dobbs 1960). Discovered in 1869, tripoli was first mined in 1871, and the first grinding mill was constructed in 1885. The American Tripoli Company was formed in 1888, and it continues to produce a wide range of microcrystalline silica products today as American Tripoli Inc. Deposits exist in Newton County, Missouri, and in Ottawa County, Oklahoma. Now mining is limited to exposures southeast of Peoria, Oklahoma, although inactive mines exist along the border between the two states and northeast of Seneca, Missouri.

Tripoli in the Missouri–Oklahoma border district occurs in bedded units of the Warsaw Formation and, to a lesser extent, in the underlying Burlington-Keokuk Limestone. Both formations are Mississippian in age. Tripoli is confined to these two formations, but the deposits do not seem to be limited to specific stratigraphic intervals within them. Cherty limestones host all of the deposits, which are thin, and range between 1.3 and 6.6 m in thickness. The mines are all open-pit operations, and overburden is typically less than 3.3 m of red clay, chert, and impure tripoli (Fellows 1967). A flint-like caprock overlies some deposits. The lateral extent of individual deposits tends to be small, generally a few tens of meters across. In contrast, a deposit south of Peoria, Oklahoma, encompasses approximately 3.6 ha. Deposits occur on broad, flat-topped hills in the region. The color of the tripoli ranges from cream to rose, depending on the iron content. The rose tripoli contains more alumina, iron oxide, and titania than do the cream deposits. The concentration of chert nodules within the deposits is important, because if they are too abundant the deposit cannot be processed into an acceptable product. Secondary silica has been deposited along some of the steeply dipping fractures in the deposits.

Several explanations have been offered over the past 90 years to account for the origin of the Missouri–Oklahoma tripoli deposits. All of them include the removal by solution of some of the carbonate material from the sedimentary rock to form the tripoli. Quirk and Bates (1978) suggested that beds formed by the deposition of colloidal silica and alkali salts were subsequently attacked by weathering processes, which removed the salts and concentrated the silica. This explanation follows the earlier formation hypothesis of Siebenthal and Mesler (1908), who suggested that the original rock was a siliceous limestone from which all of the carbonate had been dissolved, resulting in a local concentration of tripoli. Using acid, they dissolved a siliceous limestone to produce a poor grade of tripoli. The volume reduction from this process was extreme. It has not been possible to trace laterally a bed of tripoli into fresh, unaltered rock, and surprisingly no fossils or relict bedding structures can be identified in the tripoli deposits. Siebenthal and Mesler (1908) mentioned the occurrence of cherty slickensides within some of the tripoli deposits, which suggests that secondary silica was introduced into fractures produced by volume reduction along which there was renewed movement.

A third explanation, presented by Perry (1917), calls for the extensive weathering of a thick homogeneous chert bed. About 3 km north of a tripoli deposit, a persistent chert bed is exposed in approximately the same stratigraphic position. The outer margins of the tripoli deposits are always observed to grade into chert. Scanning electron micrographs of chert from these deposits show a tripolitic rim on hard chert cores, indicating that at least some of the tripoli formed by the alteration of chert (Keller 1978).

Arkansas Tripolitic Novaculite District

Tripoli mined from the Arkansas Novaculite is a homogeneous, white to tan, mostly poorly to well cemented, friable rock, composed almost entirely of microcrystalline quartz (Berg and Steuart 1994). Novaculite was first mined near Hot Springs, Arkansas, in the eastern Ouachita Mountains from a very hard, white, siliceous rock for use as sharpening stones (Holbrook and Stone 1978). Griswold (1892) described the fine-grained whetstone known as the Arkansas Stone as a "true novaculite satisfying all the necessary conditions regarding homogeneity, grittiness, finely granular structure and siliceous composition; it is translucent on the edges and has a marked conchoidal fracture." Keller, Vele, and Johnson (1977) proposed that the word novaculite be used to describe only a thermally metamorphosed chert that shows polygonal triple-point structure.

Tripolitic novaculite is restricted to the Upper Division of the Arkansas Novaculite, and Hass (1951) identified it as early Mississippian in age, based on his study of a conodont fauna at Caddo Gap, Arkansas. The Upper Division of the formation is thickest in the vicinity of Hot Springs and thins rapidly to the north and more gradually to the south and west. Recognizable beds vary in thickness from several centimeters to 1.3 m. Not all of the Upper Division rock is tripoli bearing. Much of it is calcareous, appearing variably weathered to light brown or buff rotten rock with a gritty texture. Weathered novaculite varies from a firm, slightly porous rock, which looks much like a siltstone, to soft Tripoli, depending on the amount of carbonate present in the original rock. The carbonates found in fresh rock amount to as much as 30% and consist of calcite, mangiferous calcite, rhodochrosite, or ankerite. These tripoli deposits attain thicknesses of more than 33 m. Particle sizes range from 0.5 to 10 μm , and individual grains are equidimensional. Color ranges from white through lighter shades of tan and brown, depending on the quantity of iron and manganese oxides and clays present.

Charles Steuart (personal communication) points to structural preparation as the most important reason for the development of commercial deposits of tripoli within the Upper Division of the Arkansas Novaculite. Every good locality is related to the intersection of two or more high-angle faults and, interestingly, all of the good tripolitic novaculite is mined from overturned beds. Originally the tripoli in the Arkansas Novaculite was deposited by direct precipitation of silica by chemical or biogenic means. In all likelihood, deposition occurred in a deep-water oceanic environment well beyond the limit of detrital debris. Radiolarian ooze and direct silica precipitation from seawater enriched in silica built up nearly pure accumulations in some areas as well as impure zones contaminated with carbonates. Regional metamorphism in the Ouachita Basin transformed the original sediment into chert, and subsequent extensive weathering along faults and in zones of significant carbonate minerals produced the commercial tripoli deposits.

Other Deposits

Large, noncommercial microcrystalline silica deposits are found in the northwestern part of Alabama. They have been formed by deep-seated dissolution of Mississippian chert-rich siliceous carbonate rocks of the Fort Payne Chert. Silica from dissolved chert was precipitated in the voids by circulating groundwater to form euhedral quartz crystals between 1 and 4 μm long. This material resembles the southern Illinois tripoli in texture and chemical purity. The color of the northwestern Alabama microcrystalline silica ranges from white to very pale orange. The deposits are typically 0.3 to 1.2 m thick, but some occurrences up to 24 m thick have been noted (Rheams and Richter 1992). In northeastern Alabama, smaller silica

beds are found in the Fort Payne Chert and in the Cambrian-Ordovician Chepultepec and Copper Ridge dolomites. Microcrystalline silica and tripolitic material from this area range in color from white to very pale orange and pinkish gray and in grade from fine grained powdery tripoli to coarse material with abundant chert. The friable microcrystalline silica is found in beds from about 1 m thick to one exposure 30 m thick. Production from northeastern Alabama occurred between the early 1900s and the 1920s, but there is no activity today.

Impure microcrystalline silica deposits (termed tripoli in the literature) similar to those in Alabama occur in Tennessee and in the northeastern corner of Mississippi. These deposits have been mined in several areas. The Wayne County, Tennessee, occurrences have been thoroughly described (Spain 1938; Born 1936) and probably have the greatest potential for economic development. The Fort Payne Chert hosts the tripoli deposits, which reach 20 m thick. The color of the tripoli is typically white with some brown streaks attributed to secondary iron oxides. The texture of the Tennessee tripoli ranges between compact and more friable material. The origin of these deposits is believed to be the result of preferential dissolution of the carbonate portion of siliceous limestones along structural lineaments, accompanied by the mobilization of dissolved chert and its reprecipitation (Rheams and Richter 1992). The role of the lineaments, recognized in high-altitude aerial photographs, is that they were important in channeling the flow of groundwater that dissolves the carbonates and controls the redeposition of the silica.

Other noncommercial microcrystalline silica deposits occur in Georgia, where minor production is documented north of Atlanta (Crickmay 1937). Texas also has a friable silica deposit, but it is composed of sponge spicules. Dietrich and Lonsdale (1958) described the spiculite deposits of central Texas. Calcite was leached at depth from the Pennsylvanian-aged Marble Falls Formation, leaving a rock composed of siliceous sponge spicules. Except for some residual clay, the spiculite deposits are essentially pure silica. Harris (1989) describes a small Tripoli occurrence located near Hartville in Platte County, Wyoming.

In Europe, tripoli is mined near the small town of Castro Urdiales in the Cantabria Province of Spain. Castro Urdiales is on the Bay of Biscay and near the towns of Santander and Bilbao. Tierras Industriales Herranz y Diez S.A. produces approximately 5,000 t of microcrystalline silica each year for use in filter media and abrasives. The deposit originated from the leaching of Mesozoic chert-rich limestones (R. Garcia, personal communication).

There is a tripoli deposit in the Kastorenskiy District in the Kursk region of the Russian Federation. It is reportedly located on the border with the Voronezh region, 10 km from the center of the Kastornoe District. A joint-stock company, Blagodatenskiy Building Materials Factory, has been formed to exploit the tripoli deposits for use in the manufacture of lightweight silica brick in a factory built in the 1940s. The unique chalk and tripoli deposit at Kotovo-Gudovskoe is situated on 101 ha, including the 36 ha of the existing chalk and tripoli pit. Another Russian tripoli deposit is near the town of Alaty, south of Cheboksary in the Chuvash Republic, a sovereign republic in the Russian Federation about 650 km east of Moscow. The tripoli here is mined for use in the manufacture of heat insulation materials.

EXPLORATION AND DEVELOPMENT

In the early years of the southern Illinois tripoli district, new deposits were identified simply by finding outcrop exposures of white material in steep erosional cuts in the many drainages. Exploratory adits, usually less than a few tens of meters long, were

driven into the steep slopes, and mines were developed when it was apparent that a deposit of sufficient size to justify development had been discovered. The district has many exploration openings and many small, abandoned room-and-pillar mines. Because of the small size of the deposits in this area, successful mine development was most likely limited to 10% of the exploratory adits. In recent years, drilling, diamond core, reverse circulation, and standard air rotary techniques have been used to locate and develop new deposits. Initially, exploration is conducted along the narrow ridge crests with a series of widely spaced holes until a significant thickness of white microcrystalline silica is discovered. Additional holes are completed on a tightening, irregularly developed grid along the ridge and on one or more drill trails constructed on the flanks of the ridge. Holes are spaced approximately 30 m apart before stripping the overburden to provide enough confidence of the continuity and quality of the deposit. When there are quality concerns or when mine development is approaching the edge of a drill-defined deposit, the drilling grid may be tightened to ensure that there is no unnecessary stripping.

Today, all mining in the Illinois microcrystalline silica district is conducted in open-pit operations. Samples collected during exploration and mine development drilling are evaluated in Unimin Specialty Minerals' Elco Plant Laboratory. The samples are obtained from open-air rotary holes that are blown clean after each 0.6 m of drill advance. The samples are bagged and placed in a line at some short distance from the hole. The geologist determines the sample increments for laboratory testing, prepares the samples, completes the drill logs, and retains small samples of each increment in permanent plastic chip trays. Particular attention is given to noting the hardness and chert content as well as the presence of clay in each sample. The color of the material in the drill samples is logged as well, particularly for iron- or manganese-stained material. Each drill-hole site is surveyed using modern global positioning system (GPS) equipment. At the laboratory, the samples are dried, crushed, split, and pulverized. Data are collected and reported for the Hunter L, a, b color parameters, and also the GE brightness value is determined. This information is added to the deposit database, the geologic model is revised, and the mine plan is updated. Geologic cross sections guide the annual stripping program, and the operations staff in the mine make daily development decisions using the quality data portrayed on the cross sections.

Deposit development, mining, and transport of southern Illinois microcrystalline silica is a simple affair. Overburden is drilled and blasted and placed on stockpiles constructed around the deposit, or it is backfilled into nearby exhausted open-pit mines. When the white microcrystalline silica ore zone has been uncovered, a bulldozer rips the soft material and pushes it into stockpiles. The bulldozer operator is the primary grade-control person for the entire operation. He or she determines, through experience and discussions with the mine superintendent, which material should be considered as ore and which must be treated as waste because of color or chert content concerns. The ore-grade tripoli is loaded into over-the-road trucks and is transported by improved gravel and paved roads to the plant at Elco, a distance of 8 to 14.5 km, depending on the route selected.

MARKETS

Important industrial markets for tripoli products exist in the historical abrasives sector, and newer applications have been recognized and exploited for a wide range of microcrystalline silica products in the paint, rubber, plastics, and resins industries. Minor microcrystalline silica uses include caulking compounds, refractory bricks, and cements.

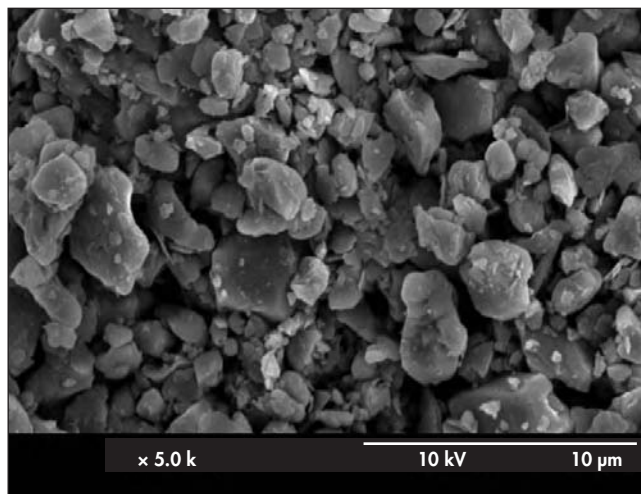


Figure 2. SEM photograph showing the textural features of Malvern Minerals' L-337 Novacite product. This material is not as finely ground as the tripoli in Figure 1 or Figure 3, and it does not tend to form grain aggregates of small clumps in the same way as other materials.

Tripoli continues to have unique and valuable uses as an abrasive agent. Polishing and buffing of metals and other surfaces requiring a cleanly scoured surface have relied on tripoli in the United States for more than 150 years. Tripoli's Mohs hardness value of 7 ensures that abrasion of most surfaces can be accomplished using a finely ground quartz compound. The extremely fine-grained and well-sorted nature of the finished products and, indeed, of some of the naturally occurring outcrop materials makes tripoli a preferred abrasive. It is used in toothpaste and dental office polishing compounds, industrial cleansers, and metal and jewelry polishing compounds. It also has a secure place in the automotive industry, which uses it in an assortment of buffing and polishing compounds in lacquer finishes.

Particle shape is very important in the abrasives industry. Pulverized or extremely finely ground (micronized) tripoli and microcrystalline silica products, unlike ground silica produced from whole-grained silica sand, do not contain quartz grains with very sharp edges. The product milled from tripoli or microcrystalline silica consists of minute clusters of very small quartz crystals in which projecting crystals present a milder abrasive action than that possible using ground whole-grained silica. Pulverizing and micronizing followed by air classifying are the major steps in producing the various particle-size grades needed by the different markets. The coarser grades for the buffing and polishing compound markets are made by air-flotation size classification following pulverizing. The finely ground grades used mainly in the functional fillers and coatings markets are micronized in attrition mills that can produce material with a 2 μm diameter.

American Tripoli of Seneca, Missouri, markets a complete line of metal finishing compounds that grade from its aggressive cutting agent, Once Ground, through its Double Ground, Air Float, Premium R-45, and C-45 products to its finest buffing compounds, R-30 and C-30. These products are used to cut and polish progressively softer metals and metal finishes. The R-30 and C-30 grades are used to polish aluminum, chromium, and brass. These grades also serve as a buffing agent for mirrored picture frames, small ornaments, display metals, coins, and other highly reflective metal surfaces.

Although most of American Tripoli's production is sold into the abrasives industry, some of their products, notably the R-15 and C-15 grades, are consumed in the plastics and polymer segments in molded epoxy compounds, where they impart higher impact resistance and higher flexural strength.

Malvern Minerals of Hot Springs, Arkansas, markets its Novacite tripoli products into the abrasives markets, citing their superior purity and a lower abrasive coefficient as compared to other naturally occurring silicas (Figure 2). Harbison-Walker Refractories Company Inc. produces crude and finished material in Hot Springs County for use in the manufacture of refractory bricks and shapes (Dolley 2002). Unimin Specialty Minerals sells virtually none of its products into the abrasives industry.

Paint formulations for exterior and interior enamels and latexes benefit from the use of microcrystalline silica in several ways. As a functional filler and extender, microcrystalline silica aids in the durability, flowability, leveling, and tint retention of paints. Particularly in enamels, it makes the painting process easier and improves the sheen of the finished surface. Because of microcrystalline silica's chemical inertness in most environments, its use extends the life of the end product and prevents chalking, which can shorten the life of calcium carbonate-filled paints. Nonreactive microcrystalline silica improves resistance to salt spray, and its durability is reflected in its improved weatherability compared to other paints. The producers of microcrystalline silica for paint fillers and extenders also point to its low oil absorption properties. This characteristic allows it to be loaded into the paint with additional pigment without seriously affecting the viscosity. Low oil absorption also makes it easier to disperse microcrystalline silica than some other pigments used in paints. The hardness of microcrystalline silica compared to other fillers such as talc, kaolin, or calcium carbonate is a clear improvement over softer and more reactive mineral fillers. The hardness of microcrystalline silica is not always a benefit, however. Its presence can cause increased wear on the sprayers used in applying highway paints, marine paints, floor paints, and other applications where a hard, durable, painted surface is desirable.

Unimin Specialty Minerals Inc., of Elco, Illinois, markets a line of Imsil grades as functional fillers and extenders to the paint, plastics, rubber, adhesives, and sealant industries. Imsil fillers range from the relatively coarse A-75 grade, which has a median particle size of 12 μm , a TAPPI brightness value of 82.0, and a surface area of 1.3 m^2/g , to the A-8 product (Figure 3), which has a median particle size of 2.1 μm , a TAPPI brightness value of 86.4, and a surface area of 2.0 m^2/g . Malvern Minerals Company also sells its three Novacite products, 325, 1250, and L-207A, into the functional fillers markets, citing an average particle size for their best grade of 35 μm and a high Hegman fineness value of 67, which ensures smooth and complete dispersion in oil- and water-based paint systems.

Microcrystalline silica is an important added ingredient in plastics, rubber, sealants, and adhesives manufacturing processes. Microcrystalline silica is much less expensive than the organic resins that are used in plastics. In electrical cable coverings and other specific applications where insulating properties are critical, the dielectric properties of quartz make microcrystalline silica a desirable filler. Microcrystalline silica acts as a white base for plastics, rubber, and many sealants and adhesives. It is opaque, allowing the material to accept pigments more effectively and to provide a good level of color saturation. Also important is the strength benefit that comes from using microcrystalline silica in a plastic formulation, because it increases the rigidity of the finished plastic. In rubber applications, microcrystalline silica is added as a nonreinforcing filler. Using microcrystalline silica in the manufacture of rubber

printing rollers improves their wear resistance. Microcrystalline silica is widely used in grouts, sealants, and high-performance epoxy cements. Up to 60 % of some epoxy compounds can be composed of this material.

REGULATORY AND ENVIRONMENTAL CONSIDERATIONS

The question of the effect of crystalline silica on human health has been one of the most important issues in the industrial minerals industry in recent years. Silicosis is the disease usually associated with exposure to crystalline silica dust; it is a debilitating, incurable, and sometimes fatal lung disease. It is also a preventable disease (NIOSH 2002). The U.S. agencies that regulate workplace exposure to respirable crystalline silica are the Occupational Safety and Health Administration (OSHA) and the Mine Safety and Health Administration (MSHA). The OSHA permissible exposure limit (PEL) and MSHA exposure limit for respirable quartz and tripoli, based on an 8-hr time-weighted average, is the fraction 10 mg/m^3 divided by the sum of the percentage of quartz or tripoli in the sample plus 2. If the respirable dust has a high percentage of quartz or tripoli, this is close to an occupational exposure limit of 0.1 mg/m^3 .

Since 1974, the U.S. National Institute of Occupational Safety and Health (NIOSH) has recommended a more stringent exposure limit of 0.05 mg/m^3 as a time-weighted average for up to a 10-hr workday over a 40-hr workweek. NIOSH had stated that its recommended exposure limit (REL) will remain at 0.05 mg/m^3 until improved sampling and analytical methods are developed to better measure exposure to respirable silica (NIOSH 2002). NIOSH also recommends that companies find acceptable substitute materials for crystalline silica where feasible, use appropriate respiratory protection when source controls cannot reduce the exposure below the recommended exposure limit, and make medical examinations available to exposed workers. The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a threshold limit value of 0.05 mg/m^3 for respirable quartz.

The microcrystalline silica industry and its customer base are well aware of the health risks posed to their workers. Some production facilities of microcrystalline silica are among industry leaders in the effort to reduce and eliminate this hazard in their workplaces.

Indeed, the silicosis health effects of silica exposure have long been recognized as problems for workers in the mining industry. Georgius Agricola (1499–1555), in his pioneering mining volumes *De Re Metallica*, published the year after his death, described diseases experienced by miners and the means to prevent them. Paracelsus (1493–1541), in his book on occupational medicine, published 15 years after his death, included a section on the lung diseases that afflict miners (Goldsmith 1994). The advent of the industrial revolution brought power tools to the workplace to improve worker productivity. These tools increased dust exposures in occupations such as knife grinding, mining and tunneling, metallurgy, flint grinding, pottery making, and sandblasting. Workers in many of these jobs developed severe respiratory ailments, and Edgar Collins, working in the early years of the twentieth century, demonstrated that silicosis was the lung disease of many dusty trades, and that it was caused by the inhalation of “free” or crystalline silica (Collins 1919). Much of modern society’s knowledge of the problem of silicosis stems from Collins’ work (Goldsmith 1994).

Research in recent decades has focused on other diseases that may be caused by crystalline silica exposure. The International Agency for Research on Cancer (IARC) concluded in 1997 that “[t]here is *sufficient evidence* in humans for the carcinogenicity of inhaled crystalline silica in the form of quartz or cristobalite

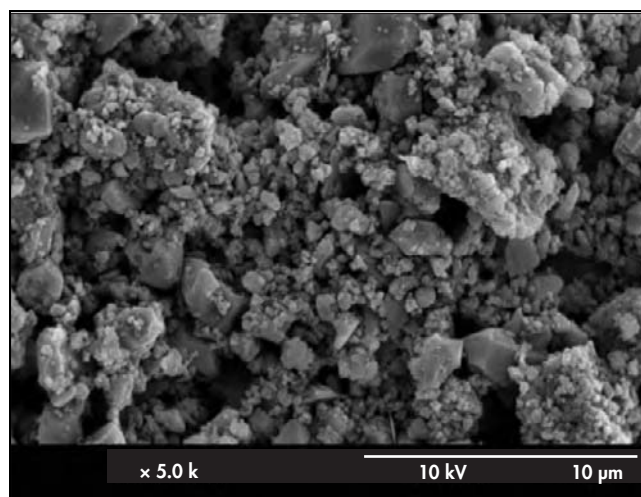


Figure 3. SEM photograph showing the textural aspects of Unimin Specialty Minerals’ A-8 lsil product. This is the most finely ground product from the plant in Elco, Illinois.

from occupational sources,” but noted that “carcinogenicity in humans was not detected in all industrial circumstances studied” and that “[c]arcinogenicity may be dependent on inherent characteristics of the crystalline silica or on external factors affecting its biological activity or distribution of its polymorphs” (IARC 1997, pp. 210–211). IARC classified “crystalline silica inhaled in the form of quartz or cristobalite from occupational sources” as “carcinogenic to humans” (Group 1) (IARC 1997, p. 211).

The 1997 conclusion by IARC followed a conclusion 10 years earlier that there is “*limited evidence* for the carcinogenicity of crystalline silica in humans” (IARC 1987b), which resulted in the classification in 1987 of crystalline silica in IARC’s Group 2A, which it terms “probably carcinogenic to humans” (IARC 1987a).

Also in 1997, the American Thoracic Society (ATS) found that “the available data support the conclusion that silicosis produces increased risk for bronchogenic carcinoma” (ATS 1997). However, the ATS noted that there was less information available concerning lung cancer risks among silicotics who had never smoked and for silica-exposed workers who did not have silicosis (ATS 1997).

The U.S. National Toxicology Program (NTP) considers crystalline silica (respirable size) to be a substance “known to be a human carcinogen” (NTP 2000).

NIOSH has also noted case reports published about autoimmune diseases or autoimmune-related diseases found in crystalline silica-exposed workers or in silicotics, as well as epidemiologic studies reporting statistically significant excesses in cases or deaths from autoimmune diseases or immunologic disorders (such as scleroderma, systemic lupus erythematosus, rheumatoid arthritis, and sarcoidosis), chronic renal disease, and subclinical renal changes in persons exposed to crystalline silica. Other adverse health effects have been reported as well (NIOSH 2002).

OSHA is engaged in a rulemaking proceeding to adopt a substance-specific rule covering crystalline silica exposure. OSHA submitted a conceptual version of the rule to the Small Business Administration in 2003 pursuant to the Small Business Regulatory Enforcement Fairness Act (OSHA 2003). MSHA has stated that it is considering several options to reduce miners’ exposure to crystalline silica (MSHA 2003).

In 2000, the U.S. Environmental Protection Agency (EPA) added silica (crystalline) to the list of substances that it proposed to study for addition to EPA's Integrated Risk Information System (IRIS) (EPA 2000). In 2004, EPA announced that it had removed silica (crystalline) from the list of substances to be added to IRIS because of limited EPA resources and lower overall priority (EPA 2004).

OUTLOOK AND FUTURE TRENDS

In the coming decade, all significant microcrystalline silica and tripoli production in the United States is expected to continue. Minor production in Spain and Russia has been noted, but nothing is known regarding any future activities. Exports from the United States to other industrialized countries will persist and perhaps increase slightly, especially with respect to the finest ground, highest value products that fill important market niches in the high-durability, high-strength, extended-life paint markets; the high-strength plastics markets; and other special applications functional fillers markets for rubber, sealants, and adhesives. Mining techniques will probably not change significantly in the near future because they are what might be considered commonly employed techniques for a variety of commodities. The introduction of open-pit mining in 1983 and the closing of the underground mine in the Illinois District represented a significant change in one district. It seems likely that the most significant changes in this industry over the next 10 years will be found in new developments in the processing of these commodities and perhaps the development of new specialized markets. Improved sophisticated processing techniques now used may allow production of even brighter and finer-sized products. Processes such as wet grinding, chemical leaching, and high-intensity magnetic separation could be used if the high end of the market justified these additional costs.

The future trend of tripoli and microcrystalline silica use is downward, in large part because of the stringent warnings against exposure in the workplace to crystalline silica dust in excess of the NIOSH-recommended exposure limit of 0.05 mg/m^3 . NIOSH is likely to reduce the REL as soon as reliable sampling and analytical methods are developed to better measure exposure levels below the REL. Other, less objectionable, finely ground abrasives and functional fillers will probably continue to substitute for tripoli and microcrystalline silica where possible. Competing minerals such as kaolin, talc, calcium carbonate, nepheline syenite, and mica are ever-present competitive challenges in the filler and extender markets.

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Vermiculite

James R. Hindman

INTRODUCTION

Vermiculite is the mineralogical name generally applied to the group of minerals commonly formed by the alteration of biotite and iron-bearing phlogopite. Vermiculite retains the micaceous form and sheet silicate atomic structure of the parent mica, but differs in that a change in the net charge of the silicate sheets results in the tightly held potassium atoms in the mica structure being replaced in whole, or in part, by other cations and their associated hydrate shells. In microscopic particles, vermiculite is differentiated from other clay minerals by a high silicon:aluminum (Si:Al) ratio of approximately 3:1, and a higher layer charge that results in a generally higher cation-exchange capacity. Commercial vermiculite, the vermiculite that is mined, beneficiated, and discussed in this chapter, is an important industrial mineral. Vermiculite possesses a number of important properties that include high aspect ratio particles in a range of sizes from less than 50 μm to more than 1 cm, a high ion-exchange capacity, directional intumescence, and an active crystal surface with catalytic properties.

Within the internal structure of vermiculite lie water molecules that, when rapidly heated to high temperature, transform into steam, causing the vermiculite particles to increase in volume. This process of thermal exfoliation produces a lightweight product that finds use in various construction products and in agricultural, horticultural, and other industrial applications. In exfoliated form, it has the low density and biological inertness of expanded perlite, while maintaining a chemically active surface. Most of the vermiculite mined worldwide is ultimately consumed in the thermally exfoliated form.

In addition, the cation-exchange potential of vermiculite and its layer-silicate structure are properties that can be used as the basis for numerous products, including intumescent coatings and gaskets and inorganic films, and for the treatment of nuclear and other toxic waste. When chemically and physically modified, it possesses some properties common to organoclays and synthetic compounds. In high-purity concentrates and manufactured products, these properties can be altered and optimized in applications to produce superior performance.

GEOLOGY Mineralogy

Thomas H. Webb first described vermiculite in 1824. He believed vermiculite to be a variety of talc and described its diagnostic property of thermal exfoliation thusly (Webb 1824, p. 55): "If subjected to

the flame of a blowpipe, or that of a common lamp, it expands and shoots out into a variety of fanciful forms, resembling most generally small *worms* having the *vermicular motion exact*." It is difficult to give a short and precise definition of vermiculite, but in the following discussion, vermiculite will refer to that industrial mineral commodity that has been formed by the alteration of biotite and iron-bearing phlogopite by groundwater, and macroscopic particles of which are deformed by exfoliation when heated rapidly to temperatures well above 374°C.

The vermiculite Webb studied was from a locality near Worcester, Massachusetts, but Brush (1866) later pointed out that vermiculite had been known for some time in Japan as a children's novelty. Because the techniques for mineral analysis used then were somewhat primitive compared to those routinely available today, and because the structure and crystal chemistry of the micas and related minerals were not widely understood, the early literature generated at least 20 "new" minerals that were nothing more than variations in the color and chemistry displayed by vermiculite. Trade names such as Dugarlite, Mandolite, Stro ng-Lite, and Zonolite are sometimes used to denote commercial vermiculite, thermally exfoliated vermiculite, and their related products.

Vermiculite particles resemble mica and vary in color from colorless through tan and green to black, depending on the chemical composition. Most physical and optical properties are close to those of biotite, with perfect basal cleavage, hardness between 1.5 and 2.5 on the Mohs scale, and specific gravity between 2.2 and 2.8. Fine-sized particles will feel talcose, especially when wet. For commercial vermiculite, however, the diagnostic test is thermal exfoliation.

Vermiculite can display a wide range of compositions, depending on the composition of the original mica and the change of chemistry during weathering and ion exchange. Table 1 gives chemical data for some commercial vermiculites and an average analysis based on a composite of 65 published analyses. Numerous analyses for vermiculite exist in the literature, and the analyses of vermiculites from commercial deposits fall within the range of values reflected in average analysis in the table. Many analyses separate the adsorbed water (H_2O^-) from crystalline water and water as hydroxyl (H_2O^+). The basis of separation of adsorbed water is generally considered to be 100°C, although molecules of water associated with cations within the vermiculite interlayer begin to be lost at 75°C and sometimes lower. Therefore, measured water content and loss on ignition are combined in the table as $\text{H}_2\text{O}^{\text{[total]}}$.

Table 1. Selected chemical analyses of vermiculite*

Analysis	A-65	V-1	V-2	V-3	V-4	V-5	V-6	V-7	V-8	V-9
Li ₂ O	0.03	NR†	NR	NR	NR	0.03	NR	NR	NR	NR
Na ₂ O	0.74	2.00	0.10	1.61	1.95	0.80	0.03	NR	0.34	0.40
K ₂ O	2.11	0.50	0.50	5.97	1.36	2.46	2.56	4.24	3.85	2.40
MgO	20.34	19.20	23.60	24.22	17.16	23.37	21.39	20.04	19.71	25.2
CaO	0.79	0.21	3.80	0.93	2.18	1.46	0.20	0.75	2.28	0.86
BaO	0.17	NR	0.20	NR	NR	NR	0.03	0.12	0.27	NR
MnO	0.23	0.18	NR	0.05	0.18	0.30	NR	0.07	0.14	0.05
FeO	1.58	NR	NR	1.54	0.48	1.17	3.56	NR	NR	NR
Al ₂ O ₃	13.86	14.50	10.20	12.68	14.23	12.08	10.01	17.36	12.67	12.4
Cr ₂ O ₃	0.33	NR	NR	NR	NR	NR	0.20	0.50	0.21	0.02
Fe ₂ O ₃	7.59	10.50	5.80	4.60	8.07	5.45	1.90	8.45	11.78	4.69
SiO ₂	36.94	36.50	45.10	41.20	37.67	39.37	43.05	38.66	35.99	37.7
TiO ₂	1.12	0.75	0.70	1.38	0.20	1.25	1.00	NR	1.60	0.92
H ₂ O ^[total]	15.41	15.30	10.20	5.82	15.71	11.20	15.70	8.71	9.24	14.30
Total	101.24	99.64	100.20	100.00	99.19	98.94	99.63	98.90	98.08	98.94

* Values are as presented in the referenced source.

† NR = not reported. It is assumed that the lack of a reported FeO value results from total iron determinations being calculated and reported as Fe₂O₃. Analytical data thought to be associated with contamination by other minerals (e.g., P₂O₅ and CO₂) are omitted.

NOTES:

A-65: Average of 65 analyses statistically selected from 116 published analyses of vermiculites from various international localities.

V-1: Munglinup, Western Australia; IMDEX Minerals, Jandakot, Australia.

V-2: Massape Mine, Piaui, Brazil; Eucatex Mineral Ltda., São Paulo, Brazil.

V-3: Qieganbulake, China (Ying and Hu 1988, p. 5).

V-4: Hafafit, Egypt (El Shazly et al. 1975, p. 95).

V-5: Phalabowra, Republic of South Africa; American Vermiculite Corp., Marietta, Georgia.

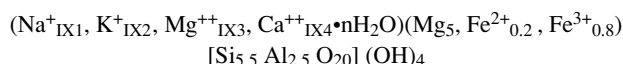
V-6: Kovdor, Russia (Justo et al. 1989, p. 512).

V-7: Enoree, South Carolina (Vermiculite Reference Manual, Zonolite Division, W.R. Grace & Company, Chicago, Illinois, p. E7).

V-8: Louisa, Virginia; Virginia Vermiculite Ltd., Louisa, Virginia.

V-9: Cavendish, Ontario; Regis Resources, Inc., Toronto, Ontario.

The average chemical component values calculated from 65 vermiculite analyses suggest a typical formula of



where the components in the first set of parentheses represent the ion-exchangeable layer, the components in the second set of parentheses compose the cations of the octahedral layer, and the components within the brackets constitute the tetrahedral layer. The actual amounts of Na⁺, K⁺, Mg⁺⁺, and/or Ca⁺⁺ in the interlayer (represented here as IX1 through IX4 for the mole contents of Na⁺, K⁺, Mg⁺⁺, and/or Ca⁺⁺, respectively) vary significantly in nature and can be easily manipulated in the laboratory by ion exchange. The total number of exchangeable cations in the interlayer is limited by the overall charge of the silicate sheets. The chemical composition of commercial vermiculite varies significantly from one mine to another, and significant variations in the chemistry of the ion-exchangeable layer can occur within a particular deposit. Generally speaking, calcium vermiculite and magnesium vermiculite are the predominate components of commercial vermiculite; potassium vermiculite also is a common component.

Many authors have investigated the crystal structure of vermiculite. The basic structure of the mineral is identical to talc and the micas: a 2:1 silicate sheet comprising two flat layers of silica and aluminum tetrahedra (the tetrahedral layers) that are joined together in a layer composed of apical oxygen atoms, and magnesium, iron, and hydroxyl molecules (the octahedral layer). Between the 2:1 sheets lies the ion-exchangeable layer. This layer differs in

thickness depending on the interlayer cation present and the arrangement of water molecules associated with it.

Interlayer water is an essential component of vermiculite. When a particle of vermiculite is rapidly heated, the interlayer water transforms into steam. The pressure of the steam forces the silicate layers apart from one another, deforming the particle from the normally flat plate into an elongated, concertina-like particle, which forms the basis of most commercial applications of this mineral. The increase in volume caused by the thermal exfoliation is normally in the range of 10 to 20 times, with typical exfoliated densities of 90 to 110 kg/m³.

The basal d-spacing of vermiculite obtained by x-ray diffraction (XRD) varies according to the composition of the ion-exchangeable layer. Mathieson and Walker (1954) detailed the arrangement of hydrated magnesium ions in 14 angstrom (Å) vermiculite. Other common basal d-spacings occur at 12 Å (i.e., barium, sodium, and strontium vermiculites) and 10 Å (i.e., potassium and ammonium vermiculites). Brindley and Brown (1980) and de la Calle and Suquet (1988) offer more detailed discussions of the crystal structures of vermiculite. These three common basal reflections represent cations with 6- and 8-fold coordinated water molecules (~14 Å), cations with water molecules in 3-fold planar coordination (~12 Å), and those structures where the exchangeable cations and water molecules lie in the hexagonal or ditrigonal cavities in the planar silicate sheet surface (10 Å). Stated another way, the 14-Å vermiculite structure has two layers of water molecules between the silicate sheets, the 12-Å vermiculite structure has a single layer of water molecules between the silicate sheets, and the

10-Å vermiculite has a single layer of water molecules embedded in the surface of the silicate sheets.

The hydrated interlayer cations are easily subject to ion exchange. Typical ion-exchange values for vermiculite concentrates are 50 to 150 meq per 100 g. If properly exfoliated, thermally exfoliated vermiculite will also have a high ion-exchange capacity that is diminished only 5% to 10% from the untreated material. The rate of ion exchange is relatively slow with potassium vermiculite, owing to the lack of interlayer separation.

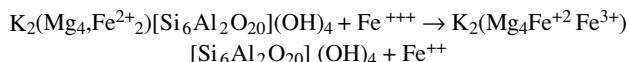
Two common misconceptions are found in much of the literature dealing with the crystal structure of vermiculite as revealed by powder XRD. Gruner (1934) used the term *hydrobiotite* to indicate regularly alternating layers of biotite and vermiculite. This mixed structure would produce a 12-Å basal reflection, which is common in commercial vermiculites. The 12-Å reflection, however, is relatively broad and does not shift after ion exchange as one would expect. For example, consider a vermiculite containing the normal sharp 14-Å reflection and the broad 12-Å reflection. After ion exchange with a sodium ion solution, the 14-Å will disappear but no 11-Å reflection is created as would be expected as a result of the alteration of 10 Å biotite and 12 Å Na-vermiculite. The broad 12-Å reflection may be caused by a combination of calcium, magnesium, or sodium ions in a single layer, and associated water molecules define the thickness of that layer.

The other common assumption in XRD studies is the assignment of the 10-Å reflection to the presence of biotite. Potassium vermiculite is a common component in commercial vermiculites and is indistinguishable from biotite using routine XRD techniques. Not all researchers are aware that potassium vermiculite does contain interlayer water. Water molecules fill structural vacancies caused by the leaching of excess potassium during vermiculitization of biotite. Many commercially desirable vermiculites will contain the 10-Å reflection in their XRD spectra, and this reflection may represent the hydrated potassium vermiculite as opposed to biotite. This misinterpretation of the XRD data may be a source of confusion in studies on the formation and ion-exchange characteristics of vermiculite.

Origin

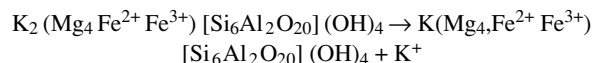
A number of studies indicate that vermiculite can be formed from a number of silicate minerals. Because the vermiculite that is mined and processed for industrial applications must produce salable concentrates of relatively large particles, however, the parent mineral is invariably an iron-bearing phlogopite or biotite. The well-known exception to this is the unique deposit at Llano, Texas, where iron-free phlogopite occurs in magne site, and the vermiculite thus formed upon weathering is a pure magnesium vermiculite variety widely used in crystallographic and geochemical studies.

The alteration of biotite into vermiculite takes place at near-surface conditions so that all known deposits are supergene in origin. Studies by Roy and Romo (1957) indicate that vermiculite will not form as a primary mineral and that it is not stable under hydrothermal conditions. The alteration of biotite into vermiculite appears to take place in two steps that can be illustrated using a hypothetical biotite and ferric iron in solution. First, the ferrous iron is oxidized within the octahedral layer:

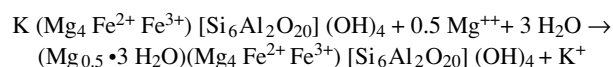


This process, unless accompanied by the loss of interlayer potassium, results in an imbalance of charge and an increased separation between the 2:1 silicate layers. The repeat distance of the crystal structure increases from the typical 10-Å value to approximately 11 Å.

The second step in vermiculite formation begins when the silicate layers of the mica are separated sufficiently to allow for ion exchange. The excess potassium content of the interlayer is taken into the groundwater according to



And finally the content of the remaining exchangeable-ion interlayer is altered to reflect the ionic content of the groundwater within the deposit, as in the case of magnesium vermiculite:



The transformation of biotite into vermiculite requires an increase in particle volume of 10% to 40%. Although not immediately obvious, this volume-increase requirement places restrictions on the size and placement of a vermiculite deposit. To form vermiculite, the alteration products of biotite must literally lift all of the overlying rock body. Unless the lithostatic pressure can be exceeded by the forces caused by the oxidation of iron within biotite and the subsequent ion exchange, no vermiculite formation can take place. This pressure has not been measured directly, although some related data are available (i.e., Norrish and Rausell-Colom 1963; Viani, Roth, and Low 1985). Empirical geological evidence suggests that the pressure will coincide with the 25- to 30-m maximum ore depth found in many deposits.

Distribution of Major Deposits

Vermiculite is currently being mined in at least nine countries. Figures 1 and 2 show those current sources, and known potential sources of commercial vermiculite in the United States and worldwide.

The first production of commercial vermiculite began in the United States in 1915 with the unsuccessful marketing of tung ash, the name given to vermiculite mined near Hecla, Colorado. Actually, vermiculite was inadvertently mined in the 1800s as a major accessory mineral in the corundum deposit in the Jenks mine in North Carolina (Cooke 1874).

The vermiculite mine started by the Zonolite Company at Libby, Montana, in 1921 was the first successful venture in the vermiculite industry. Until recently, the Libby deposit was the oldest producing vermiculite mine and had been developed and enlarged for almost 70 years. This property was closed in 1990, and that closure has had a major impact on the vermiculite industry, especially in the United States.

Vermiculite has been mined in other locations in the United States. Excellent summaries of statewide vermiculite deposits and mining have been prepared for Colorado (Bush 1951), North Carolina (Murdoch and Hunter 1946), Texas (Claybaugh and Barnes 1959), and Wyoming (Hagner 1944). Other discussions of vermiculite deposits in the United States include Bush and Sweeney (1968) on the Appalachian region and Bush (1976) for the entire country. With regard to individual deposits, doctoral dissertations have dealt with Libby (Boettcher 1966a) and with Enoree, South Carolina (Libby 1975).

Current production in the United States is restricted to mines in South Carolina and Virginia. Several mining operations are located in northwestern South Carolina. The two major producers—W.R. Grace & Company at Enoree and Carolina Vermiculite at Woodruff—account for most of the production in that state. A smaller operation, Palmetto Vermiculite, is in the same area and serves a smaller regional market.

The other major domestic vermiculite mine is near Louisa, Virginia, and is operated by Virginia Vermiculite. Virginia Vermiculite

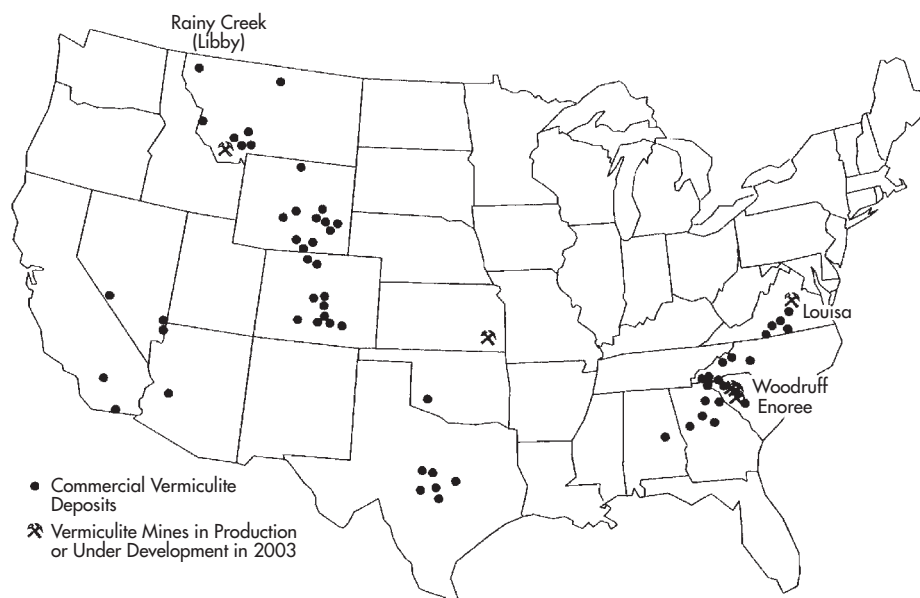


Figure 1. Major U.S. vermiculite mines and deposits

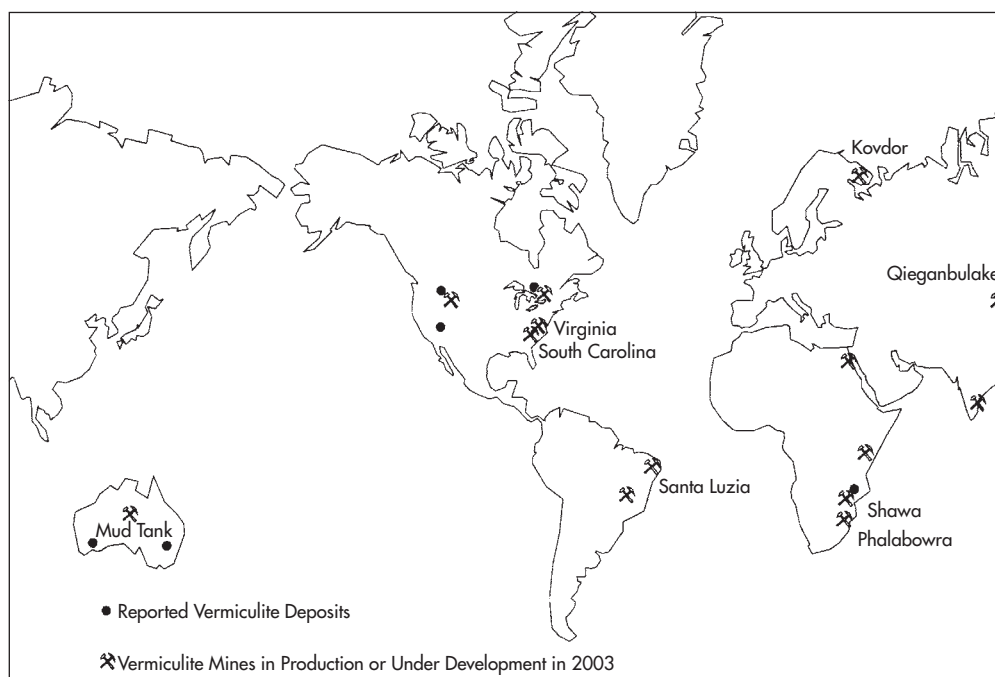


Figure 2. Major worldwide vermiculite mines and deposits

purchased Carolina Vermiculite in 1990, and the combined production capacity of the two operations is on par with the production capacity of the Grace plant at Enoree. Figure 1 shows the locations of known, major vermiculite deposits and current mining operations. Table 2 presents U.S. vermiculite production and trade data since 1980.

Vermiculite is also mined in Kansas, although the product is not considered commercial vermiculite because of its microscopic

particle size. Micro-Lite LLC operates a mine in Woodson County from which an altered lamproite with an appreciable phlogopite and vermiculite content provides a material useful in animal feed supplements.

The closure of the Libby operation left the western United States with no major domestic source of vermiculite. Several known deposits have been considered for development or reopening as mining operations. One small deposit at Elk Gulch near

Table 2. U.S. vermiculite production and trade data

Year	Production*	Exports†	Imports‡	Consumption§	Value** (Concentrates)	Value (Exfoliated)
1980	306,000	27,000	24,000	303,000	76.86	213.79
1981	290,000	28,000	24,000	286,000	90.26	235.75
1982	287,000	20,000	19,000	286,000	99.42	260.33
1983	256,000	17,000	22,000	261,000	106.32	256.88
1984	286,000	20,000	29,000	295,000	110.23	235.92
1985	285,000	17,830	32,000	299,170	113.74	204.66
1986	288,000	20,858	32,000	299,142	119.62	231.79
1987	275,000	21,599	29,000	286,878	120.42	238.84
1988	276,000	30,647	32,000	278,923	122.92	243.93
1989	249,000	41,961	45,893	255,875	122.26	250.20
1990	209,000	44,068	43,531	208,463	137.48	276.56
1991	180,000	45,840	52,163	206,323	165.41	283.00
1992	190,000	8,000	40,000	222,000	na††	328.00
1993	190,000	7,000	30,000	213,000	na	338.00
1994	177,000	7,000	30,000	200,000	na	335.00
1995	171,000	6,000	30,000	195,000	na	306.00
1996	170,000	8,000	48,000	210,000	na	334.00
1997	W‡‡	8,000	67,000	na	na	318.00
1998	150,000	11,000	68,000	207,000	na	313.00
1999	150,000	13,000	71,000	208,000	143	315.00
2000	150,000	5,000	59,000	204,000	143	322.00
2001	115,000	7,000	65,000	173,000	143	340.00
2002	110,000	10,000	56,000	156,000	143	390.00
2003	107,000	10,000	48,000	145,000	143	na

* Unless otherwise noted, all data from *Mineral Facts and Problems* and *Mineral Commodity Summaries*, USBM 1980–1995, USGS 1996–2003. Production data prior to 1985 restated as metric tons from USBM published data. Data for 2001–2003 are estimates (A. Bush, personal communication).

† Exported data 1980–1984, USBM; 1985–1989, Roskill and quoted sources; 1990–1991, U.S. Customs and other sources. Value for 1991 estimated from January–October totals. Values for 1992 onward are USBM and USGS data and represent exports to Canada only.

‡ Import data 1980–1988, USBM; 1989–1991, U.S. Customs and Port Import Export Reporting Service (PIERS). Value for 1991 estimated from January–October totals. Values from 1992 onward from USGS data.

§ Consumption calculated as Production + Imports – Exports.

** Values expressed as U.S. dollars per metric ton. All values from USBM and USGS published data except as noted. 1990–1991, average U.S. Customs values including vermiculite exported to Canada. Data for vermiculite include domestic and imported sources.

†† na = Data not available.

‡‡ W = Proprietary data, withheld by producers.

Dillon, Montana, has sporadically produced small tonnages of concentrate under different operators between 1990 and 2000. Deposits near Hamilton and Pony, Montana, near Encampment, Wyoming, and at Mica Peak in Clark County, Nevada, are periodically evaluated for their potential as new sources of vermiculite.

Within the last few years, two potential new sources of vermiculite in Ontario, Canada, have been under development. Regis Resources of Toronto recently began to ship vermiculite concentrates from a small mining operation near Buckhorn, in Carleton Place Township. The ore is found in altered red schist and gneiss associated with other Precambrian metamorphic rock types. The vermiculite ore is found in separate small zones over a relatively large area. The vermiculite from this deposit tends to have a low iron content, and the exfoliated product has a good bag yield and is often almost white.

Another vermiculite deposit in Ontario is located in Butler Township near North Bay. Some initial mining has been performed, and a small wet processing plant has been constructed at the site.

With the closure of the Libby mine and mill, the Republic of South Africa has become the leader in worldwide vermiculite pro-

duction, with production of 224,258 t in 2002 and 207,345 t in 2003. The Palabora Mining Company operates the mining operation at Phalaborwa, and copper is the primary product. The Phalaborwa deposit is also known as Loolekop and has been described in a number of papers such as Gevers (1949).

Other current vermiculite-producing countries include Australia, Brazil, China, Egypt, India, Japan, Kenya, Russia, and Zimbabwe. Recent data (Potter 2004) suggest that the top three producing countries are South Africa (46%), the United States (21%), and China (10%). Moeller (2004) suggests that worldwide vermiculite production in 2003 was approximately 425,400 t. Figure 2 shows the worldwide location of known, major vermiculite deposits and current mining operations. Table 3 summarizes worldwide vermiculite production and trade data since 1980.

TECHNOLOGY Exploration

The exploration for vermiculite deposits is straightforward because they are the products of surface and near-surface weathering. Because one criterion of commercial vermiculite is large grain size,

Table 3. Worldwide production and trade data for vermiculite*

	Argentina	Australia	Brazil	Canada	China	Egypt	India	Japan	Kenya	Malawi	Mexico	Russia	South Africa	Tanzania	Uganda	United States	Zimbabwe	Worldwide Total
1980	9,906		8,000			726	3,428	17,237	2,557				181,794	18		306,000		529,666
1981	3,227		14,307			726	3,624	17,237	2,631				175,125	18		290,000		506,895
1982	3,354		14,059			280	2,068	17,237	1,556		522		180,992			287,000		507,067
1983	3,933		9,877			300	2,411	17,237	1,179		399		139,421			256,000		430,758
1984	4,451		9,157			327	1,953	17,237	872		505		164,421			286,000		484,922
1985	4,887		9,291			488	1,805	17,237	1,515		430		177,598			285,000		498,251
1986	5,207		13,138			495	6,681	15,422	2,544		454		193,973			288,000		525,914
1987	4,990		13,608			499	3,992	15,422	2,540		454		185,838			275,000		502,342
1988													203,101			276,000		479,101
1989													195,525			249,000		444,525
1990	3,330		23,300			28	1,770	15,000	2,660		132	95,000	217,738			209,000	1,000	568,958
1991	3,950		11,000			519	1,770	15,000	2,600		117	85,000	197,768			180,000	2,320	500,044
1992	4,450		14,000			500	1,610	15,000	2,600		125	60,000	163,894			190,000	4,300	456,479
1993	4,500		1,400			500	1,410	15,000	2,600		134	50,000	161,501			190,000	5,030	432,075
1994	3,000		14,000			500	1,500	15,000	2,600		300	40,000	216,196			177,000	8,180	478,276
1995	44	2,500	18,806			483	1,696	15,000	457		225		211,965			171,000	13,742	435,918
1996	40	2,500	21,999			447	2,405	15,000	734		350		190,364			170,000	10,249	414,088
1997	822	5,000	23,000			447	4,405	15,000	1,418		295		207,070			160,000†	14,841	432,298
1998	903	10,000	24,300			12,376	4,080	15,000	353			25,000	207,337			150,000	14,804	464,153
1999	2,800	12,000	23,400		40,000	12,000	4,000	15,000	164			25,000	208,603			150,000	13,898	506,865
2000	2,800	12,000	24,074		40,000	12,000	4,200	15,000	124			25,000	208,422			150,000	18,935	512,555
2001	1,450	12,000	21,464		40,000	12,000	4,300	15,000	125	1		25,000	166,078		220	115,000	11,632	309,270
2002	1,232	12,000	21,500		50,000	12,000	4,300	15,000	100	100		25,000	224,258		664	110,000	23,803	389,957
2003													207,345		1,724	107,000		

* All data from *Minerals Yearbook*, USBM and USGS, except for South Africa production, which is from Palabora Mining annual reports. Uganda production data for 2001–2003 from the Uganda Geological Survey and Mines Department. Blanks in table indicate no data available for those years.

† Production for United States in 1997 assumed here to be average of reported 1996 and 1998 values.

exploration is directed toward geologic structures that might contain large amounts of large biotite crystals. The most common structures are ultramafic intrusives such as coarse-grained pyroxenites and metamorphic bodies containing biotite schists and gneisses.

Good vermiculite ore is friable and easily broken with a standard prospector's hammer. A small propane torch is useful for field identification purposes. The basic criterion for vermiculite ore is that the individual particles can be seen with the unaided eye and that they will exfoliate when subjected to high heat. An average content of from 20% to 35% vermiculite in the ore will produce mill feed that is easily processed with current technologies. Higher-grade feeds may allow for a smaller mill design and operating costs, whereas lower-grade ores can be processed if the quality of the concentrates obtained is acceptable. The grade, particle-size distribution, and general quality of vermiculite within an ore body may vary widely, and the larger mining operations blend ore to provide a consistent feed to the beneficiation plant. The amount of vermiculite in particle sizes less than 0.25 mm or that will pass through a 65-mesh Tyler screen are not generally included in the valuation of an ore deposit because there is no significant market for this material and it is intentionally rejected during beneficiation.

Bush (1976) classifies vermiculite into three classes. The Type 1 deposits are formed within large ultramafic intrusive masses such as pyroxenite plutons, are cut by syenite or alkalic granite, and are cut by carbonatitic rocks and pegmatites. The deposits at Libby, Montana, and Phalaborwa, Republic of South Africa, are Type 1. The rock masses in Type 1 deposits are often zoned. Type 2 deposits are formed in association with smaller ultramafic intrusive masses such as dunite and peridotite and unzoned pyroxenite. The deposits in North Carolina are of this type. The Type 3 deposits are formed from metamorphic rocks such as biotite schists and amphibole schists. The deposits at Enoree, South Carolina, and Elk Gulch, Montana, are Type 3, as are most of the deposits in Colorado, Nevada, Texas, and Wyoming.

Other classification schemes for vermiculite have been proposed. The classification of Borovikov (1962) comprises four groups: group 1—deposits in ultrabasic and alkaline rock complexes; group 2—deposits in altered carbonate rock complexes; group 3—vermiculite occurrences in reaction zones of pegmatites, talc, corundum, asbestos, and other deposits, and also in metasomatic veins in serpentines; and group 4—deposits and occurrences of vermiculite in micaceous gneisses and other metamorphic rocks. The major deposits at Kovdor and Buldym in Russia are group 1 deposits.

L'vova (1974) gives a detailed discussion of vermiculite deposits worldwide. Varley (1952) describes most of the known vermiculite deposits and discusses the technical and economic aspects of commercial vermiculite, giving information that is still applicable half a century later.

Mining and Beneficiation

The mining and milling of vermiculite depend on a number of considerations not associated with other mineral commodities. Unlike most other ores, the value of a vermiculite ore depends on the distribution and efficient recovery of relatively large particles. A vermiculite ore will normally contain vermiculite, partially altered mica, unaltered mica, and associated gangue minerals.

In the very early years of the industry, the ore bodies were selectively mined (high graded) and the sized ore was the final product of beneficiation. As these areas of relatively pure vermiculite were depleted, and the demand for coarse-sized products

increased, mills were designed to beneficiate the ore. Although high-grade areas within a particular deposit may still be encountered, modern milling techniques require feeds more consistent with the overall character of the ore body.

Vermiculite is normally mined using open-pit methods. There have been reported instances of underground mining, such as at the Quaintance deposit in Jackson County, Colorado (Goldstein 1946), but these operations were on a small scale that would not be economically feasible in today's industry.

Modern vermiculite mines are invariably developed by excavating the deposit with conventional equipment, including graders, shovels, loaders, and trucks. Drilling and blasting may be necessary in areas where dikes, sills, and other hard bodies of rock occur within the ore body. When the mill is at the mine site, large off-highway trucks transfer the ore to the mill. Some operations such as at Enoree, South Carolina, and Louisa, Virginia, use smaller capacity trucks operating on highways and improved roads to bring ore from deposits that are some distance from the mill site. In either case, the ore is taken to an area near the mill where the larger pieces of waste rock are removed and the ore is blended and stockpiled. Blending can be accomplished by a number of methods, ranging from spreading the ore with a bulldozer to using a water monitor to wash the ore from the stockpile into the mill.

Beneficiation techniques used with vermiculite take advantage of one or more properties of the mineral. These properties include shape, density, chemistry, and resistance to comminution. Some of these properties may be applicable to both wet and dry processes, but most mills do not beneficiate with both wet and dry processes.

Figure 3 is a generalized flow diagram for a dry beneficiation mill. Typically, ore processed in a dry mill requires some drying before sizing. Air classification is the normal beneficiation process in a dry mill and separation is effected by winnowing and other techniques such as air tabling. Electrostatic and high-intensity magnetic techniques may be effective in some instances, as are morphology separations using roll and slot screening.

Separating the feed into narrow size ranges that correspond to the finished concentrates assists the selectivity of air classification. Comminution primarily reduces the size of gangue minerals for removal during recycling through the air separators. In many ores, major gangue minerals are friable or possess distinct cleavage. In these cases, the vermiculite particles may pass through impact or roll crushers relatively unaffected, and the bulk of the gangue particles are reduced to sizes that are easily removed by air separators or by screening during the recycle process.

Wet beneficiation of vermiculite generally falls into two categories: froth flotation for fine particle sizes below 1 mm and beneficiation techniques based on morphology for larger particles. Because many vermiculite ores contain major amounts of dense gangue minerals, processing steps using heavy-media separation, jigs, spirals, and shaking tables can be effectively used. Simple hydroclassification may also be effective in treating fine-sized ores, and flotation circuits can be improved and possibly replaced by hydrocyclones, hydraulic classifiers, and teeter chambers in some instances.

Figure 4 shows a hypothetical wet processing circuit. Processing of fine-sized material is straightforward, and most common flotation cells and tables are effective. Processing larger particle sizes is more difficult, and most processes take advantage of the tendency of the vermiculite plates to adhere to or travel along a smooth surface. Moving water films on plates and other flat surfaces can sometimes be used with excellent selectivity. Vaplon, Erickson, and Young (1978) claim wet-roll screening to be effective in processing large particles of vermiculite. This is the separation device shown in Figure 4 as an example of beneficiation by shape.

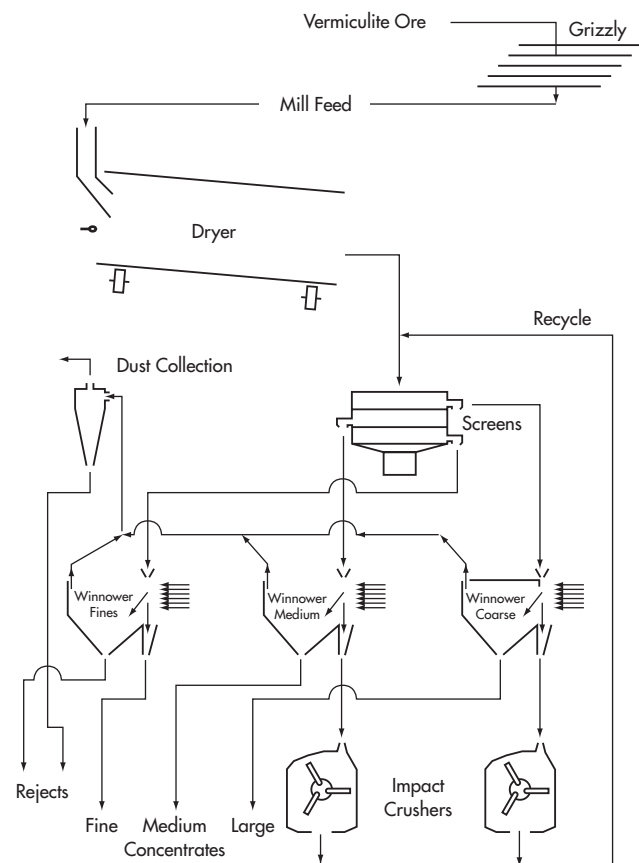


Figure 3. Processing circuit for the dry beneficiation of vermiculite ore

Vermiculite concentrates are marketed with specified particle-size distributions. The beneficiation circuitry in dry-processing plants may produce the finished product sizes without further treatment. In wet-processing plants, drying the combined mill concentrates produces the mill product. In this case, the dried concentrate is processed into the sized products in an additional screening facility.

Processing

Most vermiculite is consumed in the thermally exfoliated form. Usually, unexfoliated vermiculite concentrate, weighing 640 to 1,120 kg/m³, is shipped in 100-t hopper railcars from the mills to exfoliating plants throughout the United States and Canada. In recent years, there has been a growing trend to distribute vermiculite in smaller ton truck shipments of 10 to 20 t from centrally located distribution centers. This is especially true for vermiculite imported from China and South Africa.

In the United States, most exfoliation takes place in vertical furnaces in which the sized vermiculite concentrate falls through a hot zone produced by gas or oil burners. Exfoliation begins during the brief residence time in this zone, at 900°C or hotter, and continues during accumulation in a hopper at the base of the furnace. The temperature and residence time in the hot zone determine density and appearance of the exfoliated vermiculite and the oxidative or reductive nature of the burner flame.

Another type of furnace used to exfoliate vermiculite is a rotary drum furnace. This type of furnace is commonly used out-

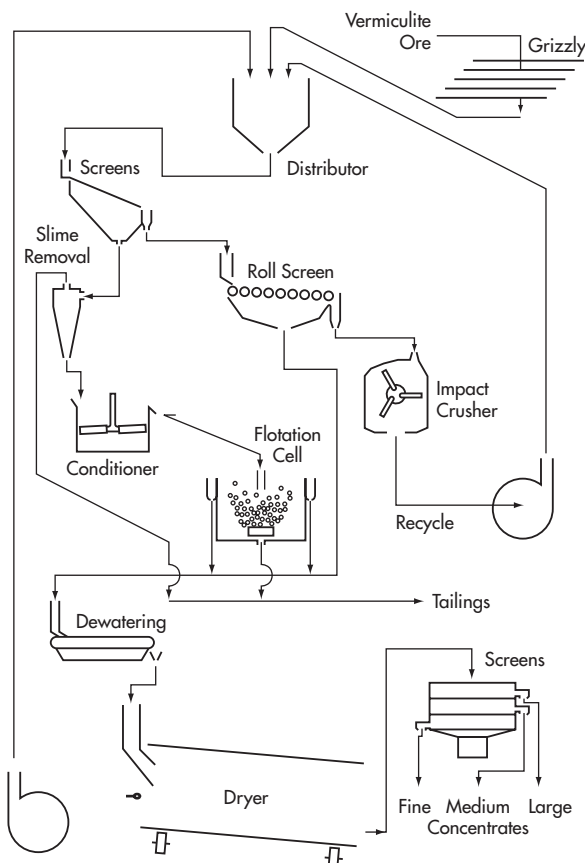


Figure 4. Processing circuit for the wet beneficiation of vermiculite ore

side North America. The sizing and design of a rotary furnace used to exfoliate vermiculite are not necessarily appropriate for the thermal expansion of perlite, and one should not assume that any furnace will process vermiculite and perlite equally well.

Other furnace types have been used to exfoliate vermiculite, and the Torbed design seems to be effective with some concentrates that require higher temperatures or longer residence times. The Torbed furnace treats the vermiculite as a rotating fluid bed. Reports of good results in processing vermiculite in Torbed furnaces have been made.

After the vermiculite has been exfoliated, an air separator removes the nonexfoliating gangue material. Purified product is then packaged in 0.1-m³ (4-ft³) paper bags for shipment. In larger plants, the exfoliated vermiculite may be ground into powder or mixed with other materials to produce horticultural blends and industrial compositions. Some exfoliation plants may also expand perlite. Table 4 lists vermiculite exfoliation plants known to be in operation during 2003.

Specifications and Testing

Vermiculite concentrates are invariably screened into various size ranges before shipment from the mill and further processing. In the United States, screening results in finished products with a mean particle diameter either one-half or double that of coarser and finer grades, respectively. Nominal top and bottom screen sizes used for various grades are 6.30 to 3.35 mm (3 and 6 mesh Tyler) for grade

Table 4. North American exfoliation plants in operation in 2003

Company	City	State or Province
United States		
Grace Construction Products	Phoenix	Arizona
Thermo-O-Rock West, Inc.	Chandler	Arizona
Sun Gro Horticulture Canada Ltd.	Pine Bluff	Arkansas
Micronized Ultra Tech Vermiculite	Richmond	California
Grace Construction Products	Pompano Beach	Florida
Verlite Co.	Tampa	Florida
Thermal Ceramics Inc.	Girard	Illinois
Whitmore Co., Inc.	Lawrence	Massachusetts
Isolatek International	Stanhope	New Jersey
Schundler Company	Metuchen	New Jersey
Southwest Vermiculite Co., Inc.	Albuquerque	New Mexico
P.V.P. Industries	North Bloomfield	Ohio
J.P. Austin Associates, Inc.	Beaver Falls	Pennsylvania
Thermo-O-Rock East, Inc.	Eagle	Pennsylvania
Vermiculite Industrial Corp.	Pittsburgh	Pennsylvania
Grace Construction Products	Woodruff	South Carolina
Palmetto Vermiculite Co., Inc.	Woodruff	South Carolina
The Scotts Company	North Charleston	South Carolina
Mandoval Vermiculite Products	Houston	Texas
Vermiculite Products, Inc.	Houston	Texas
Canada		
Grace Construction Products	Edmonton	Alberta
Grace Construction Products	Vancouver	British Columbia
Grace Construction Products	Winnipeg	Manitoba
A/D Fire Protection Systems	Scarborough	Ontario
Grace Construction Products	Ajax	Ontario
Pargro	Caledonia	Ontario
Normiska Corporation	Lachine	Quebec
Perlite Canada	Montreal	Quebec
Premier Horticulture	Riviere du Loop	Quebec

number 1; 3.35 to 1.7 mm (6 and 10 mesh Tyler) for grade number 2; 1.7 to 0.85 mm (10 and 20 mesh Tyler) for grade number 3, etc. Imported concentrates are similarly sized, except on a metric scale. Approximate top and bottom sizes for these concentrates are 8.0 to 4.0 mm (2.5 mesh to 5 mesh Tyler) for grade large; 4.0 to 2.0 mm (5 to 9 mesh Tyler) for grade medium; 2.0 to 1.0 mm (9 to 16 mesh Tyler) for grade fine, etc. The actual particle-size distributions in vermiculite concentrates from a particular processing plant may vary because of changes in the character of the ore being processed or to match market demand. There is normally no issue involved with substitution of a metric-sized product for a similarly sized American product. For a vermiculite concentrate of equal grade and quality, metric sizing will produce a slightly larger average particle size, thus a slightly better bag yield.

Ores and concentrates are normally analyzed for both grade and particle-size distributions. The dried sample is screened into various size fractions using sieves and a mechanical shaking device. In the United States, this is typically a Ro-Tap and a stack of U.S. or Tyler screens. Each screen fraction is weighed and then exfoliated in a furnace at 800° to 950°C. After cooling, the samples are again weighed and water flotation separates the exfoliated vermiculite from the gangue material. The remaining gangue is dried and weighed. The vermiculite concentrate is then calculated by simple difference or, if

the vermiculite has been well characterized, using a formula that accounts for excess moisture or overdrying of the sample.

Because of the cost of mining and beneficiation, and the cost of transportation of the finished concentrate, mining and producing high-grade ores and products is preferred. Although lower grades can be tolerated in some cases, ore feed grades are normally in the range of 20% to 35% vermiculite. Very high grade ores are sometimes encountered that contain more than 80% vermiculite.

An average grade of 90% is common for finished concentrates, and some concentrates occasionally approach 99% vermiculite. The concentrates also have specifications for the relative performance of the material during thermal exfoliation. This can be measured from samples of concentrate by laboratory exfoliation in specially designed furnaces that simulate the performance of commercial exfoliating plants.

Quality control of the exfoliated vermiculite is routinely maintained by either weighing the packaged product as 0.1-m³ or 4-ft³ bags (bag weight) or by counting the number of bags produced from known amounts of concentrate (bag yield).

USES

Vermiculite finds use in a number of diverse applications, of which a representative few are discussed here. Vermiculite is used in products and applications in three primary forms: untreated concentrate, thermally exfoliated, and the ground products of chemical or thermal exfoliation. Conventional uses for thermally exfoliated vermiculite include horticultural products such as growth media, construction products such as lightweight aggregates, high-temperature insulation, and as a primary component in cementitious coatings.

Cementitious mixtures of thermally exfoliated vermiculite and binding agents, such as gypsum plaster, have been important products. Monokote, a product marketed by W.R. Grace & Company, is applied to structural steel members in commercial buildings (Bragg and Rothfelder 1973) and has consumed major amounts of domestic vermiculite production.

Vermiculite is used in building boards of various types. Fine-sized, untreated vermiculite concentrates are included in the preparation of fire-resistant plaster board (Green and Sundberg 1971). Thermally exfoliated vermiculite can be mixed with appropriate binders and pressed into boards and other shapes (Tomandl 2002). Pressed vermiculite board could be used as a replacement for gypsum plaster board in many applications, but its primary use is for high-performance fire stops and protective enclosures.

Because of its high absorbency and chemical inertness, thermally exfoliated vermiculite has been used in industrial applications for many years. One product consists of long fabric tubes or socks filled with exfoliated vermiculite. These tubes are marketed as *pigs* by the New Pig Corporation and are distributed in the United States and exported worldwide. This product is used primarily to contain oil and similar liquids.

Ground thermally exfoliated vermiculite is produced by two domestic vermiculite companies and is also imported from the Republic of South Africa. The major use of this material is in friction materials such as a replacement for asbestos in brake linings. Ground vermiculite is also slurried with clay minerals for refractory mold release and other coatings. Ground exfoliated vermiculite is used in various refractory board products.

Dispersions of ground chemically exfoliated vermiculite are produced and marketed for various coating and film-forming applications. George F. Walker developed the first technology of vermiculite dispersions at the Commonwealth Scientific and Industrial Research Organization (CSIRO) in Australia in the 1960s. The

preparation and use of vermiculite dispersions have been the topic of a series of patents by a number of individuals, beginning with Walker (1967). Imperial Chemical Industries PLC (ICI) has done further research on preparing and using vermiculite dispersions, and product applications have been developed for increasing the thermal stability of glass cloth, flexible films, and plastic fillers. Armstrong World Industries and Hercules Incorporated have also done similar research.

W.R. Grace & Company is currently the major supplier of vermiculite dispersions in the United States, having acquired many of the patented applications and technologies of ICI. Grace markets vermiculite dispersions as Microlite, and Firespray International Ltd. manufactures and markets vermiculite dispersions as Aqualite in England.

The temperature at which vermiculite begins to undergo thermal exfoliation varies by composition of the ion-exchangeable layer. Langer and Marlor (1981) took advantage of this phenomenon to prepare intumescent gasketing material using low-temperature exfoliating NH_4^+ vermiculite. This gasketing material is used extensively in wraparound mats to cushion catalytic converter assemblies in automotive applications. Minnesota Mining and Manufacturing and the Unifrax Corporation Intumescent currently manufacture seals.

Untreated vermiculite concentrates are also used in some intumescent gasket applications and to reduce slag buildup on boiler tubes, primarily in coal-fired electric utilities (Engstrom and Bain 1983). Dearborn Chemical Company markets vermiculite used in this application as Firemate.

Although the immediate market effects of new domestic and imported sources of vermiculite are not clear, the entry of new companies into the industry should produce new opportunities for growth. Vermiculite dispersions constitute only one new area. One should expect that vermiculite, in all of its forms, will continue to find application in detoxification of water and soil, nuclear waste containment and removal, and industrial spill containment and cleanup.

ECONOMIC FACTORS

Many of the end uses of vermiculite are associated with construction and various industrial uses. Until the early 1990s, the consumption of vermiculite tracked the national economy to some extent, and the amount of vermiculite produced and consumed in the United States generally increased over a period of close to 70 years. The closure of the Libby operation in 1990 marked the end of this era of continued growth.

It is difficult to do a detailed analysis of the vermiculite market using production and trade data because most vermiculite companies treat all business data as proprietary. The U.S. Geological Survey (USGS), however, has been collecting and summarizing production and trade since 1996; before 1996 the U.S. Bureau of Mines (USBM) collected the data. It is generally acknowledged that the data from USGS and USBM are the most accurate data available for the U.S. vermiculite industry. However excellent the data may be for determining trends and qualitative evaluations, one should use caution when attempting quantitative economic analyses for several reasons. First, the USGS and USBM data have been obtained primarily from a voluntary annual survey. Response to the survey is not legally required, nor is accuracy enforceable. Second, the value-added aspect of vermiculite products may go well beyond the listed valuations of the thermally exfoliated vermiculite, such as would be the case with vermiculite dispersions.

Other sources of data and general industry reviews are available, including the annual reviews published by USGS (<http://minerals.usgs.gov/minerals/pubs/commodity/vermiculite>) and *Mining*

Engineering, the most recent of which have already been mentioned. The periodic reviews of the worldwide vermiculite industry published by Roskill Information Services (<http://www.roskill.co.uk>) are highly recommended. The Vermiculite Association (<http://www.vermiculite.org>) is an international industry organization now headquartered in London. Founded in 1948, the membership is drawn from vermiculite mining companies, exfoliation plant operators, and other industry professionals involved in the manufacture of vermiculite-based products.

The market price of vermiculite concentrates varies with particle size, with the larger-sized products commanding higher prices relative to the more abundant finer sizes. The Libby closure has eliminated the only major source of coarse-sized concentrates in the United States, and since the end of 1991 essentially all +2-mm vermiculite consumed in North America has been imported from South Africa and China, with minor amounts coming from Australia, Brazil, and Zimbabwe.

Typical market prices for domestic vermiculite concentrates currently range from \$60 to \$170/t, depending on size and grade. Prices for imported vermiculite concentrates range from \$12.7 to \$240/t, free on board (f.o.b.) Gulf Coast Port (Moeller 2004).

Vermiculite became an important industrial mineral because of uses developed for its thermally exfoliated products. Although there are significant current and developing markets for nonexfoliated and ion-exchanged vermiculite concentrates, at least 90% of commercial vermiculite is marketed after thermal exfoliation. It is not surprising, therefore, that the basic unit of vermiculite trade after leaving the mine and mill is bags, the major description of quality is bag yield, and the profitability of a processing plant is keyed to the cost per bag. The cost per bag of exfoliated vermiculite is a combination of the price of vermiculite concentrate at the mine, plus the total cost of transportation to the exfoliation plant, plus the cost of exfoliation, packaging, and distribution. The value is calculated based on the number of 0.1-m³ or 4-ft³ bags of exfoliated vermiculite obtained from the total amount of concentrate processed, including the gangue minerals (also known as grit or rock). It is not uncommon for the cost of transportation to approach 50% of the cost per bag.

The bag yield (i. e., quality) of vermiculite concentrates depends on several variables, including the grade of the concentrate and the size distribution of the vermiculite particles. Although the actual bag yield depends on the type of furnace used and the operating conditions, the amount of thermal exfoliation of a vermiculite concentrate can be measured by various laboratory techniques. The average value for all exfoliated vermiculite produced in the United States is approximately \$390/t, according to recent USGS estimates.

HEALTH ISSUES

There are no health issues reported to exist as a result of normal handling and general exposure to vermiculite. Hessel and Sluis-Cremer (1989), Addison (1995), and Chatfield (2001) discuss the relative safety of vermiculite. Although not attributed to vermiculite, one widely reported situation is linked to the asbestiform amphibole minerals found in the Rainy Creek vermiculite ore body near Libby, Montana. The health issues associated with some former workers at the former Zonolite mine and mill are complex and beyond the scope of this chapter.

INDUSTRY TRENDS

Perhaps a good indication of current trends in the vermiculite industry is the development of new products and applications for vermiculite. In 2004, there were 23 pending U.S. patent applications dealing directly with vermiculite. Of those 23 patent applications, roughly

half deal with products or uses for ~ 1 mm product sizes including vermiculite dispersions. The use of vermiculite in sprayable cementitious fireproofing products in the United States decreased in the 1990s because of W.R. Grace's introduction of MK-6 (containing shredded polystyrene) to replace MK-5 (containing exfoliated vermiculite). In recent years, other products with the same general composition and performance as the widely used MK-5 became readily available from other sources. For many years, Palabora America Ltd. (a subsidiary of the Palabora Mining Company, formerly known as American Vermiculite Company) has been the sole source of South African concentrates in the United States, and Mandoval (a former subsidiary of Palabora) has distributed the material in Europe. Mandoval produced fireproofing and related products at a plant in Texas until 1998. Currently, cementitious fireproofing products containing vermiculite are manufactured by Isolotek International as CAFCO Fire Protection products and by Southwest Vermiculite Co., Inc., as Type 5GP.

New products for waste treatment and disposal may create significant new markets for vermiculite. Major tests at an electric power plant in Ohio began in 1992 to evaluate the effectiveness of thermally exfoliated vermiculite coated with magnesium compounds to treat flue gases. Initial test work indicated significant reductions of sulfur and nitrogen gas emissions (Nelson 1988), and success of this technology on a large scale could foreshadow a significant increase in demand for the mineral. More recently, Lovell, Turchi, and Brokerick (2004) used ion-exchanged vermiculite to remove mercury from flue gas.

Vermiculite in both untreated and thermally exfoliated forms has catalytic properties. It is expected that continued research will find uses for vermiculite of both forms, and vermiculite modified for use in organic and inorganic chemical treatment, nuclear storage, water purification, and toxic waste treatment.

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Wollastonite

Sara M. Robinson, Ken Santini, and Jay Moroney

INTRODUCTION

Wollastonite is named after W. H. Wollaston (1766–1828), an English chemist and mineralogist. It is a calcium metasilicate with the chemical formula CaSiO_3 . Wollastonite is the only naturally occurring, nonmetallic, white mineral that is acicular (needlelike) in crystal habit. This crystal habit and the mineral's chemistry are the main reasons for wollastonite's rise in commercial use, which began in the 1970s and has continued to the present. As a nontoxic partial substitute for short-fiber asbestos, wollastonite became sought after in many polymer systems where mechanical strength and heat stability are needed. The end uses range from friction brake materials to fire-resistant asbestos board to ceramic tile to industrial coatings. Exterior automotive parts and under-the-hood applications have benefited from the use of high-aspect-ratio grades of wollastonite.

Until recently, the United States was the leading producer of wollastonite. In the last few years, however, China and India have emerged as major producers. In 2005, China and India were ranked the number one and two largest producers in the world, respectively. In Europe, another producer and major supplier, Partek, exited the business, and in 2005 sold only small amounts to a select customer base.

GEOLOGY

Mineralogy, and Physical and Chemical Properties

Wollastonite, a member of the pyroxenoid mineral group, has the theoretical composition of 48.3% CaO and 51.7% SiO_2 . Iron, manganese, magnesium, or strontium may substitute for some of the calcium. Associated minerals include andradite, grossular, diopside, calcite, quartz, tremolite, epidote, apatite, sphene, and plagioclase feldspar. Wollastonite is primarily chemically inert; however, it can be decomposed in hydrochloric acid as well as other strong inorganic acids. Organic acids, such as acetic acid, have little or no effect. In commercial applications, wollastonite has demonstrated effective resistance to the actions of organic solvents, including oxygenated versions.

Some wollastonite will fluoresce under shortwave or long-wave ultraviolet light, or both, with colors ranging from pink–orange to yellow–orange and, more rarely, bluish green. Wollastonite may show phosphorescence.

Because of its unique cleavage properties, wollastonite breaks down during crushing and grinding into lathlike or needle-shaped

particles of varying acicularity. This particle morphology imparts high strength, making it of considerable importance in many markets. The acicularity of particles is defined by their length-to-width ratio. Wollastonite is marketed as either low-aspect-ratio (generally 5:1 or less) and high-aspect-ratio (generally 12:1 and higher). Diameters, on the other hand, can range from a low of 2.5 μm to a high of more than 40 μm . Generally, the low-aspect-ratio grades are used as functional fillers where chemistry carries an equal value to morphology. Examples of end uses are found in architectural and industrial coatings, ceramic bodies and glazes, and foundry applications. The high-aspect-ratio grades contribute functionality, with the morphology playing a more important role than the chemistry. Examples include engineering resin compounds (such as nylon and polypropylene), phenolic molding compounds (such as friction brake materials), and rubber matrices (such as gaskets). In these applications, wollastonite has served to fill the niche originally held by asbestos.

The dry brightness and whiteness of wollastonite are also important in determining its suitability for certain filler and ceramic applications. When pure, the mineral is brilliantly white, but impurities may color it cream or gray. Brightness is determined by measuring the reflectance of finely ground powder against a standard that is assigned a brightness of 100. Magnesium oxide and barium sulfate are the two standards used. *GE brightness*, a term used in North America, refers to brightness measured with a General Electric reflectometer. Commercial wollastonite products usually have a GE brightness ranging from 85 to 95. The Hunter method is also used to measure the brightness of wollastonite.

Loss on ignition (LOI), another important property in determining applications for wollastonite, is the amount of volatile matter driven off when the mineral is heated to 1,000°C. Commercial wollastonite products have an LOI ranging from 0.5% to 2.0%.

Wollastonite's naturally high pH of 9.9 (10% water slurry) is of major importance to its use in the coatings industry. The alkaline pH has been thoroughly documented as a chief contributor to wollastonite's corrosion-inhibiting performance in heavy-duty industrial coatings. Table 1 lists some of the selected properties of wollastonite.

Origin and Mode of Occurrence

Wollastonite is formed by both metamorphic and magmatic processes that usually involve carbonate and intrusive igneous rocks.

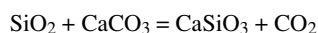
Table 1. Selected wollastonite properties

Crystal system	Triclinic
Crystal habit	Bladed masses; acicular
Cleavage	2 perfect at 84° and 1 good
Color	White, sometimes cream, gray, or very pale green
Streak	White
Luster	Vitreous to pearly
Mohs hardness	4.5–5.0
Specific gravity	2.87–3.09
Melting point	1,540°C
Transition point to pseudo-wollastonite	1,200°C
Thermal coefficient of expansion (mm/mm/°C)	6.5×10^{-6}
LOI	1,000°C
pH	10–11

Two types of deposits are known—skarn deposits (thermal metamorphic and metasomatic) and carbonatites (magmatic).

Wollastonite-rich skarn deposits are formed by the thermal metamorphism of siliceous limestone during regional deformation or as a result of local intrusive igneous activity. The mineral can also form through the metasomatism of limestone by siliceous hydrothermal solutions along contacts with igneous intrusions or along fractures and faults.

Wollastonite is formed by the following reaction:



At low temperatures, quartz and calcite will form a stable assemblage, as in certain types of marble. If the temperature rises to approximately 400° to 450°C, however, the reaction begins and proceeds to the right until the supply of calcite or quartz is exhausted, at a pressure of about 1×10^5 Pa. The carbon dioxide produced causes pressure to increase unless this gas escapes, and as the pressure rises, the temperature required for the reaction to proceed increases, possibly to as high as 950°C.

The mineral composition of each wollastonite deposit is dependent on geologic conditions, so the assemblage of associated gangue minerals differs from one deposit to another and even within a single deposit. Nevertheless, three basic assemblages are generally associated with wollastonite: wollastonite–garnet (grossular–andradite)–diopside (e.g., Lewis, New York); wollastonite–calcite–graphite (e.g., Harrisville, New York); and wollastonite–diopside–quartz (e.g., Lac St. Jean, Quebec). Each assemblage reflects the original composition of the host rock and the nature of subsequent metamorphic and intrusive igneous events.

A number of workers have studied the occurrence and origin of wollastonite deposits in the Adirondack Mountains, Essex County, New York. These deposits are held by NYCO Minerals, Inc., a subsidiary of Fording Canadian Coal Trust. The ore bodies are typified by a simple equilibrium assemblage of wollastonite–grossular–diopside (de Rudder 1962). Accessory minerals are apatite and sphene. Wollastonite is intercalated with bands and lenses of grossular–andradite and diopside–hedenbergite. The formation of wollastonite depended on the initial composition of the Precambrian Grenville carbonate rocks and was independent of silica metasomatism. Thermal metamorphism produced wollastonite in siliceous limestones, diopside in siliceous dolomites, and garnet in argillaceous limestones. Minor alumina metasomatism from adjacent argillaceous sedimentary rocks caused the development of thick grossularitic skarns bordering the ore bodies.

The wollastonite in Essex County is associated with mafic metasedimentary rocks (amphibolites and pyroxene gneisses) having mineral assemblages characteristic of both hornblende–granulite and pyroxene–granulite subfacies of regional metamorphism. de Rudder (1962) concludes that the gneissic structure of these metasedimentary rocks, their granulitic texture, the lack of recognizable metamorphic halos, and the high-grade mineral assemblages indicate that relatively high temperatures and pressures prevailed for long periods of time. The mafic metasedimentary rocks enclose a wollastonite–grossular–diopside assemblage that is considered typical of either the hornblende–hornfels or the pyroxene–hornfels facies of contact metamorphism. As a result, de Rudder proposes that the conditions of metamorphism can best be termed *thermal-load metamorphism*, and defines this term in the context of thermal metamorphism caused by the proximity of magma at great depths and very high uniform pressure.

The environment of metamorphism at NYCO's deposits must be inferred from field relations, mineral assemblages, thermodynamics, and experimental data. Based on these criteria, de Rudder (1962) believes that the range of temperature and pressure most consistent with known data is 750° to 950°C and 6 to 12×10^8 Pa. This would correspond to a burial depth of approximately 30 ± 10 km.

O'Hara (1976) disputes de Rudder's statement that the origin of NYCO's wollastonite was a contact metamorphic event triggered by the intrusion of anorthosite into granulite facies rocks at a depth of 30 km and a temperature of 750° to 950°C. Instead, O'Hara suggests that uplift occurred after regional metamorphism and before the anorthosite intrusion. Thus, the anorthosite intruded the metasediments in a low-pressure environment (e.g., about 2×10^8 Pa and 650°C). The heat from the intrusion caused thermal metamorphism of metasedimentary rocks and the crystallization of wollastonite.

Other authors (Grammatikopoulos, Clark, and Vasily 2003) attribute the formation of high-grade wollastonite skarn deposits (e.g., NYCO) to *infiltration metasomatism*. In this model, wollastonite development resulted from the interaction between infiltrating fluids, calcitic marble (possibly intercalated with dolomitic marble), and clastic, quartz-rich domains. The fluids were controlled by fractures and porosity of the original beds.

Wollastonite is also found in carbonatites, where it crystallized from carbonatite magma. Carbonatite deposits generally are found as near-surface intrusions associated with nepheline syenite or nephelinite in complexes of elliptical or circular outline. Wollastonite deposits in carbonatites are of lower grade than skarn deposits but are potentially economically valuable. It is improbable that a carbonatite would be mined for wollastonite alone, but the mineral might be obtained as a by-product.

WORLD WOLLASTONITE DEPOSITS AND ACTIVITIES

United States

Two companies in the state of New York produced wollastonite commercially in 2005. The NYCO operation is in northeastern New York (Essex County), near Lake Champlain, within the boundaries of Adirondack Park. R.T. Vanderbilt Company has an operation in northwestern New York (Lewis County), near the St. Lawrence River.

NYCO is the largest of the two domestic producers with 2004 sales of 82 kt (includes the operation in Mexico described in the relevant section in this chapter), with a value of \$34.8 million. From 1943 to 1982, NYCO mined wollastonite from the Fox Knoll deposit, initially by open-pit and later by underground methods. The deposit is approximately 4 km southwest of NYCO's processing plants at Willsboro. After the Fox Knoll deposit was shut down, the Lewis deposit, which is about 23 km southwest of the plants, became

Table 2. Selected Canadian wollastonite deposits

Name	Location	Resource
Deloro	Marmora, Ontario	2 Mt at 40% wollastonite
Mount Grove	Olden Township, Ontario	2.7 Mt containing 32% wollastonite, 63% calcite, and 5% diopside
Seeley's Bay	Kingston, Ontario	9 Mt, grading 41% wollastonite 3 Mt, grading 30% wollastonite
Lac St. Jean	Quebec	5 Mt, proven at 37% wollastonite
Montreal–Gatineau area	Quebec	Unknown; numerous deposits
Wormy Lake	Sechelt Peninsula, British Columbia	50 Mt

Table 3. Major current and past wollastonite producers in Mexico

Name	Location	Output, Finished Product, t	Markets	Current Status
General de Minerales SA (Lamosa Group)	Guadalupe, Zacatecas State	20,000 (1993)	Domestic ceramics primarily	Plant shut down in 1995; current status unknown
Minerales y Maquiles del Norte, SA	Santa Catarina, Zacatecas State	9,000	Primarily ceramics and metallurgical	Produces low-aspect-ratio grades with 85% of production for domestic consumption
Minera NYCO SA de CV	Northwest of Hermosillo, Sonora (Pilares deposit)	240,000 t nameplate capacity	Global; powder products (e.g., ceramics)	Started operations in 1997, but significantly curtailed planned production; estimated annual production of <30,000 t
Compania Minera de Cerralvo	Near Pichucalco, Chiapas State	1,000	Domestic paint industry	Wollastonite was by-product of copper operation; current status unknown

the feedstock source. Wollastonite comprises up to 60% of the Lewis ore, with 30% garnet and 10% diopside accounting for the balance. The deposit averages 49% wollastonite. Additional reserves are available at NYCO's Oak Hill deposit, averaging 45% wollastonite. A third deposit, Deerhead, grades 25% wollastonite. According to NYCO, the three deposits total 6 Mt of reserves.

All of NYCO's deposits were formed by contact metamorphism and metasomatism of Precambrian siliceous carbonates by an anorthosite intrusion. NYCO's processing plants at Willsboro produce a full product line ranging from a milled (low-aspect-ratio or powder) grade of $-45\ \mu\text{m}$ (-325 mesh) to surface-modified, $-10\ \mu\text{m}$ (-1250 mesh), high-aspect-ratio (15:1 to 20:1) products. Magnetic separation removes accessory garnet and diopside from the wollastonite. Jet mills are used for producing high-aspect-ratio products.

The R.T. Vanderbilt deposit is near Harrisville, and started production in 1977. In 2005, both underground and open-pit operations were active. The deposit was formed by contact metamorphism and metasomatism of Precambrian siliceous carbonates by a syenite intrusion. It differs from NYCO's deposits in that garnet is absent. The ore contains up to 90% wollastonite, with associated blue calcite, graphite, prehnite, magnetite, and diopside (Gerdes and Valley 1994). The ore body is differentiated, with large pods of wollastonite being separate from gangue zones. This allows selective mining of the ore zones. Wollastonite ore is crushed at the mine site and then trucked approximately 19 km to a plant near Balmat. Both low-aspect-ratio and high-aspect-ratio grades are produced. Some of the products are surface treated. Estimated production is 40 ktpy.

Other deposits, mostly in the western United States, have been explored with past attempts at starting operations. In the late 1990s, the American Wollastonite Mining Company (currently known as Previa Resources Ltd.) was evaluating and seeking investment capital for a deposit near Tonopah, Nevada. Stated reserves were more than 1 Mt at 60% wollastonite, with an aspect ratio of 16:1. Although a 10-kt pilot plant was under construction at one time, this venture had ceased as of 2005.

Canada

In Quebec, Orleans Resources reported in the 1990s that it had the potential to be a major producer. Because of certain technical and marketing problems, however, the operation ceased production by 2000, and the plant has been completely dismantled. As of 2005, only one deposit was actively being evaluated, the Seeley's Bay property owned by the Canadian Wollastonite Company. The company was seeking a joint-venture partner.

The deposits that have had the most exploration and development are concentrated in Quebec, Ontario, and British Columbia. The geology is primarily anorthosite associated with marble and calc-silicate rocks (see Table 2).

In most, if not all, of these deposits, flotation and magnetic separation would be required to process the mineral to achieve yields approaching 90% wollastonite. Most of the deposits are reported to have at least an 8:1 aspect ratio, and some aspect ratios are >20:1. Ram Petroleums Ltd. originally evaluated the Mount Grove deposit in 1990. With a stated aspect ratio range of 17:1 to 24:1, planned production called for 30 ktpy of wollastonite and 54 ktpy of calcium carbonate. The economic viability is unknown, and the project is believed to have been terminated.

Mexico

The established and known producers of wollastonite are concentrated in the states of Zacatecas and Sonora. Production in 2003 was estimated at 52 kt (Virta 2004). Other states where wollastonite has been produced include Chiapas, Durango, Morelos, and Tabasco. Table 3 shows details of the major current and past producers in Mexico.

Minera NYCO mines wollastonite from the Pilares deposit. The deposit is situated in a north-dipping sequence of Paleozoic calcitic marbles and quartzites in close proximity to granitic rocks of Cretaceous age. The San Hector deposit is near the Pilares deposit. Reserves grading more than 50% wollastonite and containing >100 Mt are represented by the two deposits combined. As of 2005, the San Hector deposit was dormant. The Minera NYCO

Table 4. Wollastonite producers in China, 2001

Name	Location (Province)	Capacity, tpy	Resource	Number of Mines
Lishu Wollastonite Mining Industry Co.	Mostly in Jilin and Liaoning	80,000	~ 20 Mt	10
Nanchuan Minerals Group	Guangdong and Jilin	30,000 and 10,000, respectively	Unknown	2
Sanyi Mining Development Co.	Jilin	60,000	Unknown	4
Jilin Wollastonite Development Co., Ltd.	Jilin	24,000 (mill capacity) 50,000 (mine capacity)	1.5 Mt	1
Xinyu South Wollastonite Industry Co., Ltd.	Jiangxi	50,000 (lump) 20,000 (milled)	Unknown	Unknown
Anhui Pioneer Mining Co., Ltd.	Anhui	20,000 (lump) 6,000 (milled)	Unknown	2
Daye Wollastonite Mine	Hubei	30,000 (lump)	Unknown	Unknown
Dayu Mineral Materials Co., Ltd.	Liaoning	20,000	Unknown	Unknown
Changxing Wollastonite Mine Co., Ltd.	Zhejiang	25,000 (lump and high-aspect-ratio)	Unknown	Unknown

facility utilizes both flotation and magnetic separation to remove calcite, quartz, and diopside from the wollastonite.

China

Approximately 50 deposits have been discovered in 19 provinces. Of these, 30 deposits have been extensively explored (Lu 1998). The deposits are concentrated in the provinces of Jilin, Yunnan, Jiangxi, Qinghai, and Liaoning. Resources are estimated at 130 Mt. China holds the largest number of deposits and mines and is considered to be the world's largest wollastonite producer (Virta 2004). Output from viable operations is believed to be about 300 ktpy, with domestic consumption approximately 100 ktpy (Moore 2003; Hawley 2004). Chinese wollastonite dominates in powder grades for ceramic and metallurgical applications and recently, high-quality, high-aspect-ratio grades have emerged.

Table 4 lists the major producers in China in 2001 (Kendall 2001; Virta 2004).

In 2004, it was reported that China produced from 60 small operations (Hawley 2004). The industry, however, has consolidated, resulting in nine companies controlling ore processing and production in 2005. The Jilin Wollastonite Development Co., Ltd. signed an agreement in 2004 with S&B Industrial Minerals S.A., pending Chinese government approval. In this agreement, S&B would have 51% control and would manage the operation (Virta 2004).

India

In 1969 the Belkappahar wollastonite deposit was discovered near the village of Khila in the Jodhpur Division of Rajasthan State. The deposit consists of three zones of wollastonite interbedded with pyroxenites and garnet-bearing gneisses that have replaced limestone. The ore contains about 96% wollastonite, associated with minor calcite, garnet, diopside, and quartz. Proven reserves are estimated to be approximately 50 Mt, and probable reserves are about 200 Mt. Wolkem India Ltd. operates two open-pit mines, one at Belka Pahar, the other at Kheratarla. The plants are at Sirrohi and Udaipur, and produce milled, high-aspect-ratio, and surface-modified grades. Wolkem serves various markets, including ceramics, metallurgical, coatings, and plastics. Production for 2003 is reported to range from 160 kt (Mahajan 2003) to 176 kt (Virta 2004). India ranks as the world's second leading producer of wollastonite.

Finland

Partek Industrial Minerals produces wollastonite as a flotation by-product with calcium carbonate. The operation is in southern Finland near Laappeenranta. At one time, the company was rated the

world's fourth largest producer of wollastonite. In 2004, however, production was only 27.5 kt. The wollastonite occurs in the central portion of an elliptical body of Archean limestone. Within the wollastonite deposit are stringers of calcite, dolomite, quartz, diopside, and lepidite. Reserves are estimated at 3 to 4 Mt at an average grade of 20% wollastonite, although the grade reaches 60% in certain areas. The company also controls another wollastonite deposit at Savitapale that is estimated to contain 20 Mt grading 25% to 35% wollastonite.

Other Countries

Other small producers of wollastonite include Estudios y Proyectos Mineros Ltda. in Chile; Kalemden in Turkey; Morocco Minerals Co. in Morocco; Atiriver Mining Ltd. in Kenya; and Namaqua Wollastonite Pty Ltd. in South Africa.

In addition to the countries listed, lesser amounts of production are reported for Pakistan and North Korea (Bolger 1998). Undeveloped wollastonite deposits have been documented in Serbia, the Czech Republic, Poland, the Commonwealth of Independent States, Lithuania, Sweden, Spain, France, Italy, Greece, Switzerland, Namibia, Cuba, New Zealand, Australia, and Japan (Bauer, Copeland, and Santini 1994).

TECHNOLOGY

Exploration and Evaluation of Deposits

Exploration for commercial wollastonite deposits begins with defining the target parameters, which include the desired location, mineralogy, and minimum tonnage. A hypothetical example might be Ontario, Canada, with 5 Mt averaging +50% wollastonite with no calcite. The next step is to develop an exploration plan, which may include researching known deposits, mining districts, and other areas with a geological environment suitable for wollastonite formation. Favorable geological features may include igneous intrusions, such as anorthosites and syenites within a Precambrian metamorphic terrane containing calc-silicate rocks, such as those found in New York, Canada, and Finland. Jurassic and Cretaceous granites within a Paleozoic metamorphic terrane containing calc-silicate rocks, such as in the western United States and Mexico, are another example.

Once exploration targets have been established, an initial reconnaissance geologic examination of the selected areas is conducted. Geologists use various exploration techniques, including field checking for host lithologies based on existing geologic maps; geologic mapping of host lithologies using aerial photos; stream-sediment sampling (e.g., for associated garnet and diopside); grab or channel sampling or both; and mineralogical, physical, and

chemical testing of field samples. Geophysical techniques have seldom been used during regional reconnaissance, because wollastonite-rich rocks exhibit no pronounced gravimetric, electrical, or magnetic properties.

In some areas, such as NYCO's Fox Knoll, Lewis, Oak Hill, and Deerhead deposits, wollastonite-rich rock does not usually crop out, partially because of its relatively low resistance to weathering in humid climates. This can impede the early stages of exploration. In such areas there may be geomorphological features that can be used in tracing wollastonite horizons. Wollastonite that is very coarse grained or contaminated with quartz (or both) can remain exposed after long periods of chemical weathering. Typically, the mineral is more resistant to weathering in arid climates, such as in certain parts of Mexico and the western United States.

After prospects have been identified, a more detailed geologic examination is conducted. This includes geologic mapping, core drilling, and trenching. Wollastonite samples generated during this phase of exploration are subjected to x-ray diffraction for mineralogical analysis and x-ray fluorescence for chemical analysis. In addition, LOI, brightness, and aspect ratio are determined. Petrographic examination of thin sections from selected samples can be useful as well.

If the exploration phase yields favorable results, it is then necessary to extract a bulk sample of representative material from the deposit for additional testing to determine what marketable products can be produced. The bulk sample is subjected to the same tests as the drill core samples. Based on analytical results, the bulk sample may be beneficiated by dry or wet laboratory-scale methods to upgrade the material to standard commercial specifications by removing gangue minerals. Laboratory-scale test work may include combinations of the following steps depending on whether a dry or wet process is required: hand sorting, crushing, screening, pebble or ball mill grinding, flotation, high-intensity magnetic separation, thickening, filtration, drying, and pebble and jet mill grinding. Products resulting from beneficiation tests are subjected to the same analyses as the core samples. In addition, products are tested for surface area, bulk density, oil absorption, and particle size distribution. Scanning electron microscope (SEM) photographs of each product are also taken.

Mining

Wollastonite deposits are mined by open-pit and underground methods. Drilling and blasting are necessary to fragment the wollastonite. At the wollastonite deposits in New York's Essex County (held by NYCO), for example, both mining methods have been employed. Open-pit mining at the Fox Knoll deposit began in 1951. Increasing overburden combined with the dip of the wollastonite horizon resulted in higher stripping ratios, requiring mining operations to move underground in 1959. The deposit was mined by underground methods until it was closed in 1982. Production shifted to the Lewis deposit, which is mined by open-pit methods with bench heights of 10 m. Wollastonite is crushed at the mine site and transported to the plants at Willsboro, New York, for further processing.

Processing

Because the mineralogy of wollastonite largely determines whether it can produce high-purity concentrate, that mineralogy is the key issue in evaluating a deposit. Ideally, an ore-processing system should be capable of recovering a concentrate of at least 97%—if not 99%—wollastonite. Important mineralogical factors include the type of gangue minerals present, the grain size, and the extent to which grains of constituent minerals are intergrown.

Deposits of wollastonite commonly contain garnet and diopside, which are nonwhite and must be removed. Both of these minerals are weakly magnetic, and therefore can be removed from the wollastonite using high-intensity magnetic separators. Wollastonite is often associated with large amounts of calcium carbonate, which must be removed by flotation.

The general flowsheets in Figures 1 and 2 display the dry and wet methods employed to process wollastonite. In New York, NYCO uses the dry method; in Mexico, the company uses the wet method.

Other minor components are present in such small amounts, typically 0.5% and less, that they do not contribute to any wollastonite performance issues and do not need to be removed. MgO, MnO, TiO₂, and Al₂O₃ are examples of these components.

If a deposit is to supply all of the wollastonite markets, it must be able to yield high-aspect-ratio as well as milled (low-aspect-ratio or powder) product grades. Equally important is the particle size at which high-aspect-ratio grades can be produced. For example, it is possible to produce a 14:1 aspect-ratio grade with a diameter of 2.3 µm and another grade with the same aspect ratio that has a diameter of 9.0 µm. In this example, both will differ in average length of particles. To ensure optimum performance of high-aspect-ratio grades, controlling the top size and the amount of fines is also part of the processing technology.

Processing improvements integral to new product development focus on the following target markets:

- High-aspect-ratio, fine-particle-size grades used as reinforcements to compete against milled glass fiber, synthetic fibers, and whiskers
- Fine-particle-size, high-aspect-ratio grades to compete against other mineral reinforcements, such as talcs and clays, in thermoplastic compounds
- Incorporation of new coupling agents to expand the usefulness of wollastonite into emerging markets, such as wood composites

Specifications and Typical Reported Properties

Wollastonite specifications and typical reported properties follow:

- Milled grades: Particle size, including top and median diameter, are measured either by optical measuring devices or by sedimentation methods. Wet and dry screen retentions are commonly reported. Other specifications can include color (whiteness), brightness, oil absorption, LOI, loose and tapped bulk density, and particle size distribution.
- High-aspect-ratio grades: In addition to measurable particle size properties, loose and tapped bulk density are determined. Other properties can be screen analysis, surface area, and oil absorption. In one application (fire-resistant cement boards), sedimentation value is frequently requested as a specification.
- Chemically modified wollastonite: In addition to the specifications and properties listed in the first two bullets, the type of chemical and amount of residual active ingredient can be specified. Percentage of moisture is often noted as well.

Wollastonite By-products and Coproducts

An often critical aspect in the development of an industrial mineral deposit is the potential for selling by-products or coproducts. This is somewhat true of wollastonite, but is probably not as important as for other minerals.

In at least one operation, the Partek operation in Lappeenranta, Finland, wollastonite itself is the coproduct. The wollastonite occurs in a calcium carbonate deposit, which is the principal material

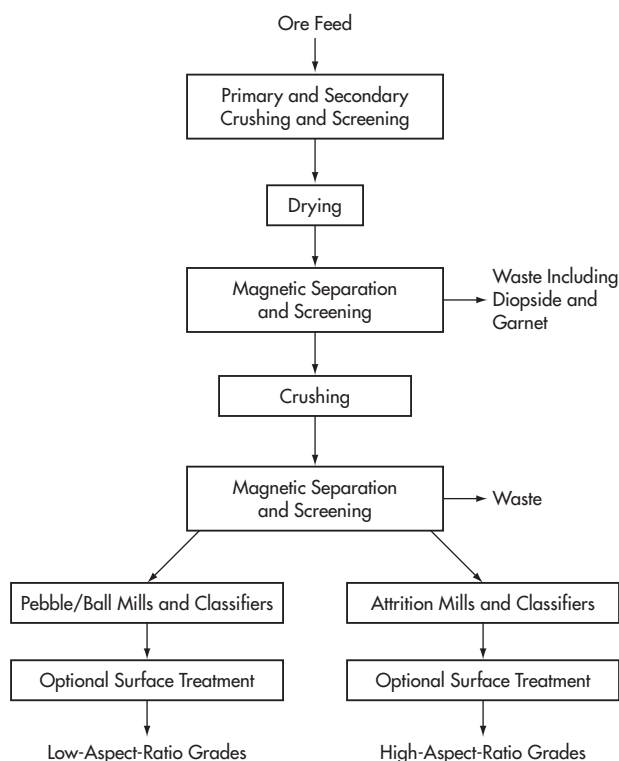


Figure 1. Wollastonite processing (dry)

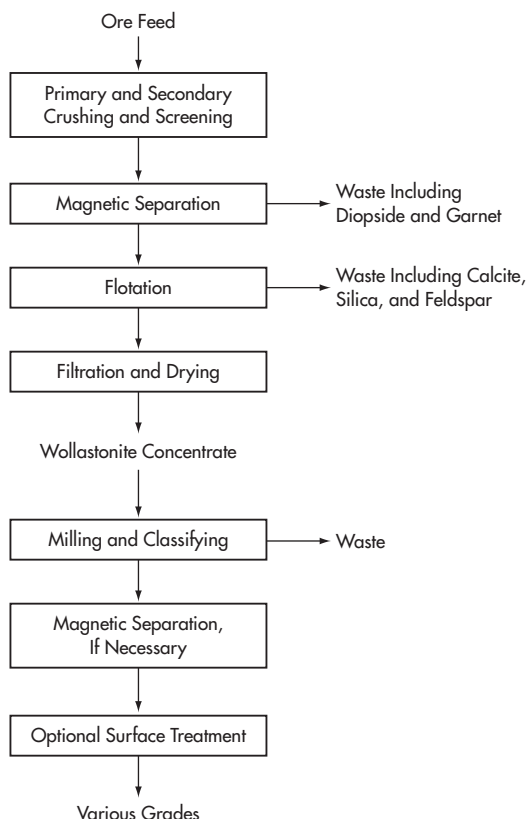


Figure 2. Wollastonite processing (wet)

coproduced. In this case, wollastonite would have to be mined and wasted if it were not recovered as a coproduct. Partek has successfully marketed and sold this high-quality form of wollastonite.

In another example, NYCO has successfully removed the garnet and diopside by-products at its operation in Willsboro, New York. These by-products are created by using high-intensity magnetic separation to remove the garnet and diopside from the wollastonite. The garnet is a substitute for silica sand in abrasive blasting and multilayer water-filtration systems.

In other operations around the world, the generation of by-products is less important. In some locations, however, wollastonite is found associated with calcium carbonate, which is removed using flotation. Once recovered, it is a source of lime for agricultural uses.

Synthetics

Synthetic calcium metasilicates have been produced commercially for many years in various parts of the world, including the United States, Denmark, Germany, Italy, and Brazil. Most of the synthetics are hydrous, and in contrast to naturally occurring calcium metasilicate, they have high absorptivity and lack the characteristic acicular shape.

The synthetic calcium metasilicates made in Denmark are produced from silica sand and chalk under the trademarked name of Synopal. Basically the process is slurring the chalk and silica sand with small amounts of dolomite, which acts as a flux. The slurry is heated to about 1,560°C in a kiln, forming a viscous paste that is then water cooled. When solidified, the material is crushed and screened, then reheated in a second kiln at 1,250°C, which facilitates crystallization. The finished product is subangular, white, and opaque, and consists of about 50% wollastonite and 50% gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$) and akermanite ($\text{MgCa}_2\text{Si}_2\text{O}_7$). The Synopal wollastonite has been used in road surfacing, mosaic tiles, flooring, and roof tiles.

In Italy, a synthetic product has been produced in a method similar to the Danish process. Additional uses that have been mentioned include road material, abrasives, and ceramics. In Brazil, a synthetic calcium metasilicate had been produced for the welding rod flux, ceramics, and refractories markets. Recent reports, though, suggest that the company that produced this material is no longer providing the synthetic form.

In the United States, both hydrous and anhydrous calcium metasilicates have been manufactured by PPG Industries (Silene grade), and by Manville Products Corporation (Micro-cel). Many grades are reported to have been made of both types, and the typical manufacturing process is autoclaving lime, silica sand, and dolomite slurries at high pressures and temperatures.

In 2003, a U.S. patent was granted that disclosed synthetic calcium metasilicates and methods for producing them (Withiam, Conley, and Yannul 2003). The calcium metasilicates were described as having low aspect ratios (1:1 to 2.5:1) and oil absorptions from 20 mL/100 g to about 220 mL/100 g. In this patent, the end uses for the synthetic wollastonite are described as being a veterinary pharmaceutical preparation, a formed food product, a formed agricultural product, and a formed home care product.

Other uses for synthetic wollastonite have been those where the natural form has been used. The deciding factor is proximity of natural wollastonite, especially if the quality is high. Because of the necessity for purity of chemistry, the ceramics industry and the refractories industry have had to rely on the synthetic version in the past, although this seems to have declined in recent years. Synthetic calcium metasilicate is believed to be used in some flat glass manufacturing. A companion product, synthetic diopside, is made as a

source of magnesium. Other uses for the synthetic form have been as a flow aid in powdered materials, in foam manufacture, and in mineral wool.

ECONOMIC FACTORS

Demand and Consumption

According to Virta (2003), the major domestic supplier of wollastonite, NYCO, indicated that sales from its combined operations in Mexico and the United States were 75 kt in 2003. This is 11% less than reported in 2002. Reasons cited were global oversupply and offshore competition from suppliers in China and India. End-use sectors reporting declines in wollastonite consumption from the same study were ceramics (using calcium carbonate as a low-cost and local substitute) and metallurgical uses (lower steel production and using either lower-cost minerals or lower-cost imported wollastonite). Sales did increase to 82 kt in 2004.

Hawley (2004) reported the distribution of U.S. consumption of wollastonite for 2003 to be plastics (37%); ceramics (28%); paint (10%); metallurgical (10%); friction products (9%); and miscellaneous (6%). This latter category includes fire-resistant cement board (a type of wallboard), adhesives, sealants, and caulks. New markets are developing in cement and concrete compositions, and in selected rubber-based polymer sealants.

Demand for wollastonite is steady, with single-digit growth expected through 2010. Some sectors could experience more aggressive growth into double-digit figures, but the average of all industries is likely to be in the single digits. Competitive mineral products have influenced some of the consumption of wollastonite, especially in the engineered plastics market. The introduction of very fine talcs and nanoclays and other nanoparticle-size minerals into the plastics market has impacted the use of wollastonite. This has been noticed especially in the production of nylons and thermoplastic olefins (TPOs). Surface-modified versions of wollastonite, however, will continue to be strong market participants. In recent years, new offerings of organosilanes have expanded the use of wollastonite in the rmoplastics. The automotive industry greatly influences the consumption of value-added grades of wollastonite. If automotive manufacturing is growing because of increased sales of new models, for example, development of new plastic parts with mineral reinforcement will require wollastonite. Additionally, other industries tied to automotive manufacturing and sales, such as friction brake products and rubber-based gaskets, will continue their demand for wollastonite as well.

Supply

In the last several years, the North American market has seen the expansion of one traditional supplier, R.T. Vanderbilt, into new grades of both low- and high-aspect-ratio grades, including surface-treated versions. As previously mentioned, Vanderbilt mines and processes wollastonite at its location in Lewis County, New York. This same market has seen the major supplier, NYCO, bring a plant (240 ktpy) onstream in Sonora, Mexico during 1998, only to curtail production a few years later. This leaves NYCO again heavily dependent on its original operation in Essex County, New York (capacity of 110 ktpy).

Imports of wollastonite into North American markets have been active for many years. India and China have introduced high-quality grades to various markets. Currently the Indian material is available in low- and high-aspect-ratio forms, as well as in surface-treated grades. Apparent markets are for thermoplastics and thermoset compositions. Chinese wollastonite has been successfully introduced into metallurgical and ceramics applications. In addition, specialized toll processors of Chinese ore have been successful in

supplying high-aspect-ratio, surface-treated grades for plastics applications. At least one source (Hawley 2004) has reported that there are more than 60 wollastonite operations in China, but most likely less than 10 are active in exporting outside of China or the Asian Pacific basin.

Other wollastonite deposits in North America that may be active in the future can be found in British Columbia and Ontario.

Pricing

The U.S. Geological Survey (USGS) minerals yearbooks for 2002 to 2004 (Virta 2002, 2003, 2004) give prices for wollastonite that range from \$50/t for lump to \$1,700/t for ultrafine, surface-treated wollastonite. Prices for domestically produced wollastonite are

- 200 mesh, ex works, \$226/t
- 325 mesh, ex works, \$273/t
- 400 mesh, ex works, \$303/t
- Acicular, high-aspect-ratio, ex works, \$380/t

Prices for wollastonite from China (all free on board [f.o.b.]) are

- 200 mesh, in bulk, \$80 to \$100/t
- 325 mesh, in bulk, \$90 to \$110/t
- 250 mm lump, \$50 to \$60/t
- 150 mesh, bulk or big bags, \$65 to \$80/t
- 200 mesh, bulk or big bags, \$70 to \$85/t
- 325 mesh, bulk or big bags, \$75 to \$90/t

Historically, the selling prices of wollastonite have been largely determined by the grade versions and the amount of acicularity (as in aspect ratio). Furthermore, because economic wollastonite deposits are not widespread, freight costs for transporting it to users tend to be higher than for more widely found minerals (such as calcium carbonate and silica sand).

The addition of surface-modifying chemicals (coupling agents) can add a significant amount to the price of wollastonite. Some grades have been reported to have prices close to \$2.00/kg as the result of adding chemicals.

Prices reported here are only guidelines used to determine the value of wollastonite as a mineral. Actual prices can depend on contractual terms between suppliers and consumers.

MARKETS

Historically, wollastonite has been used to replace short-fiber asbestos, a use that began its growth as a commercial mineral. Beginning in the 1970s, this growth continued into 2005. Worldwide consumption of wollastonite has significantly increased since its early days. In 1959, world production was approximately 34 kt. By 2004, world production was approximately 575 kt (Virta 2004).

The major uses for wollastonite are fire-resistant products, ceramics, metallurgy, paints and coatings, plastics, friction brake materials, and natural and synthetic rubber (including elastomers).

Fire-Resistant Products

This group of products includes interior and exterior construction boards, roofing tiles, shingles, and slates, shaped and formed insulation, extruded sheets and slabs, corrugated sheets, and siding. The prevalent types are calcium-silicate-based, fiber-cement-based, or asbestos-fiber-cement-based. The typical production methods are slurry, slurry-net, extrusion, or spray processes.

The benefits of wollastonite to these products include

- Improved thermal stability, including fire resistance
- Reinforcement, including microreinforcement

Table 5. Key properties and benefits of wollastonite use in ceramics

Property	Benefit
Mineral chemistry of combined CaO and SiO ₂	<ul style="list-style-type: none"> • Performs like a natural frit • No outgassing • Amount of silica can be reduced, which means better opacity control in matte or opacified glazes
High melting temperature	<ul style="list-style-type: none"> • Lower vitrification temperatures • More efficient melting control
Acicular particle shape	<ul style="list-style-type: none"> • Improved sintering, strength, and thermal expansion control • Stronger body
Firing temperatures	<ul style="list-style-type: none"> • Acts as flux at high temperatures to accelerate even melting at lower temperatures • At lower temperatures, acts as a refractory in matte glazes • Glaze melting improved because lesser amounts of flint added to glaze batch
Source of calcium	<ul style="list-style-type: none"> • Improved color strength
Low LOI	<ul style="list-style-type: none"> • Reduced number of pin-hole defects

- Improved flexural toughness and ductility of Portland-cement-based binders
- Improved water drainage
- Improved dimensional stability and reduced shrinkage and warping
- Reduced cracking and chipping
- Improved green strength

Globally, this end use has been and still likely remains the single largest market for high-aspect-ratio wollastonite.

Ceramics

Wollastonite has had a long history in ceramic use, especially whitewares. It has been used predominantly in ceramic tiles, sanitary ware, tableware, and artware. Within ceramic tiles, wall tile has been the major use area. In this application, wollastonite promotes dimensional uniformity, low shrinkage and warping, strength, low moisture expansion, and fast firing. This last property became crucial when the tile manufacturing trend moved toward rapid-fire bodies. As a result, wollastonite is found in both body and glaze formulations. Table 5 lists the key properties and benefits of wollastonite use in ceramics.

In sanitary ware, wollastonite has demonstrated that its acicular shape can improve the green strength of the body, enhance drying by allowing water vapor to escape more rapidly, and contribute to reduction of fluorine emissions. In a patent granted in 2000, Robinson and Craig claimed that the impact resistance at the drying stage was increased by more than 40% and also noted the improved drying and reduced vitrification temperature.

Metallurgy

Wollastonite's chemical composition enables it to perform as a low-temperature flux when used as part of continuous casting mold powders for steel casting. Another important use for wollastonite is in slag conditioners.

In continuous casting, a ladle containing molten steel is poured into a tundish. When the level of molten steel reaches a specified level, the cast is started by introducing the steel into the mold. A flux

composite powder is pushed onto the molten steel, and because the powder is designed to melt at very high temperatures, it will melt within minutes of contact. This casting flux functions by providing thermal insulation, preventing reoxidation, absorbing nonmetallic inclusions, providing lubrication, and offering uniform heat transfer. Wollastonite is generally 10% to 35% of the flux formula, depending on individual producer formulation. The high melting point of wollastonite (1,540°C) supplies uniform heat transfer and the SiO₂ within wollastonite contributes a silica source.

In continuous casting operations, a mixture of oxides resides on top of the molten steel. This mixture, known as *slag*, helps to condition and purify the steel. This combination of slag conditioners helps to absorb impurities such as sulfur. Wollastonite, as a source of CaO, provides a more effective way of introducing CaO than does lime. Although it is more expensive than lime, wollastonite has a lower melting point and thus liquefies faster than lime.

Tire cord steel is another end use that has been described as benefiting from wollastonite use. Advantages of wollastonite are believed to include modification of Si-Mn deoxidation inclusions to form anorthite inclusions, controlling the oxygen content of the steel, and providing a source of Ca.

The typical grades of wollastonite used in metallurgical applications are the low-aspect-ratio or powder forms, at either -200 mesh or -325 mesh sizes.

Paints and Coatings

Wollastonite has an extensive history in paints and coatings. Starting with the introduction of water-borne polymers to replace linseed oil-based house paints, and continuing into the present with new polymers, the benefits of wollastonite have proved to be numerous.

In architectural or trade sales paints, the low-aspect-ratio powder (or milled) grades are generally used. Improved properties are typically reported as film reinforcement and hardness, tint retention, low-temperature touchup, scrubability, mildew resistance, gloss reduction, and weatherability. In architectural coatings, the milled grades are not surface-modified, and the typical sizes range from -325 mesh to -1250 mesh.

In textured coatings, such as block fillers and stucco coatings, and in aluminized and asphaltic roof coatings, the high-aspect-ratio grades are used. The attraction here is wollastonite's acicular shape, which contributes reinforcement, sag resistance, and microcrack propagation control.

In liquid industrial coatings, especially those designed for anticorrosion performance, wollastonite offers the following improvements:

- Reduced water permeability
- Impact and chip resistance
- Alkaline environment that discourages corrosion
- Intercoat adhesion
- Blister resistance
- Flash and early rust resistance

In these coatings, surface-modified wollastonites are used. Organosilanes are the more common chemistries employed, and amino and epoxy versions dominate. In recent years, the growth of wollastonite in this coatings segment has increased primarily because toxic metallic inhibitive pigments can now be controlled. The synergistic effect of wollastonite with nontoxic corrosion-inhibiting pigments to improve corrosion resistance is well documented.

Industrial powder coatings are categorized into two major groups, functional and decorative. The decorative category consists

Table 6. Processing properties and effects of wollastonite in plastics

Property	Untreated	Chemically Modified
Viscosity	Increase	No effect to moderate increase
Melting flow	Decrease	No effect to moderate decrease
Processing temperature	Increase needed	Little or no effect
Injection pressure	No effect or slight increase	No effect or slight decrease
Flow in mold	Moderate reduction	No effect or slight improvement
Mold shrinkage	Decrease	Decrease
Mold cycle time	Decrease	Decrease

Adapted from Bauer 1990.

mainly of those coatings applied to automobiles, furniture, and appliances. The functional grouping consists of those applied to pipe, such as that used in gas and oil exploration, and certain mechanical housings. Wollastonite is used in both areas, but the largest use is probably in functional powders. In this application, the mineral offers several benefits—control of “orange peel,” gloss reduction and control, film integrity, and durability and weatherability.

Coatings formulators worldwide are increasingly using low volatile organic compound (VOC), waterborne, and high solid-liquid coatings. Wollastonite continues to be selected as one of the filler raw materials as coating formulations evolve.

Plastics

Essentially all the grade types of wollastonite that have been produced have been utilized in plastics. The defining characteristics are aspect ratio, particle size, and surface modification.

Wollastonite is principally a reinforcing functional filler. Several properties of the mineral make it attractive for use in polymer systems: low water absorption, good thermal conductivity, low resin demand, consistent chemistry, and needlelike particle shape.

Table 6 gives processing properties and effects of wollastonite in plastics.

The benefits of wollastonite can generally be categorized by the type of polymer system in which it is incorporated. To discuss benefits, it is important to first note load levels, because the load level of the mineral can vary and depend on polymer type. Table 7 shows the typical load levels of wollastonite in polymers.

Table 8 summarizes the expected benefits of using wollastonite in polymers.

Friction Brake Materials

One of the earliest commercial uses for wollastonite was in friction brake materials. The mineral was found to be a suitable replacement for short-fiber asbestos, which had become strictly regulated—at least in the United States—as a probable carcinogen. Even though wollastonite could not totally replace asbestos, it played a major role for reinforcement. Wollastonite can replace chopped glass in phenolic-based polymer systems. In some formulations the glass replacement percentages can be as much as 15% to 20%, kilogram for kilogram.

One growth area for wollastonite has been in the nonasbestos organic (NAO) friction materials sector. Principal end uses include drum brake applications for passenger cars and light trucks, and brake blocks for heavy-duty truck use.

As in the plastic polymer systems, the key characteristics of wollastonite in friction applications are particle shape, chemistry, mineralogy, high melting temperature, and high temperature stability.

Table 7. Typical load levels of wollastonite in polymers

Polymer	% by Weight
Nylon	22–40
Phenolics	25–45
Polyurethane/polyurea	18–25
Epoxy	15–30
TPOs 25–40	
Polypropylene (PP)	20–40
Polyester	5–35
Polycarbonate	15–20

Table 8. Expected benefits from wollastonite use in polymers

Polymer	Benefits
Nylon	<ul style="list-style-type: none"> • Cost-effective reinforcement versus certain glass fibers • Dimensional stability • Uniform shrinkage • Improved surface appearance • Improved melting flow
Phenolics	<ul style="list-style-type: none"> • Reinforcement • Heat stability • Improved mold cycle time • Improved dimensional stability • Improved physical and electrical properties at high temperatures • Resistance to microcrack propagation
Polyurethane/polyurea	<ul style="list-style-type: none"> • Cost-effective reinforcement for milled glass fiber • Improved surface appearance • Low moisture absorption • Lower shrinkage
Epoxy	<ul style="list-style-type: none"> • Excellent heat stability • Mechanical strength • Cost-effective substitute for chopped glass fiber
PP and TPOs	<ul style="list-style-type: none"> • Overall mechanical strength • Improved balance of impact and stiffness • Improved shrinkage control • Improved melting flow rate and viscosity • Improved mar and scratch resistance
Polyester (including polyethylene terephthalate [PET])	<ul style="list-style-type: none"> • Improved mechanical strength • Heat stability • Nonopacidity
Polycarbonate	<ul style="list-style-type: none"> • Improved flow-line strength • Improved modulus of elasticity • Good thermal resistance • Improved processing behavior

Benefits typically seen with wollastonite are

- Cost efficiency
- Reduced cracking
- Reduced rotor wear
- Improved lining life
- Enhanced processing efficiency
- Improved high-temperature fade and recovery
- Enhanced green strength

Table 9. Primary benefits of using wollastonite in rubber-related elastomers

Property	Benefit	Polymer
Acicular shape	<ul style="list-style-type: none"> • Reinforcement • Stiffness 	Nitrile rubber
Chemistry (including organosilane surface modification)*	<ul style="list-style-type: none"> • Prevention of sponging during press cure 	Fluoroelastomers
Chemistry (with and without surface modification)	<ul style="list-style-type: none"> • Increased modulus • Increased tensile strength • Increase durometer and tear strength • Improved compression set 	Ethylenepropylenediene rubber (EPDM)

* Silane treatment choice is dictated by cure agent used in system.

In some applications, surface-modified forms of wollastonite have been tested and found to improve dispersibility and resin bonding, yielding a stronger matrix. The most commonly used surface-modifying agent has been amino silane.

Other uses within this market segment include piston linings, transmission and clutch plates, and disc brakes.

Natural and Synthetic Rubber (Including Elastomers)

Although wollastonite is not commonly used in rubber-related elastomers, it is important when it is incorporated into these elastomers. For the most part, wollastonite has been used as a reinforcement replacement for fibers with questionable health issues. For instance, in polytetrafluoroethylene (PTFE)-based gaskets, wollastonite replaced asbestos. In other fluoroelastomers, wollastonite can contribute to improved compression set resistance and stability. Typical end use products are resilient rolls, O-rings, seals, and gaskets.

Table 9 summarizes the chief benefits of using wollastonite in elastomers.

Wollastonite, similar to other fillers, is typically incorporated into the mix using the following methods:

- Beater addition—a continuous process where materials are mixed to form a slurry.
- Calendaring—a noncontinuous process carried out in steps. The fully blended mix is then forced between two rolls moving in opposition, and the mix is drawn out as a sheet.

FUTURE OUTLOOK

North American wollastonite producers will continue to place greater emphasis on sales of higher value acicular and surface-treated products in the future (Virta 2003, 2004). Plastics represent the highest potential growth market for domestic producers. Sales of wollastonite for friction products and automotive plastic applications are forecasted to increase slightly as a function of automobile sales. Sales to paint, ceramic, and steel markets should be similar to the last few years, with nearly flat growth. Although China has been the major supplier of lower value wollastonite grades imported into the United States in recent years, these imports may decrease slightly because of increased transportation costs from China and increased prices for Chinese wollastonite. As Wolkem (India) and the Chinese companies improve quality and produce high end, high-aspect-ratio and surface-treated grades, they will provide increased competition to current suppliers of these products. Worldwide consumption of wollastonite is forecasted to increase at a low rate in the near future, as consuming markets slowly expand in response to population growth.

Future challenges to the wollastonite industry in terms of ore quality and product grades are likely to be as follows:

- Providing consistent ore quality in order to achieve proper chemistry and morphology

- Improving ore processing to produce grades that offer consistent particle size distribution and elimination of undesirable contaminants
- Producing grades that are demanded by market needs
- Selecting surface-modifying agents for maximum efficiency
- Understanding completely how minerals (natural and synthetic) must work together in a mixed filler compound to achieve maximum mechanical properties
- Working with consumers to continue development of new grades and applications

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Zeolites

Ted H. Eyde and David A. Holmes

Zeolites are crystalline, hydrated aluminosilicates that contain alkali and alkaline-earth metals. Their crystal framework is based on a three-dimensional network of SiO_4 tetrahedra with all four oxygens shared by adjacent tetrahedra. The alkali and alkaline earth cations are loosely bound within this structure and can be exchanged by other cations or molecular water. Most zeolites can be dehydrated and rehydrated without any change in volume. More than 48 natural zeolite minerals have been identified (Tschernich 1992), and more than 100 zeolites have been synthesized. Zeolites have unique physical and chemical properties that are utilized in many important commercial applications.

Though zeolites were first identified more than 200 years ago, it was not until the middle of the twentieth century that their widespread occurrence in sedimentary rocks and economic potential were recognized. Since then, thousands of articles have been published in the technical literature. In the past 40 years, the zeolite mineral group has changed from a museum curiosity to an established industrial mineral commodity.

According to Breck (1974), the important physical and chemical properties of zeolites are

- High degree of hydration
- Low density and large void volume when dehydrated
- Stability of the crystal structure of many zeolites when dehydrated
- Cation exchange properties
- Uniform molecular-sized channels in the dehydrated crystals
- Ability to adsorb gases and vapors
- Catalytic properties

Molecular sieves are materials that can selectively adsorb molecules on the basis of their size, shape, or electrical charge (Clifton 1987). Commercial applications of zeolites are based on the following properties: molecular sieving, ion exchange, adsorption, and catalysis. Most zeolites are molecular sieves, but not all molecular sieves are zeolites. Activated carbon, activated clays, aluminum oxide, and silica gels are also molecular sieves. Activated synthetic and natural zeolite molecular sieve products, however, have displaced many of these substances because of their selectivity.

Potential commercial utilization of zeolites includes hundreds of possible applications. The principal uses at this time are

- Ammonium-ion removal from sewage and industrial effluents, aquariums, and commercial fish farms

- Odor control in animal absorbents, floor and carpet cleaning products, and industrial floor absorbents
- Removal of heavy metal ions from nuclear, mine, and industrial effluents
- Agricultural applications as soil conditioners and animal feed supplements
- Desiccants used to adsorb water vapor in sealed containers and packaging
- Carriers for bacteria and enzymes
- Gas separation
- Catalysis

About 3.5 Mt of natural zeolites were produced and consumed worldwide in 2003. Construction and agricultural applications consumed most of the production, especially in developing countries. Consequently, the total production obscures the significant increases in industrial and commercial applications. The estimated production in North America in 2003 was 42 kt. Most of this was consumed in odor mitigation, aquaculture, agriculture, carriers, desiccants, radioactive barriers, effluent treatment, and other ion-exchange applications. Seven companies in the United States and two in Canada produced the zeolite mineral clinoptilolite. Two companies produced the zeolite mineral chabazite from the Bowie, Arizona, deposit (Eyde 2003).

HISTORY

In 1756, Baron A.F. Cronstedt, a Swedish mineralogist, identified zeolites as a new group of minerals. He named the minerals zeolites from the Greek words *zein* and *lithos*, meaning “boiling stones,” because of the bubbling and frothing achieved by heating the minerals with a blowpipe. There was no real interest in zeolites until the crystal structure of chabazite was determined, followed by the discovery that chabazite selectively adsorbs smaller organic molecules and rejects larger ones, a property described as *molecular sieving*. Following these discoveries, research on the zeolite minerals began in the laboratory of the Linde Company, a division of Union Carbide Corporation, a producer of industrial gases. Initially the researchers at Linde recognized that molecular sieving could be used to separate gases and that this could be used in their air products business. Later they discovered that zeolites could also separate the components of gasoline.

Although the synthesis of zeolites was reported as early as 1862, Barrer (1938) first successfully synthesized analcime-type

zeolites and confirmed them by x-ray diffraction (XRD). He was unable to synthesize either chabazite or mordenite, but instead produced a synthetic zeolite now designated as Linde type A, which is still one of the most commercially important synthetic molecular-sieve adsorbents. The Molecular Sieve Department of the Linde Company commercialized the technology to manufacture Linde type A as well as other synthetic zeolites.

Historically, natural zeolites were considered mineralogical curiosities that mostly occurred as amygdules in basaltic volcanic flows. Subsequently, Regnier (1960) and others discovered large sedimentary deposits of natural zeolites in the western United States. Later exploration identified other, very large zeolite deposits, particularly of clinoptilolite, in the western states and in more than 40 other countries in sedimentary, volcanoclastic rocks and also in hydrothermal deposits.

Synthetic zeolites have supplied many of the markets that natural zeolite products might have served because the synthetics were available first. Natural zeolite producers attempted to displace synthetic zeolites from uses and applications where natural zeolites would have been a better choice, but they lacked the product development and marketing skills needed to compete with the synthetic producers.

In 2003, worldwide production of synthetic zeolites for all applications was more than 2.2 Mt. Synthetic zeolites can be chemically tailored to meet stringent industrial specifications, whereas natural zeolites have a more fixed range of properties. This is changing with the recent introduction of heat-treated and surface-modified natural products. In many applications, natural zeolites have a significant price advantage over synthetics. Also, in some uses their performance is superior to synthetics, such as the use of chabazite from the Bowie deposit as an adsorbent in the treatment of acidic gases.

Mumpton (1983) described Linde's natural zeolite exploration in North America from 1957 through 1962. Shell Canadian began exploration for natural zeolites that could be used as petroleum catalysts in 1962. Mobil Oil Corporation also had a natural zeolite program and mined erionite from the Jersey Valley, Nevada, deposit. Efforts to develop extensive natural zeolite reserves and new products in North America led Anaconda Minerals Company and Occidental Minerals Corporation into major exploration and product development programs between 1974 and 1983. Tenneco Corporation and Phelps Dodge Corporation were late entrants to the zeolite business. None of these companies, however, generated significant sales, and they left the zeolite business.

Neither the oil nor mining companies understood that millions of tons of reserves were not needed to supply a small but growing industrial business whose sales were less than 5,000 tpy. Their lack of marketing expertise was the major cause of their failure. Dow Chemical Corporation, which acquired the molecular sieve business from UOP (the successor company to Union Carbide Corporation), is now the only major corporation in the natural zeolite business. The products sold by Dow are specialty, high-value-added materials that complement their synthetic molecular sieve product lines. The other producers are small entrepreneurial companies that, to their credit, are rapidly developing the products, applications, and marketing skills needed to sell their zeolite products. The natural zeolite business is an industry in transition.

For more than 40 years, natural zeolite minerals have been described as the industrial mineral of the future. The belief that natural zeolites had a multitude of uses and applications was fostered by an enormous outpouring of research that envisioned zeolites for applications in uses from animal absorbents to zeoponics. The potential applications were oversold. Unfortunately, very little of the

research managed to cross over into product development and then into salable products. The brevity of this chapter is intended to provide more easily accessible, useful information and a more concise bibliography, but readers may wish to consult the Zeolites chapters in the 5th and 6th editions of *Industrial Minerals and Rocks* for more detailed information.

GEOLOGY

Mineralogy

The following discussion on mineralogy, chemical properties, and physical properties reviews the works of Breck (1974), Flanigen (1977), and Mumpton (1978), leaders in the study of these complex silicate minerals. Zeolites occur in a variety of geologic settings, mostly as alteration or authigenic minerals, low-temperature–low-pressure minerals in metamorphic systems, secondary minerals in weathered zones, or in veins. Commercial zeolite production is currently limited to authigenic and alteration accumulations in finely crystalline sedimentary rocks. Nine zeolites commonly occur in sedimentary rocks: analcime, chabazite, clinoptilolite, erionite, ferrierite, heulandite, laumontite, mordenite, and phillipsite. Analcime and clinoptilolite are by far the most abundant. All nine of these show a considerable range in silicon:aluminum (Si:Al) ratios and cation contents. Except for heulandite and laumontite, they generally are alkaline and more siliceous than their counterparts in mafic igneous rocks.

Chabazite, clinoptilolite, erionite, mordenite, and phillipsite are the only zeolite minerals with commercial applications today. Erionite, which has been classified as a human carcinogen, has only limited industrial applications. These five are the only zeolites that are abundant in nature and have adequate ion-exchange, absorbency, or molecular-sieving capabilities. Ferrierite and faujasite may also have economic potential, but they are rare and known to occur at only a few localities in the world. It is possible that new technology may result in applications for other zeolite minerals.

Table 1 lists the chemical composition and selected properties of some possible economic zeolites as adapted from Mumpton (1978) and based on the Breck (1974) classification.

Breck (1974) originally listed 34 natural zeolite minerals. An additional 18 natural zeolite minerals have now been identified. The potential commercial application of both natural and synthetic zeolites is a result of their fundamental chemical and physical properties.

The basic structure of zeolites consists of $(\text{AlSi})\text{O}_4$ tetrahedra, wherein each oxygen is shared by two tetrahedra; thus, the atomic ratio $\text{O}:(\text{Si}+\text{Al})$ is 2. The net negative charge of the structure is balanced by exchangeable cations, which are loosely held within the central cavities and surrounded by water molecules. Although their chemical compositions are similar, each mineral has a unique crystal structure and thereby its own physical and chemical characteristics.

Table 2 shows a classification of natural and synthetic zeolites proposed by Breck (1974). Breck's classification is based on the crystal structure of the zeolites in seven groups. In each group, the zeolites have a common specific array of $(\text{AlSi})\text{O}_4$ tetrahedra. Although the same zeolite mineral from different localities may vary considerably in chemical composition, its crystal structure will be nearly identical. Conversely, zeolite minerals with very different crystal structures can have nearly identical chemical compositions.

The dimensions and orientation of void spaces and the interconnected channels in dehydrated zeolites are important in determining the physical and chemical properties. The three types of channel systems identified are a one-dimensional system, a two-dimensional system, and two varieties of three-dimensional, intersecting systems.

Table 1. Typical formulae and physical properties of zeolite minerals and their synthetic counterparts

Zeolite	Typical Unit-Cell Formula	Crystal System	Void Volume, %	Specific Gravity	Channel Dimensions, Å	Thermal Stability	Ion-Exchange Capacity, meq/g*
Analcime	$\text{Na}_{16}(\text{Al}_{16}\text{Si}_{32}\text{O}_{96}) \cdot 16\text{H}_2\text{O}$	Cubic	18	2.24–2.29	2.6	High	4.54
Chabazite	$(\text{Na}_2\text{Ca})_6(\text{Al}_{12}\text{Si}_{24}\text{O}_{72}) \cdot 40\text{H}_2\text{O}$	Hexagonal	47	2.05–2.10	3.7×4.2	High	3.81
Clinoptilolite	$(\text{Na}_4\text{K}_4)(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 24\text{H}_2\text{O}$	Monoclinic	39	2.16	3.9×5.4	High	2.54
Erionite	$(\text{Na}_2\text{Ca}_6\text{K})_9(\text{Al}_9\text{Si}_{27}\text{O}_{27}) \cdot 27\text{H}_2\text{O}$	Hexagonal	35	2.02–2.08	3.6×5.2	High	3.12
Ferrierite	$(\text{Na}_2\text{Mg}_2)(\text{Al}_6\text{Si}_{30}\text{O}_{70}) \cdot 8\text{H}_2\text{O}$	Orthorhombic	0	2.14–2.21	4.3×5.5	High	2.33
					3.4×4.8		
Heulandite	$\text{Ca}_4(\text{Al}_8\text{Si}_{28}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$	Monoclinic	39	2.10–2.20	4.0×5.5	Low	2.91
					4.4×7.2		
					4.1×4.7		
Laumontite	$\text{Ca}_4(\text{Al}_8\text{Si}_{16}\text{O}_{48}) \cdot 16\text{H}_2\text{O}$	Monoclinic	34	2.20–2.30	4.6×6.3	Low	4.25
Mordenite	$\text{Na}_8(\text{Al}_8\text{Si}_{40}\text{O}_{96}) \cdot 24\text{H}_2\text{O}$	Orthorhombic	28	2.12–2.15	2.9×5.7	High	2.29
Phillipsite	$(\text{Na}_2\text{K})_{10}(\text{Al}_{10}\text{Si}_{22}\text{O}_{62}) \cdot 20\text{H}_2\text{O}$	Orthorhombic	31	2.15–2.20	4.2×4.4	Low	3.87
					2.8×4.8		
					3.3		
Linde A†	$\text{Na}_{12}(\text{Al}_{12}\text{Si}_{12}\text{O}_{48}) \cdot 27\text{H}_2\text{O}$	Cubic	47	1.99	4.2	High	5.48
Linde X†	$\text{Na}_{66}(\text{Al}_{66}\text{Si}_{106}\text{O}_{364}) \cdot 264\text{H}_2\text{O}$	Cubic	50	1.93	7.4	High	4.73

* Calculated from unit-cell formula.

† Linde A and Linde X are synthetic phases.

The character of the water in hydrated zeolite crystals varies, because it can include molecular clustering or direct bonding between the cations and the framework oxygen molecules. The intercrystalline volume that may be occupied by water constitutes up to 50% of the volume of the crystal. The adsorption capacity of a zeolite is generally related to the free space or pore volume as determined by the quantity of contained water when fully hydrated at a standard temperature and humidity.

Adsorption and ion-exchange capacities in both hydrated and dehydrated zeolites are related to the characteristics of the channel openings. The apertures are bounded by oxygen atoms of the connected tetrahedra. The limiting size of the aperture is governed by the size of the rings, which contain 6, 8, 10, or 12 oxygen atoms.

Gottardi and Galli (1985), as a result of their study of zeolite mineralogy, proposed a classification with 23 types of zeolite framework, each corresponding to a particular species of zeolite, and a more specific classification of five framework groups for the natural zeolites.

Figure 1 illustrates the open structure of chabazite showing the enclosed channels.

Chemical Properties

The applications that use natural zeolites make use of one or more of the physical properties, which include adsorption, cation exchange, and dehydration or rehydration. These properties are functions of the specific crystal structure of each mineral, its framework, and its cationic composition.

Adsorption Properties

Crystalline zeolites are unique adsorbent materials. The large central cavity and entry channels of the zeolite are filled with water molecules that form hydration spheres around the exchangeable cations. If the water is removed, molecules having cross-sectional diameters small enough for them to pass through the entry channels are readily adsorbed in the channels and central cavities. Molecules too large to pass through the entry channels are excluded, which results in the molecular sieving property of most zeolites.

Table 2. Breck's classification of zeolites*

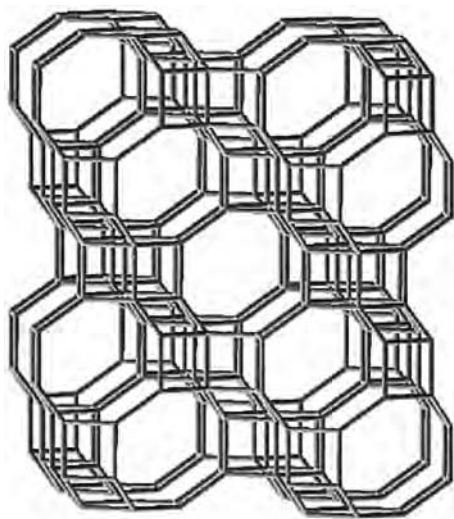
Group 1 (S4R)	Group 5 (T5O10)
Analcime	Natrolite
Harmotome	Scolecite
Phillipsite	Mesolite
Gismondine	Thomsonite
Paulingite	Gonnardite
Laumontite	Edingtonite
Yugawaralite	
Group 2 (S6R)	Group 6 (T8O16)
Erionite	Mordenite
Offretite	Dachiardite
Levynite	Ferrierite
Sodalite	Epistibite
	Bikitaite
Group 3 (D4R)	Group 7 (T10O20)
A-Type Zeolites	Heulandite
Group 4 (D6R)	Clinoptilolite
Faujasite	Stilbite
X	Brewsterite
Y	
Chabazite	
Gmelinite	

Adapted from Breck 1974.

* Expressions in parentheses refer to types of zeolite frameworks (e.g., D4R = double 4-ring, T5O10 = a unit of 5 tetrahedra).

Cation Exchange Properties

The exchangeable cations of a zeolite are loosely bonded to the tetrahedral framework and can be easily exchanged and removed by washing with a strong solution of another cation. Crystalline zeolites are very effective ion exchangers. The ion-exchange capacity is basically a function of the degree of substitution of aluminum for silicon in the framework structure. The greater the substitution, the



Adapted from *International Zeolite Association Atlas 2004*.

Figure 1. Open molecular structure of the zeolite mineral chabazite viewed along [010]

greater the charge deficiency, and the greater the number of alkali or alkaline earth cations required for electrical neutrality. Cation-exchange behavior also depends on other factors, including (1) the concentration of the specific cation in the solution, (2) the temperature, (3) the nature of the cation species (e.g., size, charge), and (4) the structural characteristics of the particular zeolite.

Cations can be trapped in structural positions that are relatively inaccessible, thereby reducing the effective ion-exchange capacity. Cation sieving may also take place if the cation in solution is too large to pass through the entry ports into the central cavities. Unlike most noncrystalline ion exchangers, the framework of a zeolite defines its selectivity toward competing ions, and different structures offer different sites for the same cation. The hydration strength of some ions prevents their close approach to the seat of charge within the framework. In many zeolites, ions having a low field strength are more tightly held and are more selectively taken up from solutions than the other ions.

Dehydration/Rehydration

Zeolites exhibit no major structural changes during dehydration; they do exhibit continuous weight loss as a function of temperature and will rehydrate. If the temperature required for complete dehydration is exceeded, the zeolite structure collapses and rehydration cannot occur. Most natural zeolites are thermally stable from 250°C to 400°C (482°F to 752°F). Zeolites with higher silica contents, such as mordenite and clinoptilolite, collapse at temperatures greater than 650°C (1,202°F).

Physical Properties

A zeolite can also be described by its physical properties and performance. The physical properties include morphology, crystal habit, specific gravity, density, color, grain or crystal size, degree of crystallinity, presence of corrosion or etching, presence of contaminants or diluents, and any other descriptive features.

Performance, which is the evaluation of the zeolite for any specific application, entails such characteristics as brightness, color, Brookfield viscosity, Hercules viscosity, surface area, internal volume, particle size and morphology, hardness, abrasion resistance,

wet abrasion durability, thermal expansion, resistance to weathering, and also cation exchange capacity (CEC).

Characterization of any zeolite requires an assessment of the mineralogical properties and the performance characteristics that are believed to be required for the specific use or application. When a specific zeolite is chosen for a commercial application, it must be tested in the environment of the planned use. The efficacy of the zeolite chosen for a use cannot be accurately predicted from properties such as bulk chemistry, zeolite content, or CEC. It is imperative to realize that “one size doesn’t fit all,” meaning that clinoptilolite from deposit A may react differently than clinoptilolite from deposit B.

Origin

Zeolite minerals occur in several geologic settings and can be formed from a variety of starting vitric or lithic materials within an extended range of physiochemical conditions. They occur in rocks deposited in diverse geologic settings and ages. Nearly all the productive deposits in North America occur in sedimentary and volcanoclastic formations of Tertiary age.

Volcanic glass of acid to intermediate composition is the most common precursor for zeolite minerals. Less common precursors include microcrystalline quartz, opal, and feldspars. Nearly all the mineable zeolite deposits in the world occur as zeolitized ash fall tuffs interbedded with lacustrine sediments, zeolitized vitroclastic tuffs in volcanic rocks, and zeolitized vitrophyres and vitroclastic tuffs as a result of hydrothermal alteration.

The development of a specific zeolite mineral depends on interrelated physical and chemical factors. Pressure, temperature, and time are three important factors that produce zeolitic alteration of the vitric precursor. The composition of the vitric component and the composition of the reactive pore water that contains cations such as H^+ , Na^+ , Ca^{++} , K^+ , and H_4SiO_4 are important factors needed to produce zeolitic alteration.

Most zeolites in sedimentary rocks formed from volcanic ash or other pyroclastic material by reaction of the aluminosilicate glass with saline-alkaline pore water. Others originated from the alteration of preexisting feldspars, feldspathoids, biogenic silica, or poorly crystalline clay minerals. Zeolites in sedimentary rocks probably formed by means of dissolution-precipitation reactions.

Earlier formed zeolite minerals can be altered to other zeolite minerals both in near-surface and in deeply buried environments. This is generally a result of changes in the physical parameters within the host rock or changes in the chemistry of the pore water. Natural zeolites have long been known to occur in basaltic rocks as veins and fillings of vugs and cavities. Only much later, because of the introduction of XRD for mineral identification, were they recognized as one of the most common groups of authigenic silicates in sedimentary rocks of volcanic origin.

Based on zeolite geologic setting, mineralogy, and genesis, Sheppard (1973) classified zeolite deposits into the following types:

- Closed system: Deposits formed from volcanic materials in hydrologically closed, saline/alkaline lake systems
- Open system: Deposits formed in hydrologically open, freshwater lake or groundwater systems
- Burial metamorphic: Deposits formed by low-grade, burial metamorphism
- Hydrothermal or hot spring: Deposits formed by hydrothermal or hot spring activity
- Deep marine: Deposits formed in deep marine environments
- Weathered zone: Deposits formed in soils, most commonly from volcanic materials

Closed System

Closed-system zeolite deposits formed in closed or partially closed hydrologic systems that had restricted movement of water out of the basin. The zeolite deposits that formed from accumulations of vitric ash fall tuffs in saline or alkaline lakes are the highest purity sources of the zeolite minerals clinoptilolite, chabazite, and erionite. Sheppard and Gude (1968, 1969b, 1973), starting with the study of a playa lake near Tecopa, California, found that tuffs deposited in such hydrologically closed basins are characterized by a later zonation: fresh ash near the margins of a basin, succeeded inward by a zone of almost complete zeolitization, a zone of analcime, and finally a central core of authigenic potassium feldspar.

The alteration to zeolites depended on high alkalinity and lake brines rich in HCO_3^- . Ash falls of glassy tuff into an alkaline-saline playa or rift lake provided the ideal setting for the formation of high-grade, closed-system deposits. Erionite, chabazite, and phillipsite characterize the saline, alkaline-lake deposits. Zeolitic tuffs in saline-lake deposits generally are from a few centimeters to a few meters thick. They commonly contain monomineralic or mixed zones of the larger pore zeolites erionite and chabazite, which are relatively uncommon in other types of deposits.

Open System

Open hydrologic systems are those in which percolating groundwater moved freely through the host rock. As the groundwater circulated, it was chemically modified by dissolution of reactive materials or hydrolysis. Clinoptilolite and mordenite are the principal zeolites of open-system deposits. The Campi anan Tuff and Neapolitan Yellow Tuff near Naples, Italy, are examples of thick, open-system zeolite deposits. These deposits were formed by alteration of volcanic ash by descending groundwater.

Burial Metamorphic

Zeolites may form in thick volcanoclastic sequences affected by metamorphism. Burial metamorphic deposits, also known as burial diagenetic deposits, are widespread in the Green Tuff region of Japan. With increasing depth, the deposits usually contain zones of (1) fresh ash, (2) alkali clinoptilolite, (3) clinoptilolite–mordenite, (4) analcime, and (5) albite that correlate with the depth of burial and related increases in temperature, pressure, and degree of metamorphism.

Hydrothermal or Hot Spring

The hot spring type includes zeolites associated with hydrothermal alteration, such as those at the East Tintic District, Utah, and especially those associated with hot springs. These occurrences show a vertical zonation and a downward succession of mineral assemblages that appears to correlate with an increase in temperature.

Deep Marine

The most common marine zeolites are clinoptilolite and phillipsite, formed from siliceous tephra and in low-silica basaltic tephra, respectively. Marine zeolites form at low temperatures and may replace as much as 80% of the marine sediments. Deep-sea drilling has found abundant clinoptilolite and phillipsite in cores from many localities in the Atlantic, Pacific, and Indian oceans.

Weathered Zone

Zeolite occurrences within weathered zones are scattered and of little economic significance. Analcime has been reported in alkaline, saline soils in the eastern San Joaquin Valley, California.

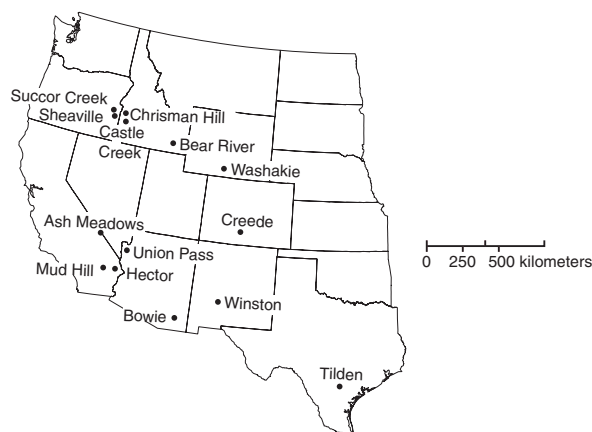


Figure 2. Locations of the producing zeolite deposits in the western United States

DISTRIBUTION OF MAJOR DEPOSITS United States

The western United States has several hundred known occurrences of natural zeolites, including all the zeolite minerals having commercial potential. Resources of clinoptilolite, mordenite, and erionite are extensive, whereas sources of chabazite and phillipsite are more limited. Ferrierite occurrences are restricted to two sites in Nevada; there are, however, no present uses or applications for this mineral. Figure 2 is a map of the western United States showing the locations of producing deposits, important explored but undeveloped deposits, and the principal zeolite minerals that occur in each of them.

Alabama–Mississippi

Low-grade clinoptilolite occurs in the Tallahatta, Nanafalia, Clayton, and Lisbon formations, the Porter Creek Beds, and the Meridian Sand in Alabama and eastern Mississippi (Reynolds 1970). Occurrences in the Porter Creek Beds and the Meridian Sand typically have less than 50% clinoptilolite. Their commercial potential is limited to soil amendments, animal absorbents, and floor sweep products.

Alaska

Mordenite, heulandite, and laumontite deposits occur in the vicinity of Sheep Mountain and Horn Mountain in the Upper Matanuska Valley of Alaska. Zeolitization is the result of burial diagenesis and regional metamorphism of volcanic rocks and related sediments of the Lower Jurassic Talkeetna Formation and the lower units of the Upper Cretaceous Matanuska Formation (Hawkins 1973).

Arizona

Forty-six natural zeolite occurrences have been identified in Arizona; they include open, closed, and hydrothermal deposits. In western Arizona, hydrothermal alteration modified some of the open-system deposits. Most of the open-system zeolites are in Cretaceous to Late Tertiary rocks. Generally, the open-system mordenite and clinoptilolite deposits are in thick sections of vitroclastic ash-flow tuffs and breccias, or clastic tuff units. These zeolite deposits are highly variable in quality because of their high content of fragmentary lithic material.

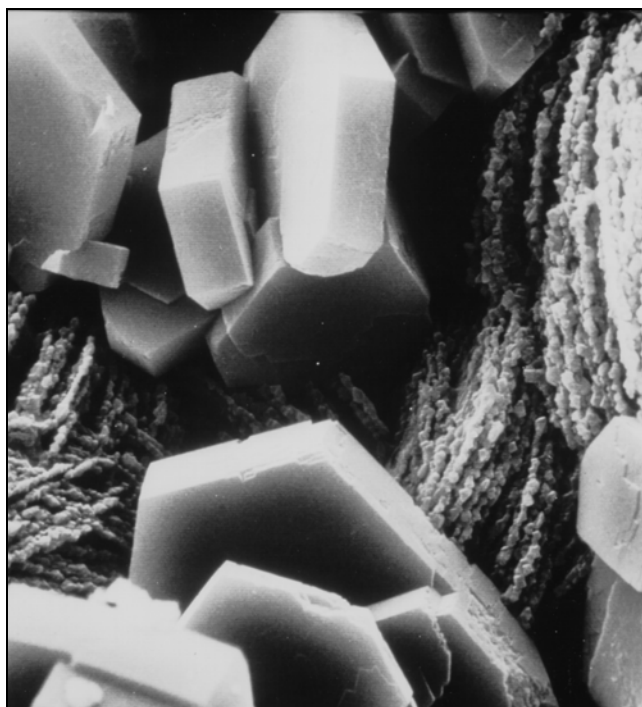


Figure 3. Chabazite "chains" and clinoptilolite crystals, Bowie, Arizona

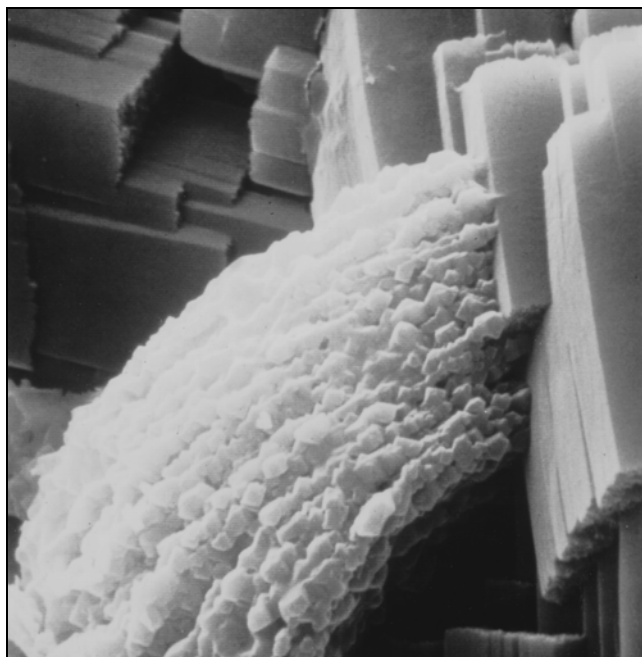


Figure 4. Chabazite "chains" and nonfibrous erionite crystals, Bowie, Arizona

Closed-system zeolite deposits occur in many of the Pliocene-Pleistocene intermontane basins in the Basin and Range Province of Arizona. These lacustrine deposits extend from the Wickenburg clinoptilolite deposit in the Big Sandy Basin in the northwest, through the Horseshoe Dam clinoptilolite deposit and the Dripping

Spring chabazite deposit in the central part, to the Bowie chabazite deposit in the San Simon Basin in southeastern Arizona.

Hydrothermal open-system mordenite and mordenite-clinoptilolite occur in Tertiary volcanic rocks in the Oatman and Union Pass areas and the Black Mountains in Mohave County. Mordenite and clinoptilolite occur in the alteration halo surrounding the Oatman gold deposit. This suggests that the zeolitic alteration was produced by the hydrothermal solutions that also transported the gold.

Union Pass Mordenite Deposit. The mine is about 32 km west of Kingman, Arizona, on State Highway 68 at the summit of Union Pass. Union Carbide Corporation shipped several carloads containing 70% mordenite from this deposit (Eyde 1977). A pink mordenite that breaks with a conchoidal fracture replaced a bed of vitrophyre and vitroclastic ash-flow tuff that contains almost no lithic fragments. The mordenite was ground, extruded, and thermally activated. It was sold as Linde AW 300 for the separation of acid gas streams.

Bowie Chabazite Deposit. A series of small strip mines produce chabazite from what was once a nearly continuous, north-west-trending, 15-km outcrop along the San Simon River, 24 km north of Bowie, Arizona. It is the largest known high-purity deposit of chabazite in North America (Sheppard et al. 1987).

The report of Lowe (1875) appears to be the earliest reference to a bedded zeolite deposit in the United States. Lowe reported an outcrop of what appears to be the marker tuff and described it as being composed of the zeolite mineral chabazite. The marker tuff bed was an airborne vitric ash that fell into a saline-alkaline lake and was subsequently altered to zeolite minerals. It is present in a section of Plio-Pleistocene lacustrine beds composed of unconsolidated clays, sand, and gravel.

The marker tuff, which ranges from 22 to 155 cm thick, is composed of varying amounts of chabazite, erionite, and clinoptilolite. It consists of a lower massive bed ranging from 10 to 20 cm thick, overlain by 4 to 135 cm of thin beds. The lower bed, designated as the ore or high-grade bed, contains nearly 100% zeolite minerals. At the northwest end of the deposit, the lower bed is more than 90% chabazite and less than 10% clinoptilolite (see Figure 3). In the central part of the deposit, the lower bed is about 80% chabazite and 10% erionite (see Figure 4). At the southeast end, the lower bed contains 90% chabazite and 10% clinoptilolite. The chabazite in the northwestern part contains more calcium than sodium; in the central part, the percentages of calcium and sodium are about equal; and at the southeastern end, sodium greatly exceeds calcium. The upper thin beds contain 60% to 70% zeolite minerals, principally chabazite and erionite.

The Linde Company acquired the deposit in 1961 and made the first shipment to its molecular-sieve manufacturing plant in North Tonawanda, New York, that same year. This was the first zeolite deposit brought into production in the United States. Several companies have produced more than 20 kt of 80% chabazite from the deposit over the past 42 years. All the production was from the lower massive bed.

The ore bed, which has been explored by more than 3,000 drill holes, has an average thickness of 20 cm. It is mined and carefully cleaned to ensure that all the upper bed and underlying clay have been removed.

The chabazite mined by Dow Chemical from the old UOP and Union Carbide property is processed into extrudates that are activated at 425°C (797°F). The chabazite products are used for natural gas purification, acid-gas drying, hydrogen drying, chlorinated and fluorinated hydrocarbon purification, hydrochloric acid (HCl) removal from by-product hydrogen streams, and the treatment of nuclear effluents. Chabazite from the Bowie deposit was

used to clean up the radioactive effluent from the damaged Three Mile Island nuclear reactor near Middletown, Pennsylvania (King and Opelka 1982; Bostick and Guo 1996).

GSA Resources crushes, screens, and thermally activates chabazite granules at a production plant in Tucson, Arizona. These products are used to remove thallium and heavy metals from mine water. As desiccants, the chabazite products maintain the motility of enzymes and bacteria used to inoculate silage and clean up sites contaminated by hydrocarbons. The upper thin-bedded unit has been used as a lightweight oil-well cement additive.

Horseshoe Dam Clinoptilolite Deposit. This deposit crops out on the east side of the Verde River near Horseshoe Dam, 89 km northeast of Phoenix, Arizona. The principal clinoptilolite bed ranges from 2.6 to 5.3 m thick and crops out continuously for 1.6 km. Most of the deposit is more than 90% white, high-brightness clinoptilolite. The clinoptilolite contains more strontium than calcium and, unlike the clinoptilolite from other deposits, adsorbs oxygen. A 5-t bulk sample was evaluated in a permeability machine pilot plant.

California

Stinson (1988) described the more than 100 known zeolite occurrences in California. Most are in Late Tertiary rocks in open or closed systems in an east-west belt in the Mojave Desert, extending from Mojave-Rosamond easterly about 190 km to Hector and Midway. A second belt of zeolite occurrences extends about 60 km from Tecopa and Shoshone north to the Ash Meadows deposit, northeast of Death Valley Junction.

Zeolite deposits of burial metamorphic or sedimentary origin are present in San Luis Obispo County, where mordenite with clinoptilolite replaced volcanic glass in tuffs of the marine Obispo Formation. Alteration by hydrothermal processes is represented by zeolitization of rhyolitic tuffs and pumice by hot-spring activity near Casa Diablo Hot Springs in Mono County.

Ash Meadows Clinoptilolite Deposit. This deposit is northeast of Death Valley Junction near the California-Nevada border. The zeolitized tuff occurs in an 8-km-long belt in unnamed Late Tertiary sedimentary rocks and extends north into Nye County, Nevada. White to yellowish-white zeolitized ash-flow tuffs and lapilli tuffs typically contain 80% or more clinoptilolite and exhibit high ammonia cation-exchange capacity. The exposed, altered tuff beds strike north-south, generally dip 25° east, and range in thickness from 100 to 130 m. Zeolitization is irregular, leaving some zones unaltered or weakly altered, which requires careful mining control (R.M. Colpitts, personal communication).

Anaconda Minerals Company drilled and developed this deposit with a small open pit, removing and stockpiling about 18 kt of material for bulk-sample testing to initiate production of the clinoptilolite (Santini and Knostman 1979). American Resource Corporation purchased the deposit from Anaconda. Their sources of clinoptilolite were the stockpile and the open pit at the California site. It was processed at the plant at Ash Meadows Rancho in Nevada, where it was crushed, screened, and bagged.

Badger Mining Corporation purchased the deposit, plant, and the assets of American Resource Corporation after the bankruptcy of the parent company, Rea Gold. The company constructed a new processing plant, purchased a packaging company, and began selling products including materials for swimming pool and spa filtration, absorbents, and deodorizers. Clinoptilolite from the Ash Meadows Deposit continues to be used at several sewage treatment plants and nuclear waste processing facilities.

Lake Tecopa Phillipsite Deposit. The Lake Tecopa phillipsite deposit is in the Pleistocene Lake Tecopa basin, between the towns

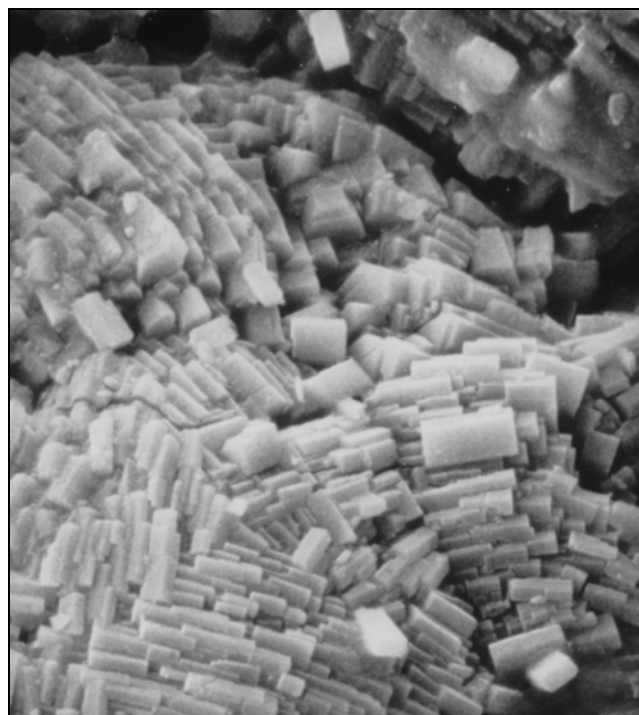


Figure 5. Phillipsite, Tecopa, California

of Shoshone and Tecopa. The Pleistocene sediments consist mostly of interbedded mudstones and altered to unaltered rhyolitic ash-fall tuffs. These interfinger with coarser clastic sediments toward the margin of the basin. Sheppard and Gude (1968) discovered that a fresh-glass facies occurs along the lake margin, succeeded basinward by a zeolite facies, and then by a central zone of potassium feldspar with sparse amounts of searlesite ($\text{NaBSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$), reflecting the changes in the chemical environment of the lake. Phillipsite is the predominant mineral in the zeolite facies, with lesser clinoptilolite, erionite, and minor analcime and chabazite (see Figure 5). Anaconda Minerals Company conducted an extensive drilling and sampling program on this deposit.

Hector Clinoptilolite Deposit. The Hector deposit is 65 km east of Barstow and 5 km west of Hector siding. The sodium-rich clinoptilolite is light green in color and attrition resistant, which makes it suitable for ion-exchange applications. This deposit produced high-purity clinoptilolite used in the treatment of radioactive effluent at the Hanford, Washington, Nuclear Test Station. Millions of liters of low-level cesium-137 have been processed through the zeolite ion exchangers at Hanford since the 1960s. At the National Reactor Testing Station at Arco, Idaho, steel drums filled with granular Hector clinoptilolite were used in ion columns to recover the radioactive isotopes of strontium and cesium.

Mud Hills Clinoptilolite Deposit. This deposit is about 13 km north of Barstow. It occurs in the Skyline Tuff unit of the Miocene-age Barstow Formation. Sheppard and Gude (1969b) described extensive clinoptilolite mineralization in the Skyline Tuff unit, which was mined at the Mud Hills open pit operated by Occidental Minerals Corporation. In 1982 the mine supplied British Nuclear Fuels Ltd. (BNFL) with high-purity clinoptilolite for ion-exchange applications. Two thousand tons of carefully mined and processed clinoptilolite were shipped to Sellafield, United Kingdom, for use in the BNFL nuclear fuel reprocessing facility. The Skyline Tuff is 3 to

5 m thick at the Mud Hills mine site and typically contains 70% to 90% clinoptilolite that has a high cation-exchange capacity. Since 1982, several successive owners have operated the mine, intermittently supplying clinoptilolite for use as adsorbents and cation-exchange media.

Colorado

The several clinoptilolite deposits in the state include the Creede deposit and the Sand Wash deposit near Craig. The latter is the stratigraphic extension of the Robin's Egg Blue clinoptilolite tuff member of the Washakie Formation in Wyoming (described in that section).

Creede Clinoptilolite Deposit. This deposit is in the Oligocene Creede Formation, about 3 km south of Creede. Altered ash-fall tuff units up to 7 m thick consist of white to light-gray, dense, massive clinoptilolite. The tuffs were deposited in a structural moat around the periphery of the Creede Caldera. Intermittent mining operations have tapped this deposit as a source for regional absorbent markets.

Idaho

Southern Idaho has several large clinoptilolite deposits in production.

Bear River Clinoptilolite Deposit. The Bear River deposit is 10 km from Preston, Idaho. Bear River Zeolite Company, a wholly owned subsidiary of U.S. Antimony Corporation, produces clinoptilolite from a green zeolitized tuff in the Eocene Salt Lake Formation that crops out over a large area in southeastern Idaho. These beds are equivalent in age and physical properties to those at the Mountain Green clinoptilolite deposit in the Salt Lake Formation east of Provo, Utah.

The company produces granular clinoptilolite products for several applications. These include a soil conditioner, cat litter, an algae control product for ponds, and preloaded zeolite fertilizers containing 2.5% nitrogen for use on turf. An absorption product manufactured by the company was successfully used to clean up an anhydrous ammonia spill from a ruptured railroad tank car. Bear River Zeolite continues to expand their customer base, both in the United States and in foreign countries (Anon. 2003, 2004).

Castle Creek Clinoptilolite Deposit. This deposit is 71 km south of Boise, Idaho. Discovered in 1962, it is the largest high-purity deposit of clinoptilolite found by the Union Carbide zeolite exploration program. The soft, fine-grained, ash-fall tuff unit in the Miocene Chalk Hills Formation is altered to fine-grained, white, high-brightness clinoptilolite. Double Eagle Petroleum and Mining Company acquired the deposit in 1976. A paper company evaluated several bulk samples of the clinoptilolite in 1982.

Sheppard (1993a) and Teague Mineral Products subsequently identified an extension of the clinoptilolite bed to the east and southeast along Castle Creek. Teague Mineral Products is actively mining and processing the clinoptilolite for sale in industrial and agricultural applications (G.A. Teague, personal communication).

Chrisman Hill Clinoptilolite Deposit. The Chrisman Hill deposit is 30 km north of Jordan Valley, Oregon. A thick, massive to thin-bedded zeolitized tuff bed occurs in the Miocene Sucker Creek Formation. The deposit consists of high-quality, white to light-gray clinoptilolite, similar in appearance to the Sheaville, Oregon, deposit 11 km to the south. The zeolitized zone is 20 m thick. It contains millions of tons of potential zeolite resources. The deposit, which straddles the Idaho-Oregon border, is mined by Teague Mineral Products to supply its processing plant in Adrian, Oregon. The Chrisman Hill deposit is on a weak hydrothermal alteration trend and shows evidence of hydrothermal alteration as well as obliteration of sedimentary structures (G.A. Teague, personal communication).

Montana

Clinoptilolite is reported from 14 localities in southwestern Montana, all in tuffaceous beds thought to be of Tertiary age and deposited in intermontane basins (Berg and Cox 2001). Clinoptilolite and mordenite occur in Cretaceous tuffs in Beaverhead County.

Grasshopper Creek Clinoptilolite Deposit. This deposit is 16 km southwest of Dillon, Montana. A section of Cretaceous tuffaceous beds is altered to clinoptilolite and minor amounts of mordenite. The cation-exchange capacity of 12 samples collected from the deposit ranges from 0.68 to 1.29 meq/g. Detailed mapping, surface sampling, and three drill holes indicate that this is a minable deposit (Berg and Cox 2001).

Nevada

Nevada has huge resources of zeolites, primarily in two geologic settings: Late Tertiary erionite-clinoptilolite-phillipsite-chabazite ash-fall tuff occurrences of closed system origin in northern Nevada; and thick Tertiary zeolitized ash-flow tuff occurrences of clinoptilolite and mordenite in central and southern Nevada.

Papke (1972) described four Late Tertiary closed-system deposits in north-central Nevada: Eastgate, Jersey Valley, Pine Valley, and Reese River. All the deposits occur in silicic ash-fall tuffs as thick as 5 m in sections of lacustrine sedimentary rocks. The principal zeolite minerals are erionite, clinoptilolite, phillipsite, and chabazite. Mordenite is less common in lacustrine tuff beds. The zeolites were formed by postdepositional diagenesis of vitric volcanic ash that fell into saline, alkaline lakes (Papke 1972).

Pine Valley Erionite Deposit. The Pine Valley deposit is 55 km south of Carlin, Nevada (Regnier 1960). Erionite and phillipsite occur in altered ash-fall tuffs in a thick sequence of Pliocene lacustrine rocks of the Hay Ranch Formation. The principal erionite bed strikes north-south, and dips 2° to 3° east. Union Carbide Corporation has operated the deposit intermittently since 1959 (Papke 1972). The principal zeolitized tuff bed is as much as 2 m thick and typically contains 80% to 90% erionite. Three to five thin beds of high-purity phillipsite occur in bentonitic sediments at the south end of the deposit.

Eastgate Clinoptilolite-Erionite Deposit. This deposit is 88 km east of Fallon, Nevada, and 5 km east of the junction of U.S. Highway 50 and Nevada Highway 2. The beds occur in the Monarch Mill Formation, an Early to Middle Pliocene sedimentary sequence (Papke 1972).

The zeolite beds are of closed-system origin in air-fall tuffs. One or more zeolite beds are present in a zone ranging in thickness from a few centimeters to as much as 5 m. The beds strike north to northwest, are exposed intermittently, and dip easterly at low angles. The most common zeolite associations are erionite and erionite-clinoptilolite accompanied by varying amounts of unaltered glass. Locally, chabazite, phillipsite, erionite-phillipsite, and mordenite are also present.

Union Carbide Corporation staked claims on the deposit in 1957 and dropped them after the Bowie, Arizona, chabazite deposit went into production in 1961. Anaconda Minerals Company staked mining claims on this deposit in 1970 and undertook a detailed exploration program. East-West Minerals, Ltd. later acquired the deposit and built a processing plant nearby. The company attempted to mine the southern part of the deposit, a short distance south of State Highway 2, and process the material for pet litter and absorbent uses. The venture was unsuccessful and the plant was dismantled and removed. In 1997 American Colloid built a state-of-the-art processing plant to produce animal absorbents at the site. Erionite was discovered in the zeolite and the plant was shut down. Badger Mining

Corporation purchased the plant and moved it to Ash Meadows (Eyde 2003).

Jersey Valley Erionite Deposit. The Jersey Valley deposit is 67 km southwest of Battle Mountain, Nevada. Ash-fall tuff beds within Late Tertiary lacustrine sediments are altered to erionite, erionite-clinoptilolite, and erionite-phillipsite-clinoptilolite in the deposit. Papke (1972) described the deposit, which has two zeolitic tuff beds that have minimum thicknesses of 2 to 3.5 m. Mobil Oil Corporation mined these zeolites by underground and open-pit methods from 1965 to 1970 to produce raw material for catalysts used in oil refining and natural gas purification.

Reese River Chabazite Deposit. This deposit is 56 km north of Austin, Nevada. Deffeyes (1959) identified chabazite, clinoptilolite, erionite, and phillipsite occurring in ash-fall tuffs within Miocene or Pliocene lacustrine beds. Eight zeolite beds thicker than 33 cm are present; one is as much as 2.5 m thick (Papke 1972). Union Carbide staked claims on the deposit in 1959 but dropped them after mapping and sampling the deposit.

Lovelock Ferrierite Deposit. This deposit is 17 km northwest of Lovelock, Nevada. Ferrierite-mordenite-clinoptilolite and ferrierite-mordenite occur in altered Miocene or Pliocene ash-fall tuffs. Clinoptilolite is a relatively minor constituent, occurring principally in the upper part of the stratigraphic section.

A remarkable concentration of ferrierite is present in the central part of the deposit. Here, a unit with an exposed thickness of about 17 m contains 75% to 95% ferrierite and minor amounts of mordenite and clinoptilolite. Apparently, this is the largest known deposit of ferrierite in the world (K.G. Papke, personal communication).

Many large deposits of clinoptilolite and mordenite occur in ash-flow tuffs, tuff breccias, and lithic tuffs in Nevada. Most of these occurrences are open system in origin, though some appear to be related to hydrothermal alteration as well. Typically, a large vitroclastic ash-flow zeolite deposit contains 30% to 80% zeolite and has abundant lithic fragments and unzeolitized crystalline and vitric material. Ammonia cation-exchange capacities are usually significantly lower than those in closed-system ash-fall tuffs.

Ash Meadows Clinoptilolite Deposit. An ash-flow zeolite deposit with large resources of high-quality clinoptilolite crops out at Ash Meadows, Nevada. The deposit straddles the Nevada-California border, northeast of Death Valley Junction, California. The deposit is described more fully in the section on California zeolites. The Nevada portion of the deposit includes a large resource of green clinoptilolite in Pliocene ash-flow and lapilli tuffs.

Beatty Mountain Mordenite Deposit. This deposit crops out on the west side of Beatty Mountain. Thick greenish-white mordenite beds are interbedded in a section of Pliocene ash-flow tuffs. Samples collected by Union Carbide contained from 70% to 85% mordenite.

New Mexico

There are two productive clinoptilolite deposits in New Mexico.

Buckhorn Clinoptilolite-Chabazite Deposit. This deposit is 58 km north of Silver City, New Mexico, and 2.5 km south of the community of Buckhorn on the west side of Duck Creek Valley. Two clinoptilolite beds crop out in the Plio-Pleistocene Cactus Flat beds. The lower bed is 1 to 1.6 m thick with 70% to 90% clinoptilolite and chabazite. The upper bed is about 30 cm thick and contains 60% clinoptilolite and a trace of erionite (Eyde 1982; Sheppard et al. 1987). Zeotech Corporation mined and shipped a few truckloads of clinoptilolite to their processing plant at Tilden, Texas.

Cuchillo Negro Clinoptilolite Deposit. The most productive clinoptilolite deposit in New Mexico is about 300 km south of Albuquerque and 6.5 km south of Winston. The deposit is in a 180-

to 240-m-thick section of interbedded tuffaceous and conglomeratic rocks that are 29 million years old (McIntosh, Kedzie, and Sutter 1991); it crops out along Cuchillo Negro Creek at the south end of the Winston graben. The zeolite bed being mined by the St. Cloud Mining Company is 4.4 to 10.7 m thick and contains 50% to 85% clinoptilolite that is more attrition resistant and has higher potassium content than most other clinoptilolite. In 2002 St. Cloud Mining Company mined and processed 14.5 kt of clinoptilolite products. These were sold into consumer, industrial, and agricultural markets throughout North America (Barker et al. 2003).

Oregon

Several natural zeolite deposits with economic potential occur in eastern Oregon. The zeolite occurrences in marine sedimentary rocks in western Oregon have no obvious commercial potential.

Durkee Chabazite Deposit. This deposit is in a closed basin near the community of Durkee, Oregon, 165 km northwest of Boise, Idaho. An area of about 18 km² is underlain by chabazite, clinoptilolite, erionite, and authigenic feldspar. Vitric ash fell in a Miocene saline alkaline lake and formed zeolite minerals at low temperature and pressure. The zeolitized ash-fall and reworked tuffs and one ash-flow tuff are interbedded with diatomite, mudstone, sandstone, siltstone, and conglomerate. The U.S. Geological Survey made several investigations of the deposit (Sheppard and Gude 1969a, 1980; Gude and Sheppard 1986, 1993).

Anaconda Minerals Company, Occidental Minerals Corporation, and Filtrol Corporation explored the deposit and identified several promising target areas containing possible large tonnages of chabazite, but their exploration results remain unknown.

The Harney Basin Clinoptilolite Deposits. The Harney-Malheur Basin is about 40 km south of Burns, Oregon. Near-surface Miocene tuffaceous rocks constitute an enormous zeolite resource. The principal mineral is clinoptilolite with lesser erionite, chabazite, phillipsite, and mordenite on the basin margins. The principal mineralized zone underlies an area of more than 20 km² (Sheppard 1993c). A massive clinoptilolite bed 20 m thick underlies much of the basin. Toward the southern margin of the basin, the clinoptilolite-rich tuff interfingers with thinner beds of erionite, chabazite, and phillipsite. The zeolite deposits of the Harney Basin formed as a result of diagenetic alteration of ash-fall tuffs and reworked tuffaceous fluvial sediments within a closed hydrologic system.

Rome Erionite Deposit. The Rome deposit is 60 km west of Jordan Valley, Oregon, near the Owyhee River and Crooked Creek in an area dissected by steep-walled canyons (Sheppard and Gude 1983, 1993b). The deposit has an extensive resource of high-purity erionite, mordenite, and mixed mordenite-clinoptilolite. The zeolites occur in several tuffaceous members of the Rome beds, a 130-m-thick Miocene fluvio-lacustrine sequence. Two zeolitized beds in the lower member initially appeared to have significant commercial potential. Each bed is about 3 m thick and contains 50% to 70% erionite. The fibrous morphology precludes its use in commercial and consumer applications.

Sheaville Clinoptilolite Deposits. The Sheaville deposits are 19 km north of Jordan Valley, Oregon, between U.S. Highway 95 and the Oregon-Idaho border. These deposits are present in at least 10 km² where the westward-flowing Succor Creek crosses the state border and the axis of a north-south trending anticline. The Sheaville District has large resources of high-quality clinoptilolite available for mining.

The Sheaville clinoptilolite sequence is in the Miocene Sucker Creek Formation, a lacustrine unit of interbedded tuff, zeolitized tuff, bentonite, and carbonaceous siltstone (Almner and Grim 1990; Sheppard and Gude 1983, 1993c).

As many as five thick, massive units of white to light gray, zeolitized ash-fall tuff crop out in the area. Clinoptilolite is the predominant zeolite, with trace amounts of mordenite. Zeolitization is most intense near the axis of the anticline (Holmes 1990).

Zeolite production by the Norton Company has been confined to the uppermost clinoptilolite bed on the western flank of the anticline. The bed is well exposed several hundred meters east of U.S. Highway 95, near the western edge of the zeolitized area. The lowest clinoptilolite bed is the thickest in the district and crops out on the south side of Succor Creek. It is as much as 22 m thick and consists of white to light-gray massive clinoptilolite. Occidental Minerals Corporation drilled this bed between 1977 and 1981 and opened a large test pit near the anticline axis in 1982.

Succor Creek Clinoptilolite Deposits. These deposits are 13 km north of Rockville, Oregon, and just south of Succor Creek State Park. Several deposits of white to light gray, massive, and sandy zeolitic tuff occur in the Miocene Sucker Creek Formation along the lower part of Sucker Creek, both within and downstream from the state park (Almner and Grim 1990).

The beds contain 30% to 70% clinoptilolite and are up to 26 m thick. These occurrences have a hydrothermal alteration overprint and generally are more variable and less altered than the Sheaville and Chrisman Hill deposits (Altaner and Teague 1993). Teague Mineral Products operates an open pit in the lower Succor Creek area to extract clinoptilolite for pet litter and odor control uses.

South Dakota

The only important occurrence of natural zeolites in South Dakota is the Sheep Mountain Table clinoptilolite deposit.

Sheep Mountain Table Clinoptilolite Deposit. This deposit is on the Pine Ridge Indian Reservation near Rockyford, South Dakota. An extensive resource of clinoptilolite occurs in zeolitic tuff in the Rockyford Member of the Miocene Sharps Formation, which caps hills and mesas in the badlands on the Pine Ridge Indian Reservation and adjacent Badlands National Monument to the north (Raymond 1986). The zeolite-rich tuffs are as much as 33 m thick and are of open-system genesis. The clinoptilolite content is in the 50% to 60% range, with ammonia cation-exchange capacity values of 0.6 to 1.40 meq/g (Desborough 1989). The deposit is not developed.

Texas

Texas has large resources of clinoptilolite in two regions (Walton, et al. 1972). In south Texas, a belt of zeolitized ash-fall tuff in the Wellborn and Yegua formations of the Eocene Jackson Group of Gulf Coast sediments extends from Zapata County on the Rio Grande River northeasterly, cropping out west of Tilden in McMullen County, and extending east toward the Gulf of Mexico.

Large resources of clinoptilolite also occur in zeolitized ash-fall tuff beds and tuffaceous sediments in the Oligocene Tascotal Formation in the Trans-Pecos region between Presidio and Marfa (Bostros 1976; Walton and Henry 1979).

Tilden Clinoptilolite Deposits. A cluster of clinoptilolite deposits is located 8 to 13 km west to northwest of Tilden. The Buck Martin pit has a flat-lying, white, flaggy, zeolitized ash-fall tuff 3 m thick containing as much as 80% clinoptilolite. The nearby Kuykendall pit has a 4-m-thick bed containing 90% clinoptilolite. The Tilden Area zeolite resources are large, but they occur in scattered deposits. Zeotech Corporation mines and processes clinoptilolite into pet litter, swimming pool filtration media, a turf treatment product, material for ion-exchange applications, and other generic absorbent products (Eyde 2003).

Utah

Zeolite occurrences have been identified at 56 localities in Utah. Six sedimentary clinoptilolite deposits may be minable.

Trenton Clinoptilolite Deposit. The Trenton deposit is located along the west side of Cache County about 35 km north-northwest of Logan, Utah, and extends northward into Idaho. It is a zeolitized ash-fall tuff in the Tertiary Salt Lake Formation. (See the description of the Bear River Clinoptilolite Deposit in the Idaho section [Mayes and Fripp 1991].)

The zeolitized green, fine-grained tuffs constitute a very large potential resource, containing as much as 70% clinoptilolite. It is a high-potassium clinoptilolite deposit, similar to the Mountain Green occurrence to the south.

The Mountain Green Area in Morgan County contains estimated zeolite resources greater than 240 Mt. The clinoptilolite content commonly is 50% to 80%.

Wyoming

Natural zeolites have been described at 88 locations in Wyoming. Potentially minable zeolites, in order of importance, include clinoptilolite deposits in the Washakie Basin, along Beaver Rim, and on Lysite Mountain (Harris and King 1990).

Washakie Basin Clinoptilolite Deposits. This deposit is about 73 km east of Rock Springs, Wyoming. Roehler (1973) discovered and described the Washakie Basin clinoptilolite. The report identified clinoptilolite and mordenite in tuffs of the Laney Shale Member of the Green River Formation and in tuffs in the Robin's Egg Blue tuff bed of the Adobe Town Member of the Washakie Formation. The Robin's Egg Blue bed is a light blue to greenish-blue zeolitized ash-fall tuff altered to 50% to 90% clinoptilolite. Extensive drilling and testing indicate that the clinoptilolite is suitable for a wide range of applications, including nuclear waste cleanup.

Rocky Mountain Energy Corporation (now Union Pacific Resources-Minerals) attempted to develop clinoptilolite in its checkerboard sections on the north rim of the Washakie Basin between 1978 and 1983. The venture also produced limited tonnages of the blue-green clinoptilolite for cat litter and other deodorant applications (Hulbert 1987).

U.S. Zeolite Corporation subsequently leased the Rocky Mountain Energy fee lands and claims and obtained state mineral leases covering other promising clinoptilolite occurrences along the rim. The company is now doing testing and marketing studies and has produced small tonnages of clinoptilolite for absorbent and industrial uses (T. van Fleet, personal communication). Adwest Minerals International acquired U.S. Zeolite and now controls the deposit.

Beaver Rim Clinoptilolite-Chabazite Deposit. The Beaver Rim deposit is near Riverton, Wyoming. Several beds of clinoptilolite, mixed clinoptilolite-chabazite and clinoptilolite-erionite occur in ash-fall tuffs in the Eocene Wagon Bed Formation in the district, in Fremont County (Boles 1968; Van Houten 1964). U.S. Energy Corporation produced and sold small tonnages of clinoptilolite during the 1980s to western aquacultural markets and to an experimental sewage treatment plant developed by ATEC Inc. in Riverton.

Zeolites Outside the United States

Natural zeolites are being produced in 37 countries and occur in another 28. Production is intermittent and figures are unreliable (Harben and Bates 1990). The major producing countries are China, Cuba, Japan, the United States, Hungary, and Bulgaria. Smaller tonnages come from Australia, Germany, New Zealand, Italy, and South Africa. More new discoveries of natural zeolite minerals are being reported. Most of the discoveries are minor

occurrences that will never be put into production because of their impurities or size. Many of the deposits being mined in developing countries supply crushed and quarried products used in agriculture and construction. Only the deposits that are in production or are being explored are described here. For more comprehensive information on the distribution of zeolites, refer to the 5th and 6th editions of *Industrial Minerals and Rocks*.

The following countries are also known to have zeolite deposits that are not being explored or developed:

- | | |
|--------------|--------------------|
| • Algeria | • Namibia |
| • Austria | • The Netherlands |
| • Chad | • Pakistan |
| • Denmark | • Papua New Guinea |
| • Egypt | • Philippines |
| • Iran | • Puerto Rico |
| • Israel | • Senegal |
| • Jamaica | • Spain |
| • Kenya | • Switzerland |
| • Malawi | • Taiwan |
| • Mali | • Tunisia |
| • Mauritania | • Uganda |
| • Mongolia | • United Kingdom |

Cuba has done extensive research on the agricultural applications for natural zeolites. In fact, most of the natural zeolite research was done in the communist Eastern bloc countries before the collapse of the Soviet Union. Since then there has been a significant transfer of technology from these countries to entrepreneurial companies based in the capitalist countries for commercialization. One of the best examples is the ZELflocc technology for sewage treatment developed in Hungary and licensed by Zeolite Australia. The company now has 14 wastewater treatment plants in operation using the process (Eyde 2000).

In the case of China, Russia, and many other countries, the information is incomplete and possibly inaccurate. Some of the information has been provided verbally, and may be lacking in credible documentation. It is presented here, nevertheless, to provide the most complete reference on natural zeolite mineralogy, occurrences, uses, and applications. Certainly, in the future, other deposits will be discovered and brought into production from deposits in countries that are not mentioned in this chapter.

Argentina

Cristamine SA processes and sells clinoptilolite from local sources for use in animal feeds.

Australia

Natural zeolites occur in Paleozoic rocks in the Drummond Basin, Queensland, and in rocks from Late Carboniferous to Tertiary age in New South Wales. Production of zeolite from New South Wales is limited to two producers with a total production of about 7 ktpy. Zeolite Australia Ltd. has produced and sold clinoptilolite from sources in New South Wales since 1988. Zeolite Australia operates the Escott mine and processing plant, 5 km southwest of Werris Creek, New South Wales. Zeolites from this deposit are being used in many parts of Australia and some are being exported. The production is about 4 ktpy (Anon. 2004).

A number of reports have been published on the occurrence of natural zeolites in New South Wales (Holmes and Pecover 1987; Crossley 2002; Cullen 2004).

Curumbin Sand and Gravel Pty Ltd. operates a zeolite mine at Willows, in central Queensland. Currently, production is 3 ktpy.

Supersorb Environmental NL processes zeolite through its crushing and screening plants at Springvale and Duaringa, central Queensland (Anon. 2004).

Bulgaria

Extensive zeolite deposits occur in Bulgaria. The principal deposits are in the Srednogorian zone south of the Balkan Mountains and the Eastern Rhodopes (Gottardi and Obradovic 1978).

In the Rhodopes, large deposits of clinoptilolite and mordenite occur in the Oligocene rhyolitic pyroclastic rocks. A bed of white clinoptilolite 35 m thick crops out near the village of Perperek. A clinoptilolite bed 110 m thick occurs in a section of Oligocene tuffaceous sediments between the villages of Beli Plast and Mest.

Clinoptilolite has been produced from the deposits in the Eastern Rhodopes for many years. Bentonite EAD in Kardjali operates a surface mine at White Hill that has a capacity of 50 ktpy. Clinoptilolite production over the past 10 years has ranged from 2 to 45 ktpy. The clinoptilolite products are used in detergents, water filtration, food additives, and gas treatment, and as soil conditioners and fertilizer carriers.

Canada

Sedimentary zeolites that were discovered in Tertiary basins in interior British Columbia during the 1980s are now being brought into production. Clinoptilolite and heulandite occurs in Tertiary sedimentary rocks in the Cache Creek, McAbee, and Battle Creek areas. The rhyolitic tuffs of Eocene age contain clinoptilolite beds that range from 1 m to 6 m thick (Read 1987).

Several companies produce clinoptilolite from deposits in the Princeton and Cache Creek basins in British Columbia. Canmark International Resources explored and began clinoptilolite production from a deposit in the Princeton Basin. Highwood Resources produces clinoptilolite–heulandite from a deposit in Cache Creek. The zeolite is processed into agricultural products at Rocky Mountain House, Alberta.

China

Clinoptilolite and mordenite deposits occur at a number of locations throughout China. Six producers are reported in the country. Most of the production is from deposits in altered volcanic rocks of open-system origin. Most of the estimated 3 Mtpy of zeolite produced in China goes into pozzolanic applications. The balance goes into agricultural and industrial applications. Chabazite, phillipsite, and erionite are reported in closed-system settings in interior desert plays.

The U.S. Geological Survey estimates that the worldwide (not including China) production of zeolites in 2002 was 3.5 Mtpy. Thus, the estimated Chinese zeolite production is nearly equal to production in the rest of the world. Assuming that the production estimate is close to being correct, China is the world's largest producer of zeolite minerals.

Cuba

Exploration for natural zeolites that began in the 1970s has developed resources of more than 300 Mt, principally clinoptilolite–heulandite and mordenite (Griffiths 1987; Fuentes and Gonzales 1991). Cuba may be the world's second largest producer of zeolites. In 1994 the Cuban International Marketing Firm for Industrial Minerals SA (CIMTEC) reported exports of 100 kt for agricultural applications.

There are at least 25 zeolite deposits in Cuba. Most deposits consist of altered volcanic tuffs within volcanogenic sedimentary rocks of Lower Cretaceous and Middle Eocene age.

Clinoptilolite–heulandite resources include the Tásajeras-Piojillo, San Antonio, Najasa, and La Pita deposits. The Palmarito and San Cayataro deposits are nearly pure mordenite. Five plants having an overall annual production capacity of 500 kt are currently processing zeolites mined from four deposits (Anon. 1988).

France

Exploration in France for economic zeolite deposits began in 1989, principally in the Massif Central region. Three areas of promising discoveries include clinoptilolite and heulandite in ash-fall sediments of the Limagne Bourbonnaise Basin and phillipsite in ash-pumice tuffs originating from stratovolcanoes of the Cantal and Mont-Dore regions (Rocher et al. 1991).

Clinoptilolite occurs in Upper Cretaceous marls and chalks in the Anjou District on the west side of the Paris Basin. It has also been detected in Paleogene marine sediments of that basin. Analcime and clinoptilolite are present in sediments containing volcanic debris in the Limagne de Clermont-Ferrand (Gottardi and Obradovic 1978).

No production has been reported from these deposits, although Materials de la Mediterranee SA processes zeolites and Poortershaven processes zeolites for animal feed at its plant in Poissy, France.

Germany

Rocks containing zeolite minerals are mined from several deposits in Germany. Nearly all the production is used as pozzolan. Clinoptilolite occurs in Upper Cretaceous marls and marly limestone. It is used in the manufacture of cement at plants near Hannover and surrounding areas in northwest Germany.

Quaternary volcanic rocks in the Bonn and Laacher See areas of the Rhine region contain zeolitized pumiceous tuffs that are mined for pozzolans. The zeolite minerals include chabazite, phillipsite, and analcime.

The largest producer of zeolites in Germany is Hans G. Hauri Mineralstoffwerk in Botzingen-Oberschaffhausen. The company produces 150 ktpy of a zeolitically altered phonolite that contains 40% zeolite. The principal minerals are natrolite, scolecite, and lesser amounts of mesolite, thompsonite, and phillipsite. Nearly all the production is sold as a pozzolan. The fines are sold to vineyards in the Rhine and Mosel valleys where they are used as a highly effective nontoxic fungicide. The fines are also used in personal care products.

Franke & Schulte GmbH, H.J. Schmidt Mineraltechnik GmbH & Co., and Carl Spaeter GmbH custom process and sell zeolite products.

Greece

The Institute of Geology and Mineral Exploration and the Institute of Geological and Mining Research identified zeolitically altered tuffs on the islands of Milos and Polyaeos, and also in the Evros Area in mainland Greece (Tsirambides, Filippidis, and Kassoli-Fournarakis 1993; Tsolis-Katagas and Katagas 1990).

Silver & Baryte Mining Company SA began producing zeolite from the Evros deposits in 1996. The deposits are estimated to contain 6 Mt of 75% clinoptilolite. The company produces five clinoptilolite products that are used as supplements in animal feeds, soil amendments and conditioners, water treatment, animal litter, and absorbents.

Hungary

Major deposits of clinoptilolite and mordenite occur in the zeolitically altered Sarmatian rhyolitic tuffs and ignimbrites in the Tokay

Mountains. The zeolite deposits contain 65% to 95% clinoptilolite (Gottardi and Obradovic 1978).

Clinoptilolite is mined from the Ratka deposit and mordenite is mined from the Bodrogkeresztúr deposit. Hungarian production of natural zeolites was estimated to be 40 to 50 kt in 1987 (Griffiths 1987). In 1997 the production was estimated to be 15 kt.

The principal markets for the clinoptilolite products are feed supplements, products for ammonia–nitrogen removal from aquariums, and cat litter. The specialty products sold in Hungary include a deodorizer for wineries, a kitchen scrubbing compound, and a bathroom cleaning and deodorizing product.

Indonesia

Altered volcanic rocks hosting natural zeolites have been identified on several islands in Indonesia. Several recently developed clinoptilolite deposits are providing zeolite products to regional agriculture and aquaculture industries.

Eastmet Ltd. is developing a clinoptilolite deposit at Mt. Ratai and Tarahan in Lampung Province, Sumatra. Another zeolite deposit 20 km south of Panjung, the major port in Lampung Province, is currently producing crushed and screened clinoptilolite product for use in local aquaculture markets. Clinoptilolite and mordenite are produced from a mine on Java and made into products for sale throughout the eastern Pacific Rim.

Italy

Italy has a great number of zeolite occurrences, ranging from the extensive Neapolitan and Campanian zeolitic tuff systems in central Italy near Naples and Rome to zeolites of marine origin in Sicily. Burial metamorphic and hydrothermal origin zeolitic tuffs occur in the Apennines in northern Italy.

The Neapolitan Tuff, the Campanian Tuff, and equivalent volcanic formations crop out over extensive areas around Rome and the Gulf of Napoli. The deposits in these tuff beds are the economically important ones in Italy. Both tuffs contain phillipsite and chabazite in beds from 20 to 120 m thick and have been used since Roman times as dimension stone (Aiello 1993). Both are sources of raw materials used in a wide range of industrial and agricultural applications. Coarse pyroclastic rocks from the Roccamonfina Volcano, about 50 km northwest of Naples, contain significant amounts of chabazite and analcime and are quarried as building stone.

Tuff layers in a thick Quaternary pyroclastic sequence from the calderas of the Vulcano Laziale, about 20 km east of Rome, contain chabazite and phillipsite. Chabazite occurs in altered zones in tuffs and ignimbrites within Quaternary calderas in the Latium region near Rome. Lenzi and Passaglia (1975) described chabazite occurrences at Bracciano Lake that constitute more than 50% of the tuff.

Mineraria del Mediterraneo Italia Srl. produces 4 ktpy of chabazite and phillipsite from its mine in Sorano, Grosseto, about 100 km north of Rome. Its zeolite products are used in water treatment and animal feeds.

Japan

As a leading producer of natural zeolites, Japan is also a world leader in development and application of zeolite technology. It utilizes zeolites for a wide range of agricultural, industrial, and consumer uses. Annual production has ranged from 60 to 100 kt since the mid-1960s. Torii (1978) and others studied Japanese natural zeolite deposits and described their uses and applications. Zeolites occur in rocks ranging from Triassic to Quaternary in age, but the majority is in Miocene pyroclastic and volcanogenic

sedimentary rocks. Most zeolite occurrences in Japan are related to low-grade metamorphism. Many occurrences show zonation typical of burial metamorphism; others show zoning caused by hydrothermal alteration related to igneous intrusion.

Clinoptilolite and mordenite are the only zeolite minerals mined in Japan. Both minerals have been used for industrial and agricultural applications since 1949. Both minerals occur in the Green Tuff belt of metavolcanic rocks, but clinoptilolite is the most important zeolite mineral in Japan.

Eighteen companies produce between 140 and 160 kt per year of natural zeolites in Japan. Only eight produce significant quantities, and only three produce more than 10 ktpy. Clinoptilolite is produced at the Itaya mine in Yamagata Prefecture, Honshu, and processed by the Zeaklite Chemical & Mining Company, Ltd. for use in agricultural and other applications. The company produces at least 60 ktpy and is Japan's largest zeolite producer. Sun Zeolite Ind. Co., Ltd. produces clinoptilolite from its deposit in Akita Prefecture for agricultural use (Griffiths 1987). Nippon Kasseihakudo Co., Ltd. produces by-product clinoptilolite from its calcium-bentonite operations. The company also produces synthetic zeolite A using clinoptilolite as the raw material.

Smaller Japanese producers include Shinshinden Development Co., Ltd. (mordenite and montmorillonite), Hamamichi Kohsan Co., Ltd. (zeolite and montmorillonite), and Asahi Kasei Kogyo Co., Ltd. (mordenite) (Griffiths 1987). Other markets for Japanese zeolites are adsorption and water treatment.

Korea

Clinoptilolite-heulandite and mordenite deposits occur in both countries on the Korean peninsula. In the Democratic People's Republic of Korea, zeolites occur in Pliocene acid volcanic rocks in the Kilcho-Mjong Chong Province, which is in the northeastern part of the Korean peninsula. Clinoptilolite- and mordenite-rich tuffs also occur in the northeastern part of the province, near the villages of Han Zin and Phoha. Two clinoptilolite deposits in the southwestern part of the province contain clinoptilolite, heulandite, phillipsite, and chabazite (Han et al. 1985).

Clinoptilolite and mordenite occur within altered Miocene tuffs and tuffaceous sediments in the Guryongpo Area in the Republic of Korea (Noh and Kim 1982). The Kuryong mine at Kuryong and the Dalsin mine at Tonghai, both in Kyongsangbuk Province, produce 110 ktpy of clinoptilolite products.

Mexico

Natural zeolites occur in altered Tertiary volcanics and lacustrine beds in Mexico. A chabazite-erionite bed 12 to 14 cm thick occurs in Plio-Pliocene lacustrine beds in the extension of the Santa Barbara Valley south of Agua Prieta, Sonora. The deposit is nearly identical to the Bowie, Arizona, chabazite deposit 120 km to the north, both in extent and mineralogy. The erionite from the deposit was tested for use in petroleum-cracking catalysts and radioactive waste treatment.

A clinoptilolite-mordenite deposit near Rancho Tetuache, 20 km south of Arizpe, Sonora, is a zeolitized vitroclastic tuff more than 200 m thick that contains 80% to 90% combined clinoptilolite and mordenite. A 20-ton bulk sample was used to treat the runoff from cattle feed lots. There are several other zeolite occurrences in the state of Sonora.

Zeolite deposits occur at Etla and San Antonio, Oaxaca, and in the states of San Luis Potosí, Puebla, and Guanajuato. Over four centuries, large buildings in southern and central Mexico, including a cathedral at Oaxaca, have been built of clinoptilolite-mordenite-rich tuffaceous rocks because of its strength, workability, and durability.

Geoexplorers International began processing test lots of clinoptilolite at a toll-processing facility in the city of San Luis Potosí. The clinoptilolite is mined from the Escalera deposit in the state of San Luis Potosí and the Almandina deposit in the state of Guanajuato (Eyde 2000).

New Zealand

Natural zeolites are abundant in the Waitemata Group, an Early Miocene sedimentary sequence in Auckland Province. The main part of the group consists of sediments where clinoptilolite and chabazite occur in interbedded volcanoclastic rocks. NZ Natural Zeolite has begun producing zeolite products. It supplies a range of products used as adsorbents in ion-exchange applications and fertilizer carriers (Eyde 2000).

Republic of South Africa

Clinoptilolite is produced from altered Jurassic volcanic rocks at the Pratley Perlite Mining Co. Pty. Ltd. mine at Hluhluwe in what is now the province of KwaZulu-Natal. Both clinoptilolite and mordenite are associated separately with perlite and white calcium bentonite, which are also mined and processed (Griffiths 1987).

Romania

Large deposits of clinoptilolite and mordenite occur in Late Tertiary tuffs in the Transylvanian Basin and in the Precarpathian zone. These tuffs are commonly tens of meters thick and have been used for hundreds of years as building stone. They are of open-system origin and offer significant economic potential (Istrate 1980).

Russia

Research done in the former Soviet Union developed a wealth of potential applications for zeolite minerals. In fact, the Soviet Union was probably ahead of Japan in technological capability to develop new zeolite-based products, but the Soviets, unlike the Japanese, did not have the product development and marketing expertise needed to sell their products. Most of the Russian zeolite production is used in agricultural applications. The widespread radioactive contamination of soil and water caused by the Chernobyl nuclear reactor disaster required the development of decontamination techniques that utilized natural zeolites (Chelishchev 1993).

Gottardi and Obradovic (1978) presented a cursory overview of Soviet natural zeolite occurrences and geology. Tsitsishvili (1988) summarized earlier information on Soviet zeolite research and commercial application, including zeolite synthesis.

Salavatnefteorgsintez and Bashneftekhinzavody I Shimbay Special Chemical Catalysts produce zeolites in Russia. Both of these plants are in the Bashkortostan region. Production at Bashneftekhinzavody is about 8 ktpy of clinoptilolite used as a pozzolan in cement.

Serbia

Zeolites occur in open, hydrothermal, and burial metamorphic deposits in Serbia. Clinoptilolite and mordenite are present in altered pyroclastic rocks of Triassic to Late Tertiary age. Clinoptilolite is mined for local use, mostly for agricultural, from several deposits.

Slovakia

Natural zeolites were discovered at Nizny Hrabovec in eastern Slovakia in 1976. Reserves of more than 7 Mt ranging in grade from 40% to 60% clinoptilolite have a mean cation-exchange capacity of 0.78 meq/g. K.S.K. (Kosice) mines between 7,000 and 12,000 ktpy of clinoptilolite from a deposit at Bystra Nad Toplou.

Slovenia

Zeolites are mined and processed at Zaloska Gorica. The operation produces ground and micronized clinoptilolite for pozzolan and agricultural use.

Spain

Mordenite occurs in an Upper Miocene bentonite sequence near Cabo de Gata, about 14 km from Almeria. Montmorillonite is the major component of the bentonite, with mordenite the next most common mineral. Minas Volcan SA has capacity to mine 10 ktpy of zeolites from quarries in Almeria Province. Bentonitas Especiales SA mines and processes zeolites in Madrid Province in conjunction with its bentonite mining operations.

Turkey

There are several very large deposits of clinoptilolite in the central part of the Bigadic Basin. The largest deposit is reported to have an extensive reserve of 82% clinoptilolite. About 9,000 tpy are produced by Yapi Insaat ve Ticaret AS and Zeolitas Turizm Yapi Ticaret ve Sanayi AS (C. Turner, personal communication).

Ukraine

Several large clinoptilolite deposits are present in the Ukraine. The Sokimitsa deposit in the Transcarpathian Ukraine contains 60% clinoptilolite that has a cation-exchange capacity of 1.44 meq/g. The Zatisyansky Chemical plant at Zakarpaty produces about 15 ktpy of clinoptilolite.

TECHNOLOGY

Exploration Techniques

Most productive deposits occur in zeolitized vitroclastic tuffs or tuffaceous sediments of Tertiary or, to a much lesser extent, Mesozoic age. Though deposits in other geologic settings may be developed in the future, it is almost certain that bedded deposits will remain the principal source of natural zeolites.

Exploration for zeolite deposits is a challenge. When the Union Carbide exploration program began in 1958, no one had ever explored for zeolite deposits. In fact, almost no one except for company geologists knew where zeolite deposits occurred, much less what the outcrop of a zeolite deposit looked like.

Union Carbide used a simple but effective technique to locate the white to yellowish-white outcrops of zeolite deposits in the intermontane valleys of the western United States. Geologic maps of the Tertiary formations in the valleys were nonexistent. The geologists flew in light aircraft at an altitude of about 150 m above the terrain and posted the light-colored outcrops on 1:250,000 scale topographic maps. The outcrops were sampled, and if the sample adsorbed carbon dioxide in the portable field adsorption unit, the outcrop was extensively sampled and mapped. The samples were then sent to the Linde Company laboratory in Tonawanda, New York, for oxygen adsorption and XRD analysis.

The exploration program based on visual analysis from aircraft was effective. The program discovered every zeolite deposit now in production. Unfortunately, the Molecular Sieve Department of the Linde Company was interested only in chabazite, erionite, and mordenite—the zeolite minerals that adsorbed oxygen and could be used as adsorbents. Therefore, there was no interest in clinoptilolite, which is now the zeolite with the greatest commercial potential.

This kind of exploration program for zeolites would still work well in undeveloped areas without undertaking a costly grassroots exploration program. Zeolites are difficult to identify in the outcrop

because they are so finely crystalline they cannot be identified with a hand lens. Zeolites resemble fine-grained tuffaceous rocks, bentonite, diatomite, freshwater limestone, and fine-grained sediments. Nevertheless, with a little experience, zeolites can easily be identified in hand specimens, but XRD analysis is needed to identify the specific zeolite minerals.

One exploration technique is to examine and sample known zeolite occurrences and then examine adjacent areas for outcrops that appear to be similar in appearance. Many of the known zeolite deposits in the world, especially in North America and Europe, have not been sampled and characterized adequately, so there are many opportunities to develop new zeolite deposits without undertaking a costly exploration program.

As the uses and applications of natural zeolites are expanded, new and innovative exploration methods may be required to locate new sources. Exploration programs will be developed that identify exploration targets based on the geology of the region, known zeolite occurrences, and the desired characteristics of a deposit that might yield specific zeolite products.

Field exploration for zeolites depends on careful geologic examination and sampling. Zeolitized tuffs usually appear to be altered rocks, but locally may not be distinguishable from unaltered rocks. Outcrops of zeolitized tuffs are commonly yellowish-white to gray, massive and blocky, and generally resistant to weathering; they may also exhibit distinctive surface textures. Natural zeolites may contain iron oxides or other minerals that produce outcrops with various shades of red, brown, yellow, or green.

XRD analysis of outcrop and drill samples is the most effective technique available to identify zeolite minerals. Specific zeolite minerals or mixtures of minerals may be identified, and semiquantitative estimates can be made of their abundance. Ammonia CEC determination of samples is also a very effective early screening technique for zeolitized tuffs believed to contain clinoptilolite, chabazite, erionite, or phillipsite. This screens out heulandite and analcime, which have similar appearances but almost no commercial potential.

Samples of mordenite, chabazite, and erionite require XRD and adsorption or separation tests to determine their zeolite content. The least expensive method of determining the purity of a zeolite mineral is to measure its adsorption capacity for water vapor at the standard temperature 25°C (77°F) and 40% relative humidity. The sample is heated to about low red heat in a porcelain crucible, then cooled and weighed. It then is placed in a desiccator overnight at the standard temperature and humidity and weighed again. The weight gain is compared to the increase of weight of a standard sample of known purity of the same zeolite mineral.

Once a zeolite deposit is identified, it must be sampled, mapped, and drilled to determine its consistency in mineralogy and purity and its vertical and horizontal extent. With this information, the geologic and minable reserves can be calculated. The deposit must then be bulk sampled. These samples are used for pilot-plant testing and also to provide samples for customer acceptance of the suitability of the product for specific uses and applications. If all these are satisfactory and a market has been established, the deposit can be brought into production.

Mining Methods

Both bedded sedimentary and thick vitroclastic zeolite deposits are mined by surface methods. Conventional earth-moving equipment, including scrapers and loaders, are used to mine the zeolite bed. Selective mining and blending during removal or stockpiling controls any variations in the purity of the ores. Sampling drill holes, the area being mined, the haulage truck, and the process stream are all used for quality control.



Figure 6. EZ chabazite mine, Bowie, Arizona

Zeolites for special, high-value applications require selective open-pit mining. Dow Chemical Corporation, which now owns and operates the deposit in Bowie, Arizona, manufactures high-value molecular sieve and ion-exchange products mined from the 15-cm-thick chabazite bed (see Figure 6). Before mining, the deposit is drilled on 15.25-m or 7.62-m centers. Overburden is stripped from the bed with self-loading scrapers. All the overlying thin-bedded chabazite waste is scraped off with a road grader. The bed is then pulled up with a backhoe. Any clay adhering to the bottom of the chabazite is scraped off by hand.

The chabazite from each pit is stored in a separate stockpile. Chabazite is blended from the stockpiles to guarantee that every shipment contains no less than 85% chabazite. Each railroad car shipment is sampled. The samples are sent to the processing plant so that the chabazite content of the car is known prior to its arrival at the plant.

Mining at the Mud Hills clinoptilolite deposit in Southern California recovered ore with strict specifications in 30-cm slices from a 4.6-m-thick deposit to yield a very high value product for ion-exchange media used by BNFL.

Processing

Natural zeolites are crushed and screened into granules that range from coarse to fine. Some zeolites are micronized to products with a particle size of less than 5 μm . The granules are used in soil conditioners, aquarium filters, feed supplements, animal absorbents, or cat litter. Chabazite granules used in desiccant applications are double activated at 260°C (500°F) and shipped to the customer in sealed containers. The chabazite produced for adsorption applications is ground, mixed with a binder, extruded, and activated at 424°C (795°F) (see Figure 7).

Natural zeolites can be enhanced in performance by washing them with acid or NaCl (sodium chloride) solutions to raise the H^+ or Na^+ content, respectively. Clinoptilolite products are particularly enhanced in ion-exchange capacity by washing to replace the slower reacting K^+ ions with Na^+ ions. Thermal treatment of clinoptilolite slows calcium from blocking exchange sites (Eyde 2000).

Specifications

Specifications are based on the end use application of the zeolite product. The user almost always sets the specifications. The pro-



Figure 7. Zeolite processing plant at the Ash Meadows Deposit near the California-Nevada border

ducer must guarantee that the zeolite product will meet or exceed the user's specifications. A chabazite product used in a desiccant application would specify the weight percent of water adsorbed at a specific temperature and humidity. Clinoptilolite used in cation-ion exchange would have to exchange a specific amount of the ion being exchanged.

Natural zeolites must have a specification sheet that provides information on the chemical and physical properties of the product. The American Society for Testing and Materials (ASTM) Committee No. D-32 was established to set testing methods and standard specifications for zeolites in the United States. Unfortunately, the committee has not been successful in setting testing standards for natural zeolites.

Industrial mineral producers deal with specifications in two ways—either by selling products on a custom basis to the specifications negotiated with the buyer or selling them on a product-line basis where each product has a name or number designation and specific physical or chemical standards. In the United States and Europe, zeolite products are commonly sold under a trade name rather than a mineral name. Tables 3 and 4 are sample specification sheets for chabazite and clinoptilolite products.

Testing for Zeolite Mineral Identification

Natural zeolite minerals are identified primarily by their crystal habit. Chemical analyses alone are not a satisfactory method of identification because they all have similar chemical compositions. The same zeolite from different localities or even from different parts of the same deposit may not have exactly the same chemical composition. Macroscopic zeolites, particularly those occurring in vesicles and fractures in basaltic rocks, can be identified by careful visual examination. In virtually all the deposits being mined, the minerals are of microscopic grain size. Positive identification and semiquantitative determination of such fine-grained materials can be done only by laboratory methods. The principal methods of identification are XRD and scanning electron microscopy (SEM). Neither optical microscopy nor differential thermal analysis (DTA) is particularly useful for identifying zeolite minerals.

X-ray Diffraction

XRD is the most reliable and widely used method for identifying zeolite minerals and providing a semiquantitative estimate of the

Table 3. Chabazite* properties

Typical Properties	
Form	Powder or granules
Color	Light brown (dry brightness 43)
Ring members	8
Crystal size—chabazite	Less than 1 μm
Crystallinity	+90%
Density	1.73 g/cm ³
Pore size	4.1 \times 3.7 Å
Effective pore diameter	4.3 Å
Cavity size	11.0 \times 6.6 Å
Total pore volume	0.468 cm ³ /g
Surface area	520.95 m ² /g
Crystal void volume	0.47 cm ³ /cm ³
Packing density	Approximately 577 kg/m ³ (36 lb/ft ³)
SiO ₂ :Al ₂ O ₃ ratio	Approximately 4:1
Mohs hardness	4–5
Moisture as packaged	Less than 10% by weight
Stability	pH 3–12
Ion-exchange capacity	2.50 meq/g

Typical Chemical Analysis

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	LOI†	Dominant Cation
54.6	14.9	2.28	0.22	0.60	6.67	0.90	19.4	Na

Exchange Selectivities

Tl⁺ > Cs⁺ > K⁺ > Ag⁺ > Rb⁺ > NH₄⁺ > Pb²⁺ > Na⁺ = Ba²⁺ > Sr²⁺ > Ca²⁺ > Li⁺

Exchange of Heavy-Metal Ions‡

Ag		Pb		Cu		Co	
pH	wt	% H	pwt	% H	pwt	% H	pwt
5.30	21.65	3.80	5.27	3.43	3.17	2.91	2.82

* Hydrous sodium aluminosilicate, natural herschelilite-sodium chabazite (CHA)

† LOI = loss on ignition

‡ Weight percent of heavy metals retained in chabazite after ion exchange from a 0.10 mg/mL solution AgNO₃+Pb(NO₃)₂⁺, CoSO₄, and a 0.025 mg/mL solution of CuSO₄ at the initial pH indicated for each solution.

percent present in the sample (Papke 1972). This method has a high degree of accuracy and can readily be used to identify individual minerals in mixtures of zeolite and nonzeolite minerals. A skilled technician is required to operate the XRD equipment, which may be automated and able to run multiple determinations unattended, and to interpret the results. XRD analysis is a non-destructive method, and the powder used for the analysis can be further tested. The method is least reliable in mixtures of minerals; the lower detection limit for an individual zeolite is about 1%. An experienced mineralogist is needed to interpret the diffraction trace. Papke (1972) and Slansky (1987) give more detailed descriptions of the XRD method.

Scanning Electron Microscopy

The scanning electron microscope is effective in identifying zeolite minerals and establishing their size, morphology, genesis, and mineralogic setting. Magnifications of several thousand times or more allow a visual examination of the zeolite minerals in small samples mounted on a specimen holder. Representative samples must be used to avoid misleading results. SEM analysis is relatively slow and costly.

Table 4. Clinoptilolite properties

Typical Properties*	
Silica:alumina ratio	5.8:1–6.4:1
Silicon:aluminum ratio	5.1:1–5.7:1
Bulk density (dry solid)	87 lb/ft ³ (1,394 kg/m ³)
Bulk density (dry, loose)	51–60 lb/ft ³ (817–961 kg/m ³)
Mohs hardness	5.1
Nominal channel size	4.0 \times 4.6 Å
Porosity	15%
Specific surface area	1,357 yd ² /oz (43.8 m ² /g)
Alkali stability (pH)	7–13
Acid stability (pH)	1–7
Thermal stability	1,292°F (700°C)
Crushing strength	2,500 lb/in. ² (176 kg/cm ²)
Wet attrition (average)	6%–7%
G.E. brightness (N.C. State University)	71.5

	Chemical Analysis, % (The Mineral Lab, Inc.)		Major Exchangeable Cations (USBM)†
	X-ray Fluorescence Results	Normalized to 100%	
SiO	66.9	76.7	Cs ⁺ > Rb ⁺ > K ⁺ > NH ₄ ⁺ > Sr ⁺ > Na ⁺ > Ca ²⁺ > Li ⁺ NH ₄ ⁺ >> Na ⁺
Al ₂ O ₃	10.5	12.0	
CaO	1.15	1.32	Heavy Metal Cations (USBM)†
MgO	0.57	0.65	
Na ₂ O	2.95	3.38	Ph ²⁺ > K ⁺ > NH ₄ ⁺ > Ca ²⁺ > Cd ²⁺ > Cu ²⁺ > Co ²⁺ > Zn ²⁺ > Ni ²⁺
K ₂ O	4.12	4.72	
Fe ₂ O ₃	0.92	1.05	Primary Adsorbed Gases
TiO ₂	0.11	0.13	
% MnO	0.03	0.03	NH ₃ CO CO ₂ SO ₂ H ₂ O N ₂
LOI‡	9.00	NA§	

Adapted from Ash Meadows Zeolite L.L.C.

* Total cation exchange capacity (CEC) 1.4 to 2.1 + meq/g; average clinoptilolite content >85%

† In order of selectivity for exchange

‡ LOI = loss on ignition

§ NA = not applicable

Optical Microscopy

Optical microscopes are generally ineffective in identifying zeolite minerals in zeolitized tuffs because of the very small grain size of the zeolite minerals, their low birefringence, and variation of their indices of refraction with changes in chemical composition.

Differential Thermal Analysis

DTA can be used to identify zeolite minerals, but the method is not effective when several zeolites or certain other minerals are present or when only a small quantity of a mineral is available. Variations in the exchangeable-cation content may also cause differences in the differential thermal curve. The method is very useful in distinguishing clinoptilolite from the closely related mineral heulandite. Gottardi and Galli (1985) published a comprehensive collection of DTA curves for natural zeolites.

Other Methods

Other analytical methods can be used in special circumstances but they are generally complex, very costly, and not currently practical for exploration or quality control. Such methods include infrared

absorption spectrography, Mossbauer spectroscopy, electron spin resonance spectroscopy, electron spin echo spectrometry, solid-state nuclear magnetic resonance, neutron diffraction, and synchrotron XRD (Slansky 1987).

Testing for Characterization

In characterizing zeolitic materials for commercial uses, it is important to quantify other physical and chemical properties required by the specific application. The following are physical and chemical properties and tests that may typically be required: wet chemical analysis; CEC; specific gravity and bulk density; brightness, whiteness, and color; hydration/dehydration; gas adsorption; attrition in water; internal and external surface area; pore size; and volume.

By-products and Coproducts

Deposits containing two or more zeolites may yield several individual varietal products or mixtures of the zeolite minerals. For example, zeolite products from the Itaya mine in Japan, a clinoptilolite and mordenite deposit, include mordenite, clinoptilolite, and mixed mordenite-clinoptilolite products depending on the selectivity of mining and processing.

Zeolite mining may yield bentonite as a by-product or coproduct. Bentonite commonly occurs in the same geologic setting as natural zeolites. At the Teague Mineral Products operation in Oregon, both minerals are mined from nearby pits and processed in the same grinding plant.

USES

Agricultural Products

Zeolites are used as soil conditioners and fertilizer extenders, particularly in Japan, Cuba, and the former Soviet bloc countries in Eastern Europe. Zeolites increase the cation-exchange capacity, improve moisture retention, and, because of their high pH, buffer acidic soils. Zeolites act as a slow-release media for ammonia and to a lesser extent potassium. Zeolite soil conditioners preloaded with nitrogen are now available. The zeolite crystal structure shields the ammonium ion from rapid consumption by nitrifying bacteria (Ferguson 1984), allowing a reduction in the amount of nitrogen fertilizers applied to the soil. Chabazite and clinoptilolite are effective carriers of herbicides, pesticides, fungicides, enzymes, and bacteria because of their high ion-exchange and adsorption capacities.

Zeolite-polymer blends are being used to improve water retention in sandy soils. In fields watered by pivot irrigation systems, the production of corn increased by 30% and water consumption decreased by nearly an equivalent percentage (R. Salestrom, personal communication). A test plot on tailings from a large open-pit copper mine in Arizona was treated with a mixture of clinoptilolite-polymer blend and dry municipal sewer sludge. Native desert vegetation established itself on the test plot without being either seeded or irrigated (S.A. Bengston, personal communication).

Zeolites also act as scavengers for heavy-metal ions such as cadmium (Cd), copper (Cu), lead (Pb), and zinc (Zn) in soils, particularly those contaminated by industrial wastes. Clinoptilolite added to soils contaminated with strontium-90 and cesium-137 reduces the uptake of these radioisotopes by plants in areas contaminated by radioactive fallout, such as around the damaged Chernobyl reactor.

Animal Nutrition

Adding clinoptilolite to animal feeds in controlled amounts increases utilization of feed and decreases ammonia stress in animal digestive systems. Controlled feeding of clinoptilolite to chickens,

turkeys, and swine has increased growth rates, improved feed efficiency, reduced the incidence of diarrhea and related health problems, and produced a drier and less odoriferous excrement. Also, excrement and sewer sludge treated with zeolites are more effective fertilizers because their slow-release properties prevent fertilizer burns on the plants. The zeolite-treated manure is drier and less odoriferous than composted manure.

Feeding clinoptilolite, and to a lesser extent mordenite, to animals is an accepted practice in Japan, Cuba, Bulgaria, and Hungary (Griffiths 1987). The use is growing slowly and steadily in the United States and in Russia, but it is still not widely accepted (Pond 1993).

Clinoptilolite fed to broiler chickens in amounts of 1% to 3% of the total feed increases feed efficiency and lowers the time required to reach a marketable size. Laying chickens fed supplemental zeolite took fewer days to the first egg, had increased numbers of eggs, and had general improvement in health through a reduction in fecal bacteria (Griffiths 1987).

Clinoptilolite also reduces the incidence of post-weaning diarrhea when added to the starter diet of young pigs. A zeolite used as a feed supplement may also reduce the levels of antibiotics needed in feeds, particularly for swine.

Aquaculture

Zeolites are used in aquariums, fish farms, and fish hatcheries to avoid the buildup of ammonia to toxic levels. Fish hatcheries are using self-contained systems that recycle water to reduce downstream contamination from their effluent. Clinoptilolite is highly effective in the removal of ammonia from recirculating fish culture systems. In oxygen-poor environments, concentrations of less than 1 ppm ammonia can damage gill tissue, increase the incidence of gill disease, reduce the rate of growth, and increase mortality (Mumpton 1977).

In Alabama and Mississippi, clinoptilolite is being used to remove ammonia from catfish ponds (Williford, Reynolds, and Quiros 1991). Ammonia-removal kits containing granular clinoptilolite as the ion-exchange media are available in many pet supply stores for home aquarium use. The U.S. Fish and Wildlife Service has also successfully used clinoptilolite-charged systems for recirculating water in tank trucks transporting live fish.

Catalysis and Petroleum Refining

Zeolites with large channel sizes have large internal surface areas and can catalyze many types of reactions (Dwyer 1984). Though natural zeolites have been used in sorption applications in the petroleum and petrochemical industries, synthetic zeolites are generally used because of their larger channel sizes, greater adsorption capacities, and uniformity. Chabazite is used to remove water, carbon dioxide, and hydrogen sulfide from gaseous hydrocarbons, to remove HCl from gas streams, and to dry hydrogen and chlorine.

Desiccants

Activated chabazite is used as a carrier and desiccant in packaged enzymes and bacteria used to inoculate silage. Partially activated clinoptilolite and chabazite are used as anticaking agents in cattle feeds containing mineral and organic supplements and other bulk agricultural and chemical products shipped in pneumatic containers. Small amounts of zeolite desiccant are blended with animal feed, fertilizers, and hygroscopic chemicals before sealing the products into bags.

Dimension Stone

Zeolitic tuffs have been used for thousands of years as lightweight, durable dimension stone. The physical properties of such stone are

important. Zeolitic tuffs have low bulk densities, are weather resistant, have superior insulating properties, and can be easily cut into attractive stone.

Many buildings in ancient and modern Rome and Naples have been constructed from local zeolite sources, particularly from the Neapolitan Yellow Tuff (Aie llo 1993). In central Europe, many buildings and cathedrals were constructed with blocks of zeolitic tuff. Quarries in the Laacher See Area in Germany, Kurdzali in Bulgaria, and Tokaj in Hungary produced blocks of zeolitic tuff for dimension stone used in building construction.

Several sources in Japan have produced zeolitic dimension stone for centuries, particularly from pumiceous marine tuffs in the Green Tuff region, Tochigi Prefecture. The principal source is a quarry near Otsunomiya City, where a green tuff bed 108 m thick has been mined for hundreds of years (Mumpton 1978).

In the United States, the use of zeolitic tuff dimension stone has been limited to a few areas in Nevada and Oregon, where several structures were constructed from blocks of zeolitic tuff from local quarries. The old Nye County courthouse, St. Patrick's Catholic Church, and several commercial buildings in Tonopah, Nevada, were built with blocks of zeolitic tuff.

Gas Separation

Zeolites are used to separate nitrogen and oxygen to produce a gas stream containing up to 95% oxygen. Mordenite appears to be the best natural zeolite for oxygen generation, although clinoptilolite and chabazite have also been used; pressure swing adsorption (PSA) plants using synthetic zeolites have displaced the compression-expansion air-separation systems.

PSA plants that use mordenite were designed and used principally in Japan to supply oxygen for basic oxygen furnaces in steel mills. PSA plants supply oxygen to municipal wastewater treatment plants, hospitals, and other users. Perhaps the most important application is the small oxygen generators used in homes to provide continuous oxygen to patients with pulmonary diseases. Natural zeolites have been displaced in virtually all the industrial and medical applications by synthetic zeolites, which have significantly higher adsorption capacities than natural mordenite.

Ion-Exchange Applications

The ability to exchange cations is one of the most important properties of zeolites. Cation-exchange capacity is a measure of the number of cations per unit weight available for exchange, usually expressed as milli equivalents per gram or milli equivalents per 100 grams of zeolite. The ammonia ion is most commonly used for CEC testing. The result is referred to as the ammonia ion-exchange capacity.

Both chabazite and clinoptilolite are used to treat mine water and metallurgical effluents. Because chabazite has a higher selectivity for thallium than any other natural zeolite or ion-exchange resin, it is used to remove thallium from mine water. Sodium chabazite modified with ferrous iron removes arsenic from solution without first converting it to arsenate (Eyde 2000). The ZELFLON technology uses clinoptilolite to treat municipal sewage (Eyde 2000).

NSF International approved clinoptilolite for use in swimming-pool filtration systems. In these systems, granular clinoptilolite replaces the sand in the filter. Clinoptilolite is superior to sand because it removes chloramines, heavy metals, urea, and organic matter from the pool water.

Synthetic zeolites are used in detergents. This is because natural zeolites are not uniform in purity and composition; are inferior in color, brightness, and CEC; and have smaller channel sizes and higher percentage of iron and other impurities. Natural zeolites are superior to synthetic ones for uses such as the treatment of radio-

active waste or the removal of metals from low-pH solutions because of their hardness and resistance to attrition and degradation by intense radiation.

Fine grinding of zeolitic materials can improve their CEC by increasing their surface area, especially when the zeolite (usually mordenite) has a low permeability. Zeolite minerals with high CEC include clinoptilolite, erionite philipsite, chabazite, and mordenite. Minerals with low CEC include heulandite, laumontite, and analcime.

Medical and Personal Care Applications

The U.S. armed forces uses zeolite products that stop bleeding from wounds by promoting clotting (Healy 2003). Clinoptilolite has been used successfully as a polishing agent in fluoride-containing toothpaste by allowing a higher level of fluoride to remain in anionic form (Kato et al. 1970). Clinoptilolite is encased in tampons to control odor and reduce the incidence of sepsis. Because of its ability to absorb ammonia ions from air and water, clinoptilolite has been used in products such as baby powder and filler in disposable baby diapers, and as an ammonia control product in diaper pails.

Natural Gas Purification

Chabazite has been used to separate carbon dioxide, hydrogen sulfide, and other gases from methane produced from natural gas and oil wells (Mumpton 1978). Other sources of methane that use either synthetic or natural zeolites to remove noncombustible gases and contaminants include municipal wastewater treatment plants, sanitary landfills, and animal waste treatment facilities. NRG Corporation constructed two gas treatment plants in the Los Angeles, California, area that used the NuFuel PSA process to produce pipeline quality methane. The Palos Verdes Landfill plant treated gas containing about 50% methane and 40% carbon dioxide to produce about 30,000 m³ of methane per day. The other NRG Corporation plant treated casing head gas at the Farmers Market oil field. Both plants used activated extrudates produced from chabazite mined at the Bowie, Arizona, deposit (Anon. 1975).

Nuclear Waste Treatment and Handling

Chabazite and clinoptilolite are used in the treatment, handling, and containment in engineering structures for the storage of nuclear wastes (Grant, Skriba, and Saha 1987; Grant et al. 1988, 1989). Natural zeolites have the unique ability to selectively remove Sr⁹⁰, Cs¹³⁷, and other dangerous isotopes from solutions containing high concentrations of competing ions. Natural zeolites are less expensive than organic ion-exchange resins and much more resistant to degradation from radiation. Zeolites melt at low temperature into a stable silicate glass, which greatly reduces the volume of the radioactive waste. By encapsulating the radioactive glass in concrete, the radioactive cations can be safely stored in a secure disposal site.

The Hanford Laboratories of Battelle Pacific Northwest Laboratory in Richland, Washington, initially demonstrated the high efficiency of clinoptilolite from Hector, California, in removing radioactive Cs¹³⁷ and Sr⁹⁰ from low-level waste streams at nuclear facilities. Radioactive solution treatment at Hanford has processed millions of gallons of solutions. A comparable Sr⁹⁰/Cs¹³⁷ waste treatment is used at the National Reactor Testing Station at Arco, Idaho; West Valley, New York; and other nuclear facilities. Chabazite products IE-95 and IE-96 from the Bowie deposit were used in the cleanup of the Three Mile Island nuclear power plant site (King and Opelka 1982; Bostick and Guo 1996).

Ion-exchange treatment utilizing clinoptilolite has also been used for nuclear-waste treatment in other countries, including Russia, Ukraine, Japan, Hungary, Bulgaria, Canada, Italy, the United

Kingdom, France, and Germany. Large tonnages of clinoptilolite were used in direct application to contaminated soils at the devastated Chernobyl nuclear power plant to contain radioactive contaminants spilled during the accident (Griffiths 1987; Chelishchev 1993).

Mixed clinoptilolite and mordenite have been used for Cs¹³⁷ removal in Japan (Kato 1974). Clinoptilolite from the Tokaj District in Hungary has been used to encapsulate Sr⁹⁰ for solid waste disposal and removal of Sr⁹⁰ and Cs¹³⁷ from effluent waste streams (Adam, Kakasy, and Pallos 1971). In Canada, clinoptilolite was used to recover Sr⁹⁰ and Cs¹³⁷ from waste solutions in underground disposal sites at Chalk Run, Ontario (Mathers and Watson 1962).

Chabazite and phillipsite from the Neapolitan Yellow Tuff at Naples, Italy, have been used to remove Cs¹³⁷ and Sr⁹⁰ from nuclear effluents. The zeolite minerals loaded with the radioactive cesium and strontium were stored in secure underground disposal sites at Cassacig, Italy (Anon. 1972).

BNFL uses clinoptilolite from the Mud Hills deposit near Barstow, California, to selectively exchange Sr⁹⁰, Cs¹³⁷, and other radioisotopes from effluent waste streams at its nuclear fuel reprocessing plant at Sellafield, U.K. (Anon. 1990). Levels of Sr⁹⁰ and Cs¹³⁷ in the clinoptilolite-treated plant effluent, which is discharged into the Irish Sea, have dropped to very low levels.

Battelle Pacific Northwest Laboratory uses clinoptilolite in engineered sorbent barriers in containment and waste storage structures for low-level nuclear wastes (Freeman and Jones 1989).

Odor Control

Natural zeolites, particularly clinoptilolite, adsorb ammonia ions. This process suppresses odors from fecal matter and urine. Hydrated zeolites adsorb ammonia vapor; when the gas enters the zeolite pores, it bonds to or replaces crystalline water (Frederickson 1987).

In Europe and the United States, clinoptilolite is used as a pet litter and to suppress odors in horse stalls (Eyde 1987). In Japan, clinoptilolite and mordenite are used to control odors from poultry and swine. Crushed and sized zeolites, principally clinoptilolite, have proven effective in controlling the pungent odor of ammonia fumes produced when animal excrement dries (Griffiths 1987). Granular clinoptilolite is applied directly to the floors in pens and stables and in litter trays for cats and small pets. Adding clinoptilolite as a supplement to animal feeds has a nutritional benefit in addition to reducing the odor from fecal matter and urine.

Natural zeolites, notably clinoptilolite, chabazite, and phillipsite, have also been used for odor control in personal products (e.g., in athletic shoes). Room air cleaners with zeolite filters have also been used in living quarters and to remove high-ammonia urine odors in nursing homes and similar facilities. Ground clinoptilolite is effective as a dry carpet cleaner, particularly to remove pet odors.

Paper Fillers

Natural zeolites have been used as fillers in some specialty paper products. Clinoptilolite and the crystalline quartz that occurs as an impurity in the zeolitic tuffs are abrasive. In addition, clinoptilolite has a low brightness and a poor color (Kobayashi 1970). Clinoptilolite is not competitive with kaolin and calcium carbonate for either coating or filling most paper products.

Pozzolan and Cement

Pozzolan is a naturally occurring cementaceous material that can replace up to 25% of the portland cement in concrete. Pozzolans both improve the quality and reduce the cost of concrete. Zeolitic tuffs have been used as pozzolan in many places in the world. The Romans employed pozzolanic materials in aqueducts, public buildings, and high ways using the Neapolitan Yellow Tuff near Poz-

zuoli, Italy. In Europe, zeolites are being mined in Serbia, Germany, Bulgaria, and other countries for use as pozzolan. The minerals used include clinoptilolite, natrolite, skolezite, and phillipsite.

Monolith Portland Cement Company mined zeolitic ash-flow tuffs near Tehachapi, California, for pozzolan in cement. The use of pozzolanic cements in the construction of the 400-km-long Los Angeles aqueduct in 1912 saved several million dollars by enabling a 25% reduction in the amount of cement consumed.

GSA Resources and C2C Corporation developed a lightweight, oil-well cement additive that Halliburton Energy Services is evaluating. The additive is based on the chabazite in the thin-bedded horizon that overlies the high-purity ore bed at the Bowie Arizona, deposit. The additive is blended with the portland Class G cement to optimize placement within a well bore. The technology is based on research done at the Institute of Architecture, Slovak Academy of Sciences (Janotka, Krajč, and Dzivák 2003).

Sewage Treatment

Clinoptilolite and chabazite remove ammonia and some heavy metals from sewage and other effluent streams. The ammonia removed can be discharged into the atmosphere, recovered as a gas by-product, or converted to an ammonium sulfate fertilizer. Plants in Truckee, California; Rosemont, Minnesota; and Manassas, Virginia, have operated successfully for many years using clinoptilolite in tertiary sewage treatment processes to remove ammonia.

Zeolite Australia licensed the ZELfloc technology that uses zeolites for municipal wastewater treatment. The company has 14 wastewater treatment plants using the technology (Eyde 2000). Supersorb, another Australian company, has undertaken full-scale trials of an activated zeolite technology at the Water Corporation of Western Australia Kwinana Wastewater Treatment Plant in Queensland (Crossley 2000).

An improved environment is the incentive behind the increased use of zeolites in tertiary wastewater treatment. Ammonia ions should be removed because they are toxic to fish and other aquatic life and contribute to rapid growth of algae and the eutrophication of streams and lakes.

Solar Energy and Heat Exchange

Chabazite and clinoptilolite absorb and release heat from solar radiation for air conditioning, refrigeration, and water heating applications. The dehydration of the zeolite during the day and its rehydration at night result in the exchange of several hundred BTUs per kilogram of zeolite, sufficient to operate refrigerators or to cool small buildings (Tchernev 1993). The study estimated that 1 t of zeolite in solar panels spread over 19 m² of roof surface will produce 1 t of air conditioning. Recreational uses such as in beverage coolers, and use in less developed countries where power is not available to refrigerate medical supplies and food, are important applications.

Stack Gas Cleanup

Natural zeolites can be used to remove sulfur dioxide from the stack gases of coal-burning power plants. Clinoptilolite and mordenite can adsorb as much as 200 mg of SO₂ (sulfur dioxide) per gram of zeolite under static conditions and as much as 40 mg under dynamic conditions, even in the presence of high percentages of carbon dioxide. These zeolites are especially suited to the low-pH and high-temperature conditions of exhaust gas systems.

ECONOMIC FACTORS

Markets

Synthetic zeolites were produced and used for many years before Union Carbide discovered large deposits of chabazite, clinoptilolite,

erionite, and mordenite. In fact, their Linde Company subsidiary that developed and sold the first 5A molecular sieve products marketed the Bowie chabazite as their AW500 synthetic zeolite product in 1961. AW500 was sold into applications where the adsorption bed was exposed to an acidic environment in which the 5A synthetic molecular sieve quickly deteriorated.

Union Carbide was not interested in the mineral clinoptilolite because at that time it had no adsorption applications. Had the company been interested in clinoptilolite, it could have acquired all of the major deposits in the western United States. Although W.R. Grace and Company acquired the eastern part of the Bowie chabazite deposit in 1965, no major mining or oil companies acquired large zeolite reserves until they entered the natural zeolite business about 10 years later.

Natural zeolites are still an undeveloped facet of the zeolite business. Synthetic zeolite sales worldwide total several billion dollars, whereas natural zeolite sales are only a few million dollars. No formal commodity markets exist, and sales for lower value products are confined mostly to countries with zeolite resources. Higher value products may be sold internationally, but their total value worldwide is still small. Synthetic zeolites have established major, growing markets through silicate chemical manufacturers, mostly in North America, Western Europe, and Japan.

Because of their very wide range of applications, natural zeolites sell into diverse markets. Japan has a particularly wide range of zeolite markets for agricultural, industrial, and consumer uses. North American sales are principally for agricultural, ion-exchange, and pet litter applications. Markets in Western Europe, the former Eastern bloc countries, and Cuba are primarily for agricultural products, with a growing industrial market sector.

The fastest growing market sector is for ion-exchange applications. Clinoptilolite is a superior swimming pool filtration product that will displace sand as the preferred media. The new tertiary wastewater treatment systems will experience continuing strong growth.

Steady growth is anticipated for agricultural, industrial, and consumer applications. The strongest areas of market growth in North America are expected to be in water treatment, deodorants, pet litter, soil treatment, and nuclear waste treatment and containment.

Values and Costs

The cost of zeolite products depends on the type and degree of processing that must be done to satisfy targeted market specifications. Mining costs are generally fairly low, typically \$3 to \$6/t, unless very selective mining is done.

Most natural zeolites are sold into low-value industrial or agricultural markets, commonly selling for \$30 to \$70/t for granular products down to 40 mesh, and \$50 to \$120/t for ground materials in a range of -40 to -325 mesh. Consumer products such as pet litter, fish-tank media, or deodorant materials commonly sell for \$0.50 to \$4.50/kg at the retail level.

Products for specialty industrial applications, such as radioactive waste filtration media, specialty adsorbents, and surface modified products, are sold for several dollars per kilogram or thousands of dollars per ton. Specialty materials with products developed for specific markets are highly profitable even though the market for these products may be very limited.

Transportation

Zeolite products are generally transported by highway or rail carriers in bulk, in 1-t "supersacks," or in multiwall paper bags, usually

palletized. The products are not hazardous and present no special problems, subject to proper labeling and handling. Chabazite and clinoptilolite, which have been stored at high temperatures or low humidity, can adsorb several weight-percent water if their destination has a high humidity. Zeolites prepared as dimension stone are shipped as any other stone products, generally palletized and by truck.

Transportation costs strongly affect the distance a lower-value zeolite can be hauled to reach markets. Agricultural-grade clinoptilolite from the western United States can reach markets in the eastern half of the country.

Future imports from Greece, Italy, China, and other tidewater sources with low ocean freight rates could make some materials produced in the western United States uncompetitive. High-value-added zeolites can generally be shipped nationwide and even to international destinations because the freight is such a small incremental cost in relation to the cost of the product.

Alternate Materials

Natural zeolites are competitive on the basis of price and performance with other mineral products. It is difficult for a new product to displace one with performance characteristics that are known and are satisfactory to the user. There are many established alternate materials for most zeolite applications. Market entry of a natural zeolite product requires equivalent or superior performance or a significant cost advantage over the product being used.

Synthetic zeolites (molecular sieves) are natural zeolites' principal competitor. Synthetic zeolites often can be modified in physical and chemical properties to enhance their performance in specific applications. The synthetics are more uniform in quality than their natural equivalents. Natural zeolites have an advantage over synthetic materials in some applications (e.g., cesium and strontium adsorption in radioactive waste cleanup) and are also able to function at lower pH levels. They are also generally less expensive than synthetic zeolite products, which gives them a superior price performance ratio.

Activated carbon, synthetic ion-exchange resins, and similar materials can be more effective than zeolites for many ion-exchange applications. Activated bentonite, silica gel, calcium oxide, calcined gypsum, and other minerals also can be competitive adsorbents and desiccants in a comparative price range.

GOVERNMENTAL CONSIDERATIONS

Taxes, Subsidies, and Depletion Allowance

No specific taxes are related to zeolites, and the material is not subject to any government subsidies in the United States and Canada. The depletion allowance is 14% for natural zeolites mined in the United States.

Zoning and Land Use

Natural zeolite deposits experience zoning and land use restrictions similar to most other fine-grained minerals such as kaolin or diatomite. Most zeolite deposits are located in rural areas, so their utilization seldom interferes with urban development. The very large zeolite deposits around Naples, Italy, are a conspicuous exception, but the deposits are so extensive that many other sites in the region are available where disturbing residential or industrial lands is not an issue.

Environmental Regulations

Environmental regulations are always a matter of concern. Excessive regulation is always a source of conflict between government

regulators and mine operators. Natural zeolite mines and processing facilities generally present no serious environmental problems, with two possible exceptions:

1. Erionite and mordenite may be fibrous. Fibrous erionite is a Class 1 carcinogen. Mordenite is not known to be a carcinogen.
2. Crystalline silica commonly occurs in zeolite deposits, and the finely ground products may contain more than 0.1% respirable silica.

Natural zeolites are dusty materials when crushed and ground. Therefore, air quality standards should be maintained carefully during mining and processing.

Fugitive dust from mining and plant facilities may be considered a local environmental pollutant. Most zeolite deposits contain silica minerals in the form of amorphous silica such as opal or opal-CT, cristobalite, or crystalline silica. Processing plants therefore must have air-pollution control systems ranging from standard bag-house dust collectors to electrolytic precipitators to minimize worker exposure to fugitive dust at grinding mills or bagging stations and to comply with local air quality control requirements. Most zeolite production uses dry processing methods.

Zeolite processing will inevitably use water-washing and wet classification methods, requiring proper handling of plant effluent and tailings pond discharges. Zeolite minerals are generally considered to be chemically inert, and most are nonfibrous. Erionite is classified as a fibrous, acicular mineral and has been labeled a human carcinogen on the basis of medical studies of the large number of mesothelioma cases in the Cadocchia District of Turkey. Mordenite is also a fibrous mineral but is currently not regarded as a potential carcinogen.

FUTURE TRENDS AND PROBLEMS

Future Trends

The zeolite industry continues to develop new applications in both industrial and consumer markets. Most of this activity and growth, however, has been in synthetic zeolites. Most natural zeolites uses are in commodity and lower-value applications such as agriculture or pozzolan. This is changing. Specialty and consumer applications are the fastest growing segments of the natural zeolite market.

Chabazite and clinoptilolite are the only ion-exchange products that do not degrade when exposed to radiation. The zeolites used to clean up radioactive waste streams sell from \$2/kg to as much as \$14/kg. Clinoptilolite is displacing sand as a filtration media in swimming pool filters. These are applications where the physical and chemical properties of natural zeolites are superior to synthetic zeolites or other ion-exchange media.

Although the production of natural zeolites in North America is growing slowly, the value of this production is increasing more rapidly. This has occurred because of the shift from commodity to specialty and performance products. This trend will continue as more specialty products such as clinoptilolite coated with the quaternary amine hexadecyltrimethyl-ammonium are developed. (Bowman 2003). These organophilic zeolite products are now available for removing organic chemicals from ground- and surface waters. The coated zeolite products do not swell in water and therefore can displace organoclay products that swell and block circulation.

The producers of natural zeolite have characterized their products and provide specification sheets that document the physical and chemical properties. Still, no high-purity-beneficiated zeolite products are available. The technology is available to beneficiate zeolites by air separation, wet processing, or flotation. Until beneficiated clinoptilolite products become available as powders, beads,

or extrudates, natural zeolite products will be unable to gain access to many high-value-added specialty and performance uses and applications.

The highest purity zeolite product available in North America is the chabazite from the Bowie, Arizona, deposit. This unique deposit was formed when airborne volcanic ash from a distant volcanic eruption was deposited in a saline alkaline lake. By the time the ash arrived at the lake, virtually all the other minerals had been removed by natural air separation and only the glass fraction remained.

Problems

The use of inclusive generic mineral names for both the fibrous and nonfibrous varieties of erionite, phillipsite, and mordenite is inaccurate and has resulted in the designation of the nonfibrous varieties of these minerals as carcinogens. Nonfibrous erionite, phillipsite, and mordenite were identified in samples being studied for the U.S. Bureau of Mines report on size and shape characterization of fibrous zeolites by electron microscopy (Shedd, Virta, and Wylie 1982). The erionite in the Bowie deposit was judged to be nonfibrous. Yet the *Sixth Annual Report on Carcinogens* classifies all erionite as fibrous and as a carcinogen (Eyre 1996).

Because erionite has been classified as a carcinogen, it cannot be used in consumer products. The presence of even trace amounts of erionite may prevent its use or consideration for some applications. Mordenite has also been designated as a fibrous mineral but has not been classified as a carcinogen. Figures 8 and 9 illustrate the differences in the crystal morphology between fibrous and nonfibrous erionite (Eyre 1996). Natural zeolites usually contain some crystalline silica, which must be listed on the Material Safety Data Sheet.

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The zeolite chapter in the 6th edition of *Industrial Minerals and Rocks* was a carefully researched and referenced chapter that accurately summarized the content of the four outstanding individual papers in the 5th edition. This chapter has relied heavily in places on the data in the 6th edition (Holmes 1994), using some sections with no or very little change. The goal in the 7th edition is to update the previous chapters and to place more emphasis on the productive deposits and the end-use applications of the zeolites being produced. As a result, the bibliography has been updated and significantly reduced in size, a difficult task because each reference is important, and any of the references could be the inspiration for the development of a world-class natural zeolite product.

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Figure 8. Fibrous erionite, Eastgate, Nevada



Figure 9. Nonfibrous erionite, Bowie, Arizona

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Zirconium and Hafnium

Philip Murphy and Louise Frick

INTRODUCTION

Elemental zirconium (Zr) was first identified and named in 1789 by the German chemist M.H. Klaproth, who called it zirconium after the Arabic word *zarquán*, meaning gold colored. It is the 20th most abundant element in terrestrial rocks, making up 0.016% of the earth's crust. The metal was first isolated in 1824 by the Swedish chemist J.J. Berzelius, but it was another 100 years before A.E. von Arkel first processed pure zirconium in 1925. Hafnium (Hf) is so chemically similar to zirconium that it was not discovered until 1923, when D. Coster and A.K. von Hevesy detected it using x-ray spectrographic analysis.

Zirconium and hafnium occur most commonly in nature as the mineral zircon (ZrSiO_4) and less commonly as baddeleyite (ZrO_2). They are also found as a variety of other silicates. Zircon was identified as a component in alluvial and beach sands in 1895, but it was not produced in any quantity until 20 years later. During World War I, it was produced as a coproduct of beach sand mining for titanium minerals just south of Jacksonville Beach, Florida, and was patented as a refractory. It was not until the 1930s, when Zircon Rutile Ltd. began mining at Byron Bay on the east coast of Australia, that zircon was first used as foundry sand. Later in the 1940s, NL Industries and Humphreys Gold Corp. began production of zircon sands from fossil beaches in northeast Florida. Baddeleyite first became available as a commercial product in 1916, but never in comparable quantities to zircon.

MINERALOGY AND GEOLOGY

Zirconium and Hafnium Chemistry

Zirconium is a transition element with the atomic number 40. It occurs together with titanium and hafnium in Group IV of the periodic table. The similarity in the electron structure of these elements is the reason that all three have similar chemical and physical properties and invariably occur together in nature.

Zirconium forms the dioxide, zirconia (ZrO_2), along with two other oxides of lower oxidation states. It reacts with hydroxides and carbonates to form zirconates (e.g., Na_2ZrO_3). Adding alkali to zirconium salt results in the formation of zirconium hydroxide, which is readily soluble in acids. In nature, zirconium occurs most commonly as the silicate mineral ZrSiO_4 and less commonly as the dioxide ZrO_2 . It also occurs in at least 20 other minerals, either as an oxide or a silicate.

Table 1. Key properties of zircon and baddeleyite

Property	Zircon	Baddeleyite
Formula	ZrSiO_4	ZrO_2
Specific gravity	4.68	5.5–6.0
Hardness (Mohs scale)	7.5	6.5
Refractive index ω	1.923–1.960	2.13–2.20
Refractive index ϵ	1.968–2.015	
Melting point	2,200°C	
Thermal conductivity	$2.1 \text{ W m}^{-1} \text{ C}^{-1}$	
Thermal expansion	$2.5 \times 10^{-6} \text{ C}^{-1}$	
Specific heat	$550 \text{ J kg}^{-1} \text{ C}^{-1}$	
Bulk density	2,600–2,900 kg m^{-3}	5.74

Separating hafnium from zirconium is extremely difficult because of their similar chemical and physical properties, and chemical analyses of zirconium minerals for commercial applications are virtually always based on the zirconia + hafnia ($\text{ZrO}_2 + \text{HfO}_2$) content, often simply abbreviated to ZrO_2 .

Physical Properties of Zircon

Zircon is an extremely refractory mineral with a high melting point, a low and regular coefficient of thermal expansion, and high thermal conductivity (Table 1). These properties are responsible for zircon's effective performance as a refractory material and as a foundry sand. The mineral has a high hardness and is thus resistant to abrasion.

Highly crystalline zircon does not absorb or reflect any particular wavelength of visible light. Combined with its high refractive index, this allows zircon to scatter all wavelengths of light when milled to a size similar to the wavelength of visible light (0.4–0.7 μm). This unique property allows zircon to be used as an opacifier in ceramic applications. By scattering all wavelengths of visible light, the zircon makes ceramic surfaces appear white.

The effectiveness of zircon in this function is influenced by its crystallinity and chemistry. Impurities such as uranium (U), thorium (Th), and yttrium (Y) can distort the zircon crystal structure creating point defects. Similarly, radioactive decay of uranium and thorium in the zircon also distorts the zircon structure. In extreme

cases, this can result in part or all of the zircon crystal becoming amorphous, producing what is known as metamict zircon.

Geology of Zircon and Baddeleyite

Zircon is a common accessory mineral in granitic rocks and pegmatites. It is one of the earliest minerals to crystallize from a cooling magma and sometimes incorporates inclusions. Much of the zircon in these rocks crystallizes in tetragonal prisms with pyramidal terminations; however, it also commonly occurs as rounded grains in igneous rocks. It is sometimes found in metamorphic rocks such as gneiss and schists. Because it is resistant to mechanical and chemical disintegration, it appears as a detrital mineral in river and beach sands. Zircon can also occur as a gemstone and has been recognized as a semiprecious stone since biblical times.

Although zircon is a common accessory mineral, it is rarely found in high concentrations in anything other than sedimentary deposits, where it has been concentrated over time by the processes of erosion and deposited along with other heavy minerals (HM) such as ilmenite, rutile, monazite, garnet, staurolite, and kyanite. Most commercial sedimentary deposits of titanium minerals and zircon are found on Quaternary age shorelines (0 to 2 million years) on the trailing margins of continents. They include beach, or strand line, deposits and coastal Aeolian dunes.

The geology of baddeleyite deposits is very different from that of zircon deposits. Baddeleyite has recently been mined alongside a wide range of mineral products from two large, ultrabasic, geologically complex deposits. The operation in the Kovdor Complex in Russia still mines baddeleyite, but falling grades at the Phalaborwa Complex in South Africa have put an end to baddeleyite production.

A commercial supply of zirconia from the rock caldesite has been investigated in the United States, and eudialyte is of minor commercial importance.

GLOBAL OCCURRENCE OF ZIRCON AND BADDELEYITE

Commercial zircon deposits occur almost exclusively in four countries: Australia, South Africa, the United States, and India. These tend to comprise coastal Quaternary-age sedimentary deposits, but also a small number of older, highly altered, mineralogically complex deposits are often found many hundreds of kilometers from the present coastline.

Australia

Australia has been the world's principal source of zircon since production of mineral sands first started on the east coast of the country, between Broken Bay, New South Wales, and Rockhampton, Queensland. Production from this region has declined considerably, however, because of depletion of resources and environmental constraints, and the only remaining significant source is the deposits on North Stradbroke Island in Queensland.

On Australia's west coast, the Eneabba region has been the world's most important source of zircon since the late 1970s, but production from this area is now declining because of lower grades and depleted resources. Zircon also occurs south of Perth, around Bunbury and Capel, but here the HM suite is less rich in zircon than it is at Eneabba.

The Murray Basin in inland southeastern Australia is host to substantial HM sand mineralization. Many of the projects being evaluated in the region are high in rutile and zircon, and although a number of these have been known for many years, the complexity of the mineral assemblage, together with the fine grain size of the zircon and elevated levels of uranium and thorium, has so far constrained their development.

The Eucla Basin, located onshore from the Great Australian Bight, seems likely to become Australia's newest mineral sands province. Toward the end of 2004, Iluka Resources Limited announced two discoveries on the eastern margin of the basin, which suggest that the region is highly prospective for mineral sands mineralization. The mineralization that has been found to date is particularly rich in zircon, and may well prove to be comparable to the Eneabba region of Western Australia.

Africa

South Africa hosts the largest known deposits of zircon in Africa. On the east coast, the Richards Bay Minerals deposit is one of the world's largest sources of zircon. Other deposits exist along that coastline, one of which is being mined by Ticon South Africa. Farther north along the same coastline, in Mozambique, are three very large, as yet undeveloped, titanium resources that contain some associated zircon.

On the west coast of South Africa, Namakwa Sands mines zircon deposits between Standfontein and Oranjemond.

United States

The two centers of zircon mining in the United States are the Jacksonville District, which spans Florida and Georgia and includes the Trail Ridge deposit and the Green Cove Springs deposit, and the Old Hickory deposit in Virginia.

India

Because the zircon content in deposits currently mined in India is relatively low, the country is not a significant producer of zircon. Deposits in Tamil Nadu, which are currently the subject of potential development proposals, have higher zircon to titania (TiO_2) ratios and could ultimately become a new source of supply.

WORLD RESERVES

The U.S. Geological Survey (USGS) provides the only published source of zircon reserve data, and Table 2 gives the latest published estimates. Identified world resources of zircon exceed 70 Mt.

Resources of hafnium in the United States are estimated to be about 130,000 t, a available in the 14-Mt domestic resources of zircon. World resources of hafnium are associated with those of zircon and baddeleyite and exceed 1 Mt.

According to these estimates, South Africa and Australia have the largest reserves of zircon and are also the largest commercial producers. The United States has moderate reserves of zircon and is the world's third largest producer. Other important occurrences are in Brazil, India, and Ukraine.

EXPLORATION AND EVALUATION

Exploration

Zircon exploration techniques are the same as those for titanium minerals, because both occur in the same deposits. Most commonly, target areas are selected where large volumes of sand are present and where beach ridges and other features associated with shorelines are known to occur. Early explorers used USGS quadrangle maps, physiographic references, aerial photographs, and often word of mouth to find target areas. Modern methods have become much more refined since the advent of Earth Resource Technology Satellite (ERTS) imagery, manned space flight photography, and new developments in computer science. In some cases, such as at Eneabba, farmers have discovered deposits on their land.

A Geiger counter or scintillometer can be useful in detecting HM deposits where radioactive monazite is present. Although geophysical methods such as magnetometer survey and induced

Table 2. World reserves of zirconium and hafnium

	Zirconium Mine Production, kt		Zirconium		Hafnium	
	2002	2003	Reserves	Reserve Base	Reserves	Reserve Base
			ZrO ₂ , Mt		HfO ₂ , kt	
Australia 408		400	9.1	30	180	600
Brazil	21	30	2.2	4.6	44	91
China	15	15	0.5	3.7	na*	na
India	19	20	3.4	3.8	42	46
South Africa	224	280	14	14	280	290
Ukraine	34	34	4.0	6.0	na	na
United States	100	100	3.4	5.3	68	97
Other countries	9	10	0.9	4.1	na	na
World total (rounded)	830	890	38	72	610	1,100

Source: USGS Mineral Commodity Summaries 2004.

* na = not available.

polarization have been tested, they are not widely used in HM prospecting.

A variety of drilling systems are available for beach sand exploration: hand auger, vehicle-mounted power auger, and reverse-circulation drills using both water and air to force the mineral to the surface. Each has its advantage, and one is chosen because it is thought to be the best for a particular type of deposit.

Evaluation of a Deposit

Gold pans of various sizes and materials of construction as well as vanning plaques can be used in the field to estimate the percentage of HM present in a sand. Evaluating prospect samples and ores in the laboratory usually requires separating the HM as a first step. The conventional methods use heavy liquids (tetrabromoethane, bromoform, methylene iodide, or Clerichi solutions). The heavy liquids are toxic, so some risk is involved in their use, and this has caused them to be banned in some countries (e.g., England). Newly invented nontoxic tung state solutions that use water instead of organic solvents are considered to be much safer than the conventional heavy liquids. Another new development in HM separation equipment is the Magstream separator, which separates HM by specific gravity using a nontoxic ferro-solution rotating in a magnetic field. The specific gravity is set by adjusting the rotational speed of the separation tube. In addition to gravity separations, the Magstream can also make magnetic separations. It is a very useful tool in HM evaluations because it can be used to concentrate zircon and the other HM for both chemical analysis and physical testing.

Analytical Methods

For many years, wet analytical chemistry methods were used to analyze zirconium-bearing materials. This type of analysis is very difficult because zircon is inert and can be taken into solution only with fusion methods with a strong flux. Because zirconium and hafnium have almost identical chemical properties, wet chemical methods cannot be used routinely to determine composition by individual element. Instead, wet analyses report combined ZrO₂ and HfO₂ as 67.2% ZrO₂ for pure zircon. In the past 20 years, x-ray fluorescence (XRF) has replaced chemical methods of analysis almost entirely.

For many years, grain counting (point counting) was a popular and useful means of identifying minerals present in HM concentrates and determining the amounts of each. The method is fairly accurate for the major minerals present, but accuracy decreases for

the minor minerals. Development and refinements of the x-ray microprobe, scanning electron microscope (SEM), associated XRF techniques, and modern computer science have been combined to produce the most accurate and sophisticated means for analyzing HM concentrates. It is now possible to accurately identify each mineral present in a sample, measure each particle's size, chemically analyze it, and then give an accurate percentage for each individual mineral present in the sample, its average chemical composition, and its particle-size distribution.

MINING AND PROCESSING

Zircon is sourced from HM sands mining operations in which the mineralized sand (containing both zircon and titanium minerals) is mined using dredging or dry mining techniques. The choice of method depends primarily on the physical nature of the deposit and the scale of operation. Dredging is the preferred and more economical choice for large-scale operations. Dry mining methods are used for smaller-scale operations in situations where there is inadequate water; where the deposit contains hard, rocky material; or where there is a high clay content.

Such deposits contain from less than 1% HM to more than 10% HM. The remaining material is predominantly clay and silica sand. The proportion of clay, or slimes, in the HM deposits varies considerably. The slimes are first separated from the sand, and the HM are then separated from the silica sand to make an HM concentrate containing in the region of 90% to 95% total HM. These concentration processes employ wet gravity concentration techniques on spiral separators or cone concentrators. The HM concentrate is then transported to the dry separation plant, where the individual minerals are separated from one another by exploiting variations in their magnetic and electrical conductive properties. Further separations are based on either grain size or specific gravity.

The specific processes used for separating zircon from other minerals include the following:

- High-tension electrostatic separation, typically used for separating zircon from rutile
- Magnetic separation techniques, used for separating zircon from mildly magnetic minerals such as leucoxene, monazite, and altered ilmenite
- Gravity separation techniques, using spiral separators, Kelsey jigs, hydrosizers, and air tables to separate zircon from minerals such as kyanite, other aluminosilicate minerals, monazite, and quartz

In many mineral sands deposits, the grains are coated with clays and iron oxides. If these are not removed, they contaminate the final zircon product, contributing to higher iron (as Fe_2O_3) and alumina (Al_2O_3) contents, and also make separating the individual minerals more difficult. The mineral grains may also have organic coatings that can affect the mineral separation and the uses of the zircon product—for instance, in special foundry sand applications. The surfaces of zircon grains are cleaned by mechanical attritioning or by chemical means. Mechanical attritioning processes are often incorporated early in the separation plant flowsheet and are used for cleaning both zircon grains and grains of other minerals. However, with some exceptions, the chemical processes primarily clean the surfaces of the zircon grains to improve zircon product quality.

Specific chemical processes used to remove coatings from the surface of zircon grains are

- The hot acid leach (HAL) process, in which hot zircon is coated with moderately concentrated sulfuric acid and reacted in a kiln, after which the product is attritioned, neutralized, and dried
- The zircon upgrading process (ZUP), which involves heating the zircon to about 400°C , after which it is quenched in dilute sulfuric acid

Both of these processes are effective in lowering the iron content of zircon from more than 0.2% to as low as 0.04% Fe_2O_3 . It is likely that specific grain cleaning processes will become increasingly important as demand for high-quality zircon with low iron content increases and as the availability of naturally clean zircon deposits diminishes.

Iron may also be contained within the zircon grain as inclusions of ilmenite or iron oxides. In such cases, it may be possible to separate grains with high iron content using selective magnetic separation. High-gauss magnetic mineral separation may also be used in certain instances to reduce high levels of U+Th in zircon. This separation, however, usually results in relatively high loss of zircon recovery because of the slight difference in magnetism between the metamict zircons containing high U+Th and the less altered zircon grains.

In some instances, the final zircon product is calcined at approximately 900°C , principally to render the zircon product whiter. Though this does not improve the chemical quality of the material, it can provide a qualitative advantage in marketing the product for certain applications. It may also relieve crystal stresses caused by zircon's natural radioactivity and improve milling characteristics prior to use as an opacifier.

GRADES AND SPECIFICATIONS

Although its theoretical chemical formula is ZrSiO_4 , naturally occurring zircon has the variable formula $(\text{Zr,Hf,U,Th,Y})\text{SiO}_4$. Zircon always contains some Hf, commonly around 2% (as HfO_2), but it can be as high as 4%. Zircon also always contains some U and Th and rare earth elements such as Y. These impurity elements are incorporated into the zircon crystal structure and cannot be removed without destroying the individual zircon grains.

Other impurities found in zircon crystals, such as Al_2O_3 , silica (SiO_2) (other than that included in the crystal structure), and Fe, are usually the result of secondary deposition in cracks and cavities in the zircon grain as a result of precipitation from aqueous solutions. Additional impurities present in commercial zircon products are present as individual grains of other minerals.

Quality specifications for zircon are typically quoted in terms of zirconia content (expressed as $\text{ZrO}_2+\text{HfO}_2$), Fe_2O_3 , Al_2O_3 , TiO_2 ,

and, occasionally, radioactivity (U+Th). SiO_2 content may also be quoted, although it is the free silica content present as quartz that is most important. Physical specifications normally include grain sizing (either as a size distribution or AFS [American Foundrymen's Society] number), bulk density, and residual pH.

Guaranteed levels are normally quoted for the following:

- $\text{ZrO}_2+\text{HfO}_2$: minimum 65.0% to more than 66.0% for ceramic applications
- Fe_2O_3 : maximum levels ranging from as low as 0.04% for premium ceramic-grade quality up to 0.25% for foundry-grade products
- TiO_2 : maximum levels ranging from 0.10% to 0.30%, depending on the grade and application

For certain applications, specific consumers may request other guaranteed levels. For example, maximum Al_2O_3 and phosphate (P_2O_5) levels may have to be guaranteed for certain foundry or zirconia/zirconium applications.

Fe_2O_3 content is often the most common specification in determining the suitability of a zircon product for a particular application. In particular, low Fe_2O_3 content is often requested for ceramic opacifier applications. The commonly accepted maximum level for premium-grade zircon is 0.07% Fe_2O_3 , even though zircon products with higher levels of iron have been used satisfactorily in a number of opacifier applications. Iron content is controlled principally through grain surface cleaning and efficient mineral separation, minimizing contamination by leucoxene and staurolite.

The level of TiO_2 content is principally a function of the extent of contamination by titanium minerals, normally leucoxene or rutile as separate grains. This is controllable by efficient electrostatic separation, but may be affected by the degree of grain surface coatings, which affects electrostatic separation.

High Al_2O_3 content is usually an indication of contamination by aluminosilicate minerals, typically kyanite or sillimanite. These minerals are most effectively separated from zircon using wet or dry gravity separation techniques.

Silica, in the form of free quartz grains, must also be controlled, not only because it acts as a diluent to the ZrO_2 grade but also because it is considered an occupational hazard. Crystalline silica is known to cause lung fibrosis (silicosis) and has also been classified as a carcinogen. Generally, free silica must be reduced to less than 0.1% to comply with local occupational health and safety standards. Free quartz is readily separated from zircon using gravity techniques.

The radioactivity of the zircon is important to zirconium/zirconia producers who must deal with the elevation of radiation in waste streams. The level of U+Th in a zircon product may be influenced by contaminating particles of monazite, which can be removed by magnetic separation and by wet and dry gravity separation processes. However, in most clean zircon products, the U+Th content is a function of the extent to which these elements are present in the zircon crystal structure, and this U+Th cannot be removed by physical processing methods. With some exceptions, chemical processing without disturbing the grain is unlikely to be successful. Therefore, the level of U+Th in the various commercial zircon products is primarily a function of their geological setting.

MARKETS AND USES

Zircon is ultimately used in a wide range of consuming industries (see Figure 1), in varying physical and chemical forms. In its simplest form, zircon is used as a sand, directly from the mineral processing plant at the mine. Refractory products, abrasives, and foundry sands contain zircon in this form.

The majority of zircon is processed further before consumption. It is mechanically ground into either a flour (95% passing 45 μm) or an opacifier (95% passing 5 μm). In this form, zircon is consumed in ceramics, investment castings, television glass, and refractories.

Chemical processing of zircon is less common. Zircon is processed chemically to produce alumina-zirconia-silica (AZS) for use in glass refractories and a range of zirconium chemicals that are used in advanced ceramics, colored ceramic pigments, catalysts, and a wide variety of other minor applications. Zirconium metal is also produced chemically from zircon sand and finds applications in the nuclear industry.

Ceramics

The main use of zircon in the ceramics industry is as an additive to glazes used on ceramic tiles to provide opacity. It can also be added to engobes (an intermediate surface on a ceramic body) or incorporated in the main body of the ceramic body, as with gres porcellanato tiles. The sanitary-ware industry is also a major market for zircon, where it is also added to the high-gloss glaze as an opacifier. Zircon also finds some use in tableware products, but this is a smaller market because transparent glazes are widely used.

Refractories

Zircon is now a specialized refractory material because of its relative cost and availability. It is added to refractory products as zircon sand, zircon-pyrophyllite mixtures, zirconias, or AZS, depending on the industry and application. Zircon-based refractories are used in steel- and glassmaking.

Foundry

Zircon is used as a foundry sand, to form casts in investment casting, on the surfaces of die casts, and in the Cosworth process. In the first three applications, zircon is a relatively minor ingredient, but in the Cosworth casting process, which is used to cast aluminum motor engine heads and blocks, coarse-grained zircon sand is used exclusively. Additionally, some refractory paints, or mold washes, contain 60% to 70% zircon flour.

Glass

Zircon is used in the faceplate panels of color televisions and computer monitors to absorb x-rays generated in cathode ray tubes. Zircon is also used in the glass substrates of liquid crystal displays (LCDs) and plasma display panels (PDPs). These products contain about 1% zirconia but consume only small volumes because the substrates are very thin. Zircon and zirconia are also added to some specialty glasses, such as lead-free crystal glassware, special fiber-glass, and optical fibers.

Other Markets

There are a wide range of small-end-use markets for zircon and its derivatives and hafnium:

- Markets for zirconia—abrasives, electronics, oxygen sensors, gemstones, ceramic pigments, advanced ceramics, catalysts, fuel cells
- Markets for zirconium chemicals— TiO_2 pigment coating, paper coatings, paint driers, antiperspirants, printing inks, and paints
- Markets for zirconium metal—nuclear reactor fuel tubes, chemical industry
- Markets for hafnium metal—component of superalloys used in the aeronautics and space industry, neutron absorber in nuclear reactor control rods

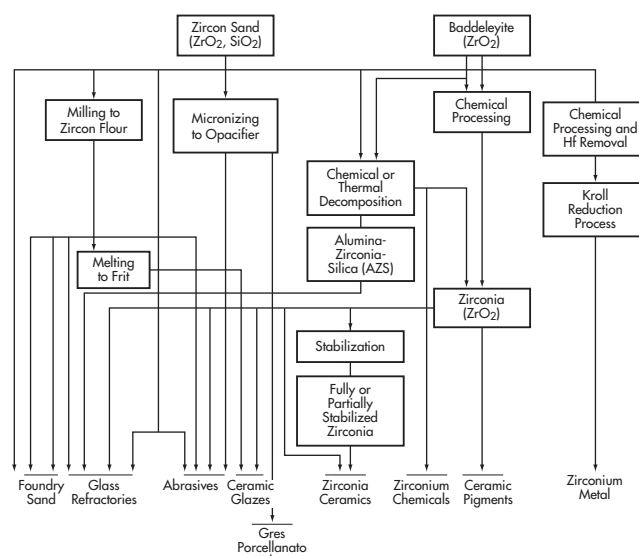


Figure 1. Schematic structure of zircon processing and consuming industries

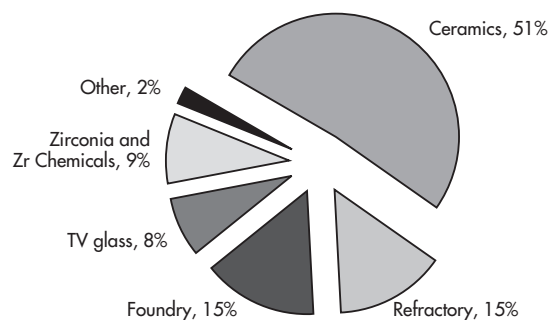


Figure 2. Zircon consumption by end-use market (2003)

Figure 2 shows the breakdown of principal end uses for zircon in 2003. The ceramics sector is by far the largest consumer of zircon sand, accounting for almost 51% of consumption in 2003. Not only is the ceramics sector the largest end-use market for zircon, it also showed steady growth with a veraging more than 5.0 % per year between 1987 and 2003. It is very clearly the principal driver of zircon demand. A key element in this sector is the role played by the zircon milling groups, principally based in Europe, that dominate the market for zircon. These consumers mill the zircon to flour for use in the manufacture of frits and to very fine opacifier for use in the manufacture of glazes.

The other large-volume markets—namely, the refractory and foundry industries—together account for a further 30% of zircon consumption. Technological advances, however, are reducing the volumes of zircon required and in some cases allowing more cost-effective materials to be used in place of zircon. Although still important markets, there is little expectation of substantial growth in demand in either the foundry or refractory sectors.

More interesting, from a zircon consumption viewpoint, are the smaller markets of zirconia, zirconium chemicals, and TV glass. These higher-value markets for zircon grew at 9% to 13% per year

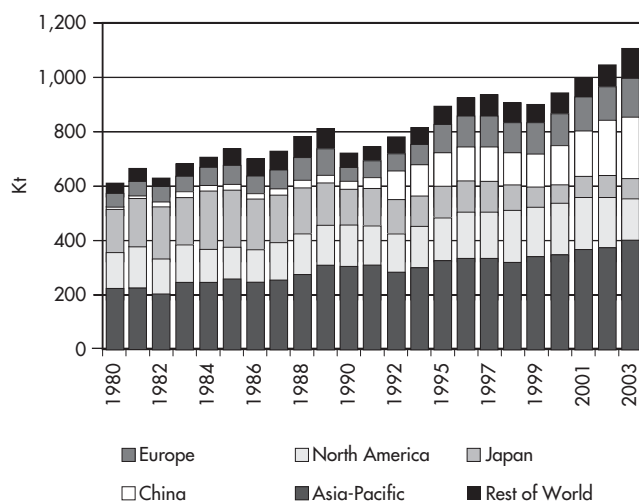


Figure 3. Zircon consumption by geographical region (1980–2003)

between 1987 and 2003, and demand is now believed to be reaching a plateau; future growth rates are forecast to be substantially lower.

Figure 3 shows the principal geographic markets for zircon from 1980 to 2003. The Asia-Pacific region dominates zircon consumption, accounting for 40.5% of the total in 2003. Within the Asia-Pacific region, China has the highest level of zircon consumption. Europe has always been a large consumer of zircon. In 2003 it was estimated that Europe accounted for more than one third of all zircon consumption, mainly because large European ceramic production centers use zircon in frits and glazes for ceramic products.

Global zircon demand has averaged 2.7% per year compound growth since 1987 and 3.8% per year from 1998 to 2003. During this 6-year period, China showed the strongest growth at 13%, as a result of strong construction activity, housing sector reform that allows private home ownership, and the 2008 Olympics—all of which are combining to boost the demand for ceramic products. The mature North American market declined by an average 4% per year over the same period.

ALTERNATIVE MATERIALS

During periods of zircon shortages, the foundry industry used South African chromite and domestic olivine as zircon substitutes.

Table 3. Zircon supply and demand (2000–2005), kt

Components of Supply and Demand	2000	2001	2002	2003	2004*	2005†
World Supply						
Australia	368	398	417	453	435	459
South Africa	317	377	420	370	355	391
United States	181	173	132	144	155	160
Other countries	151	147	164	161	166	162
Total supply	1,017	1,095	1,133	1,129	1,111	1,192
Supply‡	971	1,050	1,093	1,089	1,081	1,162
Growth in supply	1.9%	8.2%	3.5%	−0.4%	−0.7%	7.5%
Consumption by Region‡						
Europe	359	371	398	401	405	411
North America	194	186	153	175	171	167
Japan	78	79	75	68	66	64
China	167	198	220	236	248	258
Other Asia-Pacific countries	124	128	151	155	161	167
Rest of world	77	76	96	98	101	103
Total consumption‡	998	1,039	1,093	1,134	1,153	1,170
Consumption by Market‡						
Ceramics	479	511	561	582	599	619
Refractory	165	164	160	166	162	158
Foundry	170	171	161	168	166	164
Glass	80	81	85	89	94	95
Zirconia and ZR chemicals	87	91	102	105	107	109
Other	19	20	24	24	25	25
Total consumption‡	998	1,039	1,093	1,134	1,153	1,170
Growth in consumption	6.7%	4.0%	5.2%	3.8%	1.6%	1.6%
Surplus/deficit	−27	12	0	−46	−72	−9

Source: TZ Minerals International database.

* Estimate.

† Forecast.

‡ Excludes former U.S.S.R. countries.

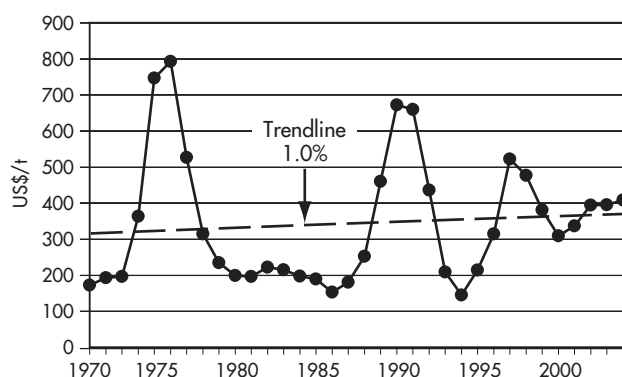


Figure 4. Zircon prices 1970–2003, real 2003 US\$

With the exception of a few special applications, the foundries returned to the use of zircon when it became available. Mullite, manufactured by calcining kaolin clay, is also used successfully as a substitute for zircon, both as a foundry sand and mold wash. Japan's steel industry has successfully replaced much of its zircon refractories requirement with high-alumina and magnesium refractory products. Dolomite and spinel refractories can also substitute for zircon in certain high-temperature applications.

Columbium (niobium), stainless steel, and tantalum provide limited substitution in nuclear applications, and titanium and synthetic materials can substitute in some chemical plant uses. Silver-cadmium-indium control rods are used in lieu of hafnium at many nuclear power plants. Zirconium can be used interchangeably with hafnium in certain superalloys; in others, only hafnium produces the desired or required grain boundary refinement.

Unless future zircon supply becomes severely limited, it is unlikely that any substitute with all of its properties will be sought or found.

OUTLOOK

All commercially produced zircon is a co-product of titanium mineral production. However, over the last 40 years, zircon has developed from a low-value by-product of titanium mining to an important co-product that typically accounts for between 15% and 35% of total revenue. Despite its increased value, zircon supply remains dependent on titanium mining. Consequently, the future supply of zircon will depend on the zircon content of the deposits that are developed to meet demand for titanium feedstocks. In recent years, supply has become very short, and this scarcity has prompted companies to promote new projects as "zircon" projects, but the fact remains that the deposits contain more titanium than zircon.

The key to the future level of demand for zircon in consumption is the ceramics industry, which is by far the largest market for zircon and which is forecast to continue at a steady pace.

Future supply may not be sufficient to meet the growing demand for zircon. This could lead to substitution of zircon in certain applications, and pricing pressures will mean that this takes place at the lower-quality end of the market spectrum, particularly in the foundry and refractory industries.

Table 3 clearly shows the imminent problem of insufficient supply, with a shortfall of 100,000 t forecast for 2004, a level likely to continue for some time unless more resources are discovered. This will clearly affect zircon prices, which exhibited a past propensity to spike (as shown in Figure 4), and prices are forecast to increase further in 2005.

The next few years will be another very interesting period in the evolution of zirconium and hafnium markets.

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PART THREE



Markets and Uses

Absorbents and Desiccants

Abbas A. Zaman

INTRODUCTION

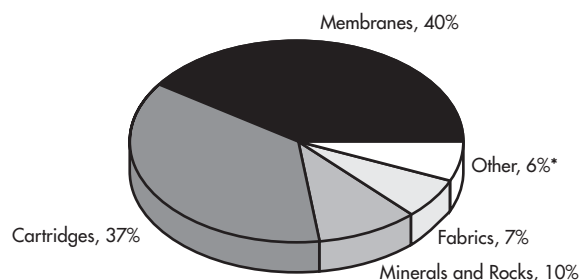
Absorbents and desiccants are the key materials in many industries dealing with purification, clarification, and separation. Adsorption, which involves the preferential concentration of solutes at an interface, is of great importance in various science and engineering fields. These include waste treatment, pet litter, cosmetics, food products, petroleum, chemical industries, pharmaceuticals, water purification, energy-related industries such as storage of hydrogen for fuel cell technology, separation technologies such as removal of carbon monoxide (CO) from hydrogen, and environmental technologies for meeting higher standards on safety issues and environmental pollutants. In addition, the use of absorbents and desiccants is a convenient method to handle liquid wastes, clean up spills, and eliminate odors.

MATERIALS

A wide range of materials are used as desiccants and absorbents. These can be categorized as industrial minerals and rocks including different kind of clays, and synthetic materials such as zeolites, silica gel, activated carbon, and activated alumina. The world market for activated carbon demand (granules, powder, and felts) is estimated at around \$2.0 billion, growing at an annual rate of 7.5% (Yang 2003). According to Business Communications Company, Inc., and R. Deshpande (2001), the approximate reported figures for annual worldwide sales of some of the adsorbents in 2001 were

Activated alumina	\$91 million
Clays	\$44 million
Granular activated carbon	\$334 million
Silica gel	\$177 million
Zeolites	\$1,100 million

Although minerals and rocks represent only a small portion of the total materials used as absorbents and desiccants, as shown in Figure 1 (Van Kouteren 1994), the most widely used material for this kind of application is activated carbon. Commercial production of activated carbon dates back to the nineteenth century (Yang 2003). During World War I, filters containing carbon black were developed to remove chemicals from air. Activated carbon is widely used in bulk separation of hydrocarbons; purification of gases such as air, nitrogen, hydrocarbons, sulfur dioxide, and halogenated organics; and liquid and water purifications to remove organics, solvents, and inorganics such as arsenic, chromium, and odor species.



*Includes fibers, powders, pulp and paper, and centrifuges

Courtesy of Celite Corp.

Figure 1. The U.S. fluid conditioning market by type of system

Silica gel and activated alumina are widely used as desiccants because of their large capacity for water adsorption (nearly 40 wt %) and also because they regenerate at low temperatures (150°C) compared with zeolites. The surface of these materials has been modified with different organic ligands for different applications (Vansant, Van Der Voort, and Vrancken 1995).

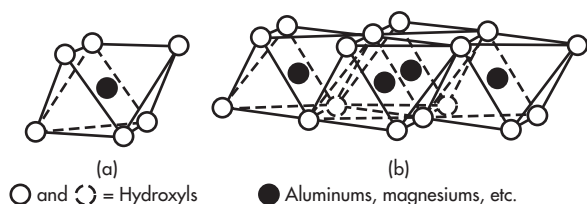
MINERALOGY

The common mineralogical trait of industrial minerals used as absorbents and desiccants is that these materials all belong to the silicate group. Silicates have an inherent chemical stability and unique molecular structures, which prove to be useful in absorbents. Silica (SiO₂) is the dominant chemical constituent and is present in many different forms. For example, in the clay minerals, it is present in complex tetrahedral and octahedral sheets and/or chains. In diatomite, it occurs in an amorphous form (Van Kouteren 1994).

Diatomite and Perlite

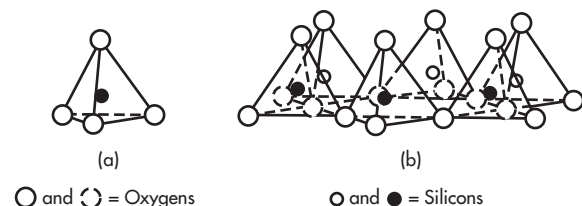
Diatomaceous silica is the preferred name for the primary mineral component that makes up the rock diatomite. Diatomite is a siliceous, sedimentary rock consisting principally of the fossilized skeletal remains of the diatom, a unicellular, microscopic aquatic plant related to algae (Kadey 1983). Fossilized diatom skeletons are made of opaline or hydrated silica (SiO₂•H₂O).

On the other hand, perlite, in its naturally occurring form, is a dense, amorphous, hydrated volcanic glass, generally of rhyolitic



Source: Van Kouteren 1994.

Figure 2. Geometric representation of octahedron showing (a) a single octahedral unit and (b) the sheet structure of the octahedral units



Source: Van Kouteren 1994.

Figure 3. Geometric representation of silica tetrahedron showing (a) a single silica tetrahedron, and (b) the sheet structure of the silica tetrahedra arranged in a hexagonal network

composition (sodium potassium aluminum silicate). Because of its commercial applications, perlite has a dual nomenclature in the industry. It is known by the same name as both the naturally occurring rock and, after processing and thermal expansion, as the lightweight aggregate (Kadey 1983).

Specialty Clays

Compared to other minerals used as absorbents, the clay minerals are much more mineralogically complex. As a general definition, clays are naturally occurring, earthy, fine-grained hydrous silicates (Patterson and Murray 1983). Collectively, they are classified as phyllosilicates, a group of silicate minerals characterized by silica-oxygen tetrahedra linked together in two-dimensional sheets (Thrush 1968).

The phyllosilicate group of clays consists of several minerals, each having different mineralogy, geologic occurrence, technology, and uses. Although the mineralogy is complex, it is easier to think of these minerals as containing crystal structures that can be broken down into two simple building blocks: tetrahedra and octahedra. These building blocks form sheets or layers by joining at the corners (tetrahedra) or at the edges (octahedra) (Moll and Goss 1987), as shown in Figures 2 and 3.

Given these basic building blocks, the variations in how the blocks are arranged yield the various groups of clay minerals. Table 1 lists the major clay mineral groups used as filters and absorbents, along with their commonly used names and mineralogical compositions. The major structural differences between these groups are imbedded in how the building blocks are layered.

Smectite Group

Smectite minerals have a three-layer structure. Two outer layers of silica tetrahedra are attached to a central octahedral layer of hydrous metal oxide (usually aluminum, sodium, magnesium, calcium, or lithium). The layers are combined in a way that the oxygen atoms at

Table 1. Classification of clay minerals including those used as absorbents

Clay Group and Commonly Used Names	Chemical Formula
Kaolinite and Serpentine Group (two-layered structure)	
Kaolinite	$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$
Halloysite	$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4 \cdot 4\text{H}_2\text{O}$
Serpentine	$\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$
Micas (three-layered structure. The charge of the three-sheet layer ≤ 2)	
Illite	$\text{K}_2\text{Al}_4[(\text{Si}_6\text{Al}_2)\text{O}_{20}](\text{OH})_4 \cdot n\text{H}_2\text{O}$
Vermiculite Group (three-layered structure with swelling capacity. The charge of the three-sheet layer = 1.2–1.8)	
Trioctahedral vermiculite	$(\text{Mg}, \text{Fe}^{2+}, \text{Fe}^{3+})_6[(\text{Si}, \text{Al})_8\text{O}_{20}](\text{OH})_4 \cdot n\text{H}_2\text{O}$
Smectite Group (three-layered structure, strongly swelling. The charge of the three-sheet layer = 0.5–1.2)	
Montmorillonite	$\text{M}^{+}_{x+y}(\text{Al}, \text{Fe}^{3+})_4\text{Si}_4\text{O}_{20}(\text{OH})_4 \cdot n\text{H}_2\text{O}$
Calcium (nonswelling bentonite)	Same as above with M^{+} being Ca^{2+}
Sodium (swelling bentonite)	Same as above with M^{+} being Na^{+}
Magnesium (saponite)	$\text{M}_x^{+}\text{Mg}_6(\text{Si}_8\text{Al}_x\text{O}_{20})(\text{OH})_4 \cdot n\text{H}_2\text{O}$
Beidellite	$\text{M}_x^{+}\text{Al}_4(\text{Si}_8\text{Al}_x\text{O}_{20})(\text{OH})_4 \cdot n\text{H}_2\text{O}$
Nontronite	$\text{M}_x^{+}\text{Fe}_4^{3+}(\text{Si}_8\text{Al}_x\text{O}_{20})(\text{OH})_4 \cdot n\text{H}_2\text{O}$
M^{+} represents adsorbed alkali cations in the interlayer space.	
Pyrophyllite and Talc Group (three-layered structure, nonswelling. The charge of the three-sheet layer = 0)	
Pyrophyllite	$\text{Al}_2(\text{Si}_4\text{O}_{10})(\text{OH})_2$
Talc	$\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$
Chlorites Group (four-layered silicate structure, nonswelling. The charge of the four-sheet layer = 1.1–3.3)	
Donbassite	$\text{Al}_2(\text{Si}_8\text{O}_{20})(\text{OH})_4 \cdot \text{Al}_4(\text{OH})_{12}$
Palygorskite and Sepiolite Group (with the layer fibrous structure)	
Palygorskite	$\text{Mg}_5(\text{Si}_8\text{O}_{20})(\text{OH})_2(\text{OH}_2)_4 \cdot 4\text{H}_2\text{O}$
Sepiolite	$\text{Mg}_8(\text{Si}_{12}\text{O}_{30})(\text{OH})_4(\text{OH}_2)_4 \cdot n\text{H}_2\text{O}$

Adapted from Konta 1995.

the tips of the tetrahedra of each silica layer are shared with the octahedral metal oxide/hydroxide layer. A small proportion of the metal cations in the central octahedral layer is replaced by cations of lower valence but similar size. This leads to an electrical charge imbalance that is corrected by the presence of cations held outside and between each of the three-layer units. The electrical charge deficiency of the three-layer units and the presence of the exchangeable cations (commonly sodium or calcium) impart the characteristic expansion properties to the smectite group of clays (Clarke 1985).

Palygorskite and Sepiolite (Hormite) Group

Hormites are markedly different in terms of their structural characteristics in that they form chain-type rather than layered structures. The chain-type yields a fibrous-like structure (Clarke 1985). Unlike the smectite minerals, which have sheets that extend laterally, the sheets in hormite minerals extend only a short distance and then flip up or flip down in a continuous pattern to yield a three-dimensional structure that includes long tubes instead of layers. Because of this structure, hormite minerals do not swell as do smectite minerals. However, crystal lattice substitutions, or exchange capacity, do occur at the broken bonds on the edges of the crystal (Moll and Goss 1987).

Kaolin Group

This group of minerals, consisting principally of kaolinite, forms a two-layer structure. The two layers are composed of tetrahedra and octahedra sheets. The tetrahedra contain silicon and oxygen and the octahedra contain aluminum, oxygen, and hydroxyl, arranged in sheets. The apexes of the tetrahedra join with the octahedra to form the two-layer structure with water molecules between the two layers. These sheets are generally neutral, but on the edges, where broken bonds exist, unbalanced charges are also found. These sites are areas where cation exchange can occur (Moll and Goss 1987).

Sand and Gravel

In the strictest sense, these two materials are defined by size rather than by composition or mineralogical makeup. Sand and gravel consist of separate grains or particles of detrital rock with a particular size range of $1/16$ to 2 mm in diameter. For filter and absorbent applications, however, sand consists mainly of pure, rounded quartz (SiO_2) grains (Davis and Tepordei 1985), and gravel typically consists of rock fragments.

Minor Minerals

Other minerals used as filters or absorbents include vermiculite, talc, ball clay, crushed limestone, gypsum, ilmenite, and garnet. Vermiculite, talc, and ball clay are also in the phyllosilicate group. As a consequence, these minerals, especially vermiculite, are commonly used in certain absorbent applications. Such heavy minerals as garnet and ilmenite (and sometimes anthracite coal) are often used as filter media in wastewater treatment plants. Calcium carbonate (especially as lime) and gypsum are two nonsilicate minerals that find limited applications as absorbents.

DOMESTIC PRODUCTION AND USE OF CLAYS

According to the U.S. Geological Survey (2004), clay and shale production was reported in 2003 in all states except Alaska, Delaware, Hawaii, Idaho, New Hampshire, New Jersey, Rhode Island, Vermont, and Wisconsin. Approximately 760 clay pits or quarries were operated by about 240 companies, and the leading 20 firms supplied about 50% of the tonnage and 79% of the value for all types of clay sold or used in the United States. Remaining essentially unchanged from 2002, U.S. production was about 39.3 Mt and was valued at \$1.6 billion. Major domestic uses for specific clays were estimated as

- Ball clay—41% floor and wall tile, 25% sanitary ware, and 34% other uses
- Bentonite—25% pet waste absorbent, 21% drilling mud, 21% foundry sand bond, 15% iron ore pelletizing, and 18% other uses
- Common clay—56% brick, 17% cement, 17% lightweight aggregate, and 10% other uses
- Fire clay—75% refractories and 25% other uses
- Fuller's earth—74% absorbent uses and 26% other uses
- Kaolin—54% paper, 17% refractories, and 29% other uses

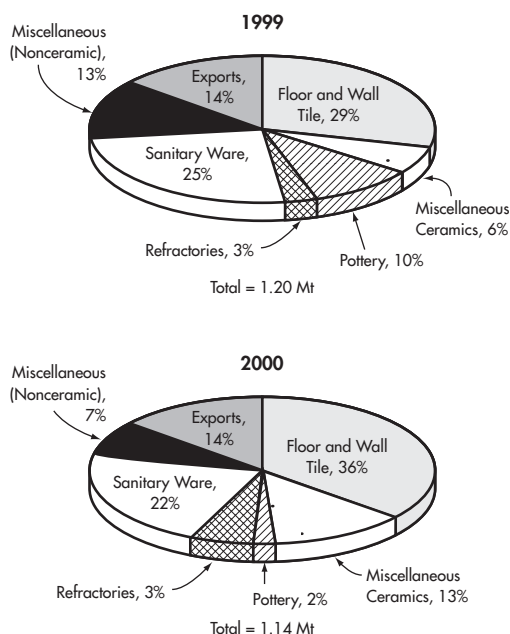
Table 2 presents data for the production, imports, and exports of different clays in the United States.

Overall production of clays in the United States, including ball clay, bentonite, common clay and shale, fire clay, fuller's earth and kaolin, decreased by 3% in 2000 to 40.8 Mt. Exports increased about 9% to 5.3 Mt, and imports increased about 6% to 96,000 t (Grahl 2002). Bentonite and fuller's earth are the clays most commonly used as absorbents. The other clay statistics are included in the table to show the overall market.

Table 2. Salient statistics—United States, kt

	1999	2000	2001	2002	2003
Production mine					
Ball clay	1,200	1,140	1,100	1,120	1,120
Bentonite	4,070	3,760	3,970	3,970	3,970
Common clay	24,800	23,700	23,200	23,000	23,000
Fire clay	402	476	383	446	446
Fuller's earth	2,560	2,910	2,890	2,730	2,730
Kaolin	9,160	8,800	8,110	8,010	8,010
Total	42,200	40,800	39,600	39,300	39,300
Import for consumption					
Artificially activated clay and earth	17	18	21	27	20
Kaolin	57	63	114	158	275
Other	16	16	13	32	50
Total	90	96	148	217	325
Exports					
Ball clay	107	100	174	127	150
Bentonite	719	761	628	722	680
Fire clay	189	216	238	251	275
Fuller's earth	152	136	146	60	50
Kaolin	3,310	3,690	3,440	3,350	3,400
Clays, not elsewhere classified	329	357	344	449	420
Total	4,800	5,260	4,970	4,960	4,980

Courtesy of U.S. Geological Survey.



Source: Grahl 2002 (reprinted with permission from *Ceramic Industry*, January 2002, Vol. 152, No. 1, www.ceramicindustry.com).

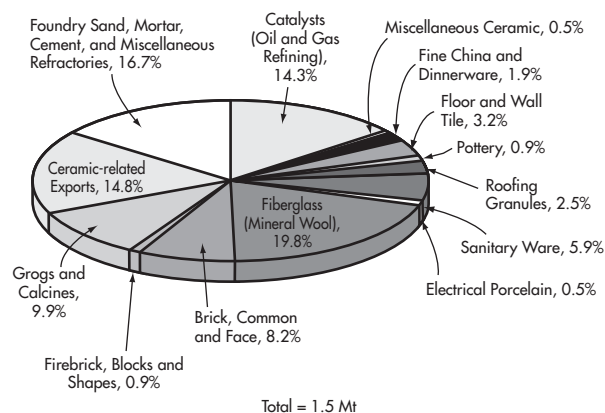
Figure 4. U.S. consumption of ball clay, 1999–2000

Between 1996 and 1999, the ball clay industry sustained an exceptional growth rate of 7.6% per year. The robust economy and associated booming construction industry prior to the latter half of 2000 resulted in healthy sales of sanitary ware and other ceramic products that use ball clay. In 2000, domestic consumption increased compared to 1999 for floor and wall tile, 12%; refractories (including firebrick, blocks, shapes, high-alumina brick and specialties, and kiln furniture), 38%; and miscellaneous ceramics (including catalysts, electrical porcelain, fiberglass, fine china/dinnerware, glazes, and mineral wool), 52%. Declines in consumption were recorded, however, for pottery (81%) and sanitary ware (12%; see Figure 4.)

The recession that began in March 2001 resulted in declining consumption of industrial products in many sectors. Construction was one of the last business segments to be affected. Major business consolidations have occurred over the past several years, resulting in five major competitors—Imerys (based in France with locations worldwide), Unimin (based in Belgium with locations worldwide), WBB Minerals Ltd. (based in the United Kingdom), H.C. Spinks (based in the United States), and Old Hickory Clay (based in the United States)—dominating the U.S. ball clay market. Competition, coupled with the slowing economy, appears sufficient to minimize any significant price increases over the next several years.

The production of common clay and shale declined slightly (4%) to 23,700 t in 2000. Of this amount, the majority was supplied from North Carolina (10%), Texas (9%), Alabama (9%), Georgia (6%), and Ohio (6%). Use of common clay and shale increased 23% in ceramic floor and wall tile, but declined nearly 40% in refractory applications. Demand for common clay and shale in heavy clay products (including extruded brick, drain tile and sewer pipe, flue linings, and miscellaneous clay products) declined about 2% compared to 1999 levels.

Production of fire clay increased about 16% in 2000 to 476,000 t, with the largest increase (53%) in heavy clay products.



Source: Grahl 2002 (reprinted with permission from *Ceramic Industry*, January 2002, Vol. 152, No. 1, www.ceramicindustry.com).

Figure 5. U.S. kaolin consumption by end use (ceramics), 2000

Production of fuller's earth also increased by about 12% to 2.9 Mt, but it was uncertain how much of that amount was used in ceramic applications. Data were unavailable for the use of bentonite in ceramics in 2000.

The kaolin industry has been mostly stagnant over the last several years. Production in 2000 slipped 4% to 8.8 Mt. Of this amount, 18% (1.5 Mt) was used in ceramic applications (see Figure 5). This was 3% lower than the share held by ceramics in 1999 (1.9 Mt), and the overall quantity of kaolin used in ceramics also decreased by about 18%. Segments posting the biggest declines were electrical porcelain (down 38% compared to 1999) and miscellaneous refractories (down 56%). Other applications for kaolin included fillers, extenders, and binders (primarily for paper and paper coatings), 53%; chemical manufacture, 0.4%; portland cement, 1%; and miscellaneous, 6%. Exports comprised 31% of overall production at 2.7 Mt, an 11% increase over 1999 levels. Import information was unavailable.

As with ball clay, kaolin consumption in sanitary ware and other ceramic products used in construction is expected to decline as the construction industry slows. Kaolin consumption in fine china and dinnerware is expected to remain relatively steady.

Despite several significant business consolidations over the last several years, approximately 25 companies in nine states mine kaolin. Ongoing competitive forces coupled with a soft economy will probably temper any desire by producers to increase kaolin prices in the near future.

DISTRIBUTION OF MAJOR DEPOSITS

United States

The United States is home to major deposits of all the industrial minerals and rocks used as absorbents. In fact, the diatomite, kaolin, attapulgite, and sand deposits are world class in terms of size and purity. These deposits, however, occur in select areas of the country. Diatomite and perlite deposits are in the West, the specialty clay deposits are in the South, and sand and gravel deposits occur in all regions, as shown in Figure 6. The biggest disadvantage in terms of deposit location and market demand is that diatomite and perlite are mined in the West and the demand is concentrated in the Midwest and the East. Table 3 is a comparison between the mine production in the United States and different countries around the world.

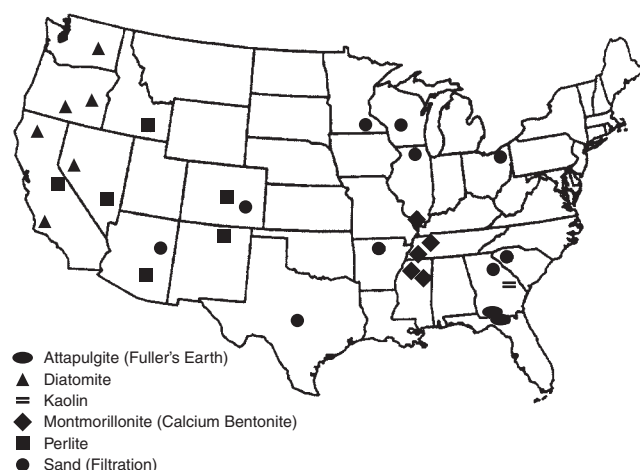


Figure 6. Major producing locations of industrial minerals and rocks used as filters and absorbents

Diatomite and Perlite

All of the commercial deposits of diatomite and perlite occur in the western United States. Diatomite is currently mined in the states of Arizona, California, Nevada, Oregon, and Washington. Greater than 50% of U.S. production is mined from the world-class deposits at Lompoc, California (Miles 1990).

New Mexico accounts for about 85% of the perlite mined in the United States, with the remaining 15% mined in Arizona, California, Colorado, Idaho, and Nevada. Because expanded perlite has a very low bulk density and the majority of perlite is consumed in the East, crushed perlite ore is typically transported to expander plants, which are located close to major end-use markets (Meisinger 1988).

Specialty Clays

Commercial deposits of specialty clays used as filters and absorbents are, for the most part, located in the Southeast. Mississippi,

Missouri, and Tennessee account for the majority of calcium montmorillonite. Florida and Georgia account for all of the attapulgite production.

Sand and Gravel

The occurrence of sand and gravel deposits are pervasive throughout the United States. From a strictly geologic view, the quantity of sand and gravel is essentially inexhaustible (Dunn 1983). Although this is true for gravel used in filtration, it is not true for sand. The sand that is used in filtration applications has rigid specifications as to the purity, size, and shape of the individual grains. As a consequence, the major deposits that naturally yield such material are limited to locations in northern Illinois and central Texas (Van Kouteren 1994).

The Rest of the World

A review of the USGS mineral production statistics indicates that no one country dominates in producing materials used as filters and absorbents. There are, however, a number of countries that are major producers of these raw materials.

PHYSICAL AND CHEMICAL PROPERTIES

Clay minerals used as absorbents and desiccants have a number of similar chemical and physical properties. They must be chemically stable with a physical structure that allows the storage and flow of liquids in the structure. Chemical analysis of the major materials used as adsorbents and desiccants is shown in Table 4 (Van Kouteren 1994). Silica, the main constituent, is responsible for chemical stability. The relatively open or porous structure of these materials results in low bulk densities.

The properties and technical application of clay minerals mainly depend on the mineral composition, size distribution, degree of consolidation, and processing conditions (Konta 1995). Properties of clay minerals depend mainly on the structure and chemistry of the crystal and also on the state and distribution of the electrostatic charge of the structural layers. The ionic substitution in the octahedral and tetrahedral sheets will result in a negative charge, which is naturally compensated by cations such as K^+ , Na^+ , Ca^{2+} , Mg^{2+} , and H^+ adsorbed in the interlayer space. Materials of

Table 3. Mine production, kt

	Bentonite		Fuller's Earth		Kaolin	
	2002	2003	2002	2003	2002	2003
United States (sales)	3,970	3,970	2,730	2,730	8,010	8,010
Brazil (beneficiated)	175	175	na *	na	1,710	1,800
Commonwealth of Independent States	750	750	na	na	5,800	8,000
Czech Republic	174	200	na	na	3,650	4,000
Germany (sales)	500	500	500	500	3,770	3,800
Greece (crude)	1,150	1,200	na	na	60	60
Italy	500	500	30	30	100	100
Korea (crude)	na	na	na	na	2,380	2,850
Mexico	400	400	150	150	680	680
Turkey	559	600	na	na	372	350
United Kingdom	na	na	140	150	2,400	2,400
Other countries	1,820	1,830	340	335	14,300	13,000
World total (rounded)	10,000	10,100	3,890	3,900	43,200	45,100

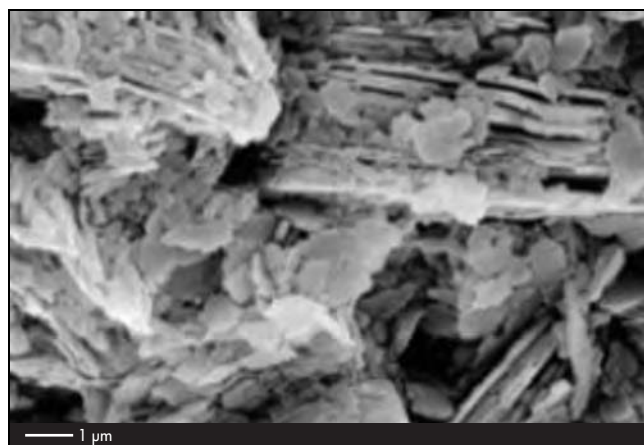
Courtesy of U.S. Geological Survey.

* na = not available.

Table 4. Approximate chemical composition of the major industrial minerals and rocks used as adsorbents and desiccants

Mineral Type	Sand	Diatomite	Perlite	Attapulgite	Montmorillonite	Kaolinite
Oxides, %						
SiO ₂	99.45	89.7	72.1	54.0	50.2	45.2
Al ₂ O ₃	0.05	3.7	13.5	8.6	16.2	37.0
H ₂ O	NA *	NA	3.0	21.4	22.7	14.4
Ignition loss	0.07	3.7	NA	NA	NA	NA
Fe ₂ O ₃	0.02	1.1	0.8	3.1	4.1	0.3
TiO ₂	0.01	0.1	0.1	0.2	0.2	1.3
CaO	0.04	0.3	0.9	2.0	2.2	0.5
MgO	0.02	0.5	0.5	10.1	4.1	0.5
Na ₂ O and K ₂ O	NA	0.7	9.0	0.4	0.3	0.8
P ₂ O ₅	NA	0.2	NA	NA	NA	NA
Other	0.34	NA	0.1	0.2	NA	NA
Total	100.0	100.0	100.0	100.0	100.0	100.0

* NA = not applicable.



Courtesy of H.H. Murray.

Figure 7. Scanning electron microscope (SEM) image of kaolin particles (bar = 1 μm)

larger pore volume with a new microstructure can be prepared by exchanging any of these cations with a desirable cation and also by removing ions from the octahedral or tetrahedral sheets (Konta 1995).

Kaolinite and Serpentine Group

The most common mineral in this group is kaolinite. Its crystal has the unit cell chemical composition of $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$ and consists of alternating layers of silica tetrahedra and alumina octahedra. Each kaolinite particle consists of several sheets of twin layers held together with hydrogen bonds. The aspect ratio of kaolin particles, which are plate-like in shape, may vary from 5 to 15, depending on the mechanical treatment of the particles (Konta 1995; Weaver and Pollard 1973; Sjöberg et al. 1999). Physical and chemical properties of kaolin, which depend on several factors such as geological conditions and mineralogical composition, determine the use of kaolin in different applications. The best commercially usable kaolin deposits are located in Georgia and South Carolina in the United States, the Amazon region of Brazil, and the Cornwall Area of southwestern England (Pickering and Murray 1994).

Kaolin is a white powder and its pure crystal, called kaolinite, is hexagonal in shape (see Figure 7). There is a significant charge difference between the basal plane and the edge of the particles resulting from the differences in chemical composition. Kaolin edges contain both silica and alumina-like charge sites, and the faces contain only silica-like charge sites, which are expected to remain negatively charged above pH 3.0. The edges are positively charged at low pH, but progress through an isoelectric point to possess a negative charge at high pH (Johnson, Russell, and Scales 1998; Johnson et al. 2000). As a result of this difference, in the absence of dispersing agents, electrostatic edge-to-face attraction causes agglomeration of the particles in the form of a cardhouse-type structure (even at very low volume fractions) depending on the pH of the dispersion (Herrington, Clarke, and Watts 1992). Results of earlier work (Zaman, Tsuchiya, and Moudgil 2002) indicate that negatively charged agents such as polyacrylic acid (PAA) adsorb on positive sites present on the edge of kaolin particles.

The main applications of kaolin is in the paper industry where it is used to improve brightness, opacity, and printability of paper; as functional fillers and extenders in different products such as plastics, rubber, paint, and ink; in ceramics in the tile, white ware, sanitary ware, insulators, and pottery markets; and as a raw material in the production of fiberglass. A relatively small amount of kaolin is used as a dust-dispersal adsorbent for pesticides (Khandal et al. 1992) and as a mildly acting sorbent in the manufacture of linoleum and other floor-cloth cement (Konta 1995).

Kaolinite is a hydrophilic material and can be dispersed in water using anionic inorganics, polyelectrolytes, and surfactants. Adsorption of polymers and surfactants as a function of pH, ionic strength, and polymer charge on the surface of kaolin has been studied (Sastry, Sequaris, and Schwuger 1995; Lee, Condrate, and Reed 1996). Understanding the interaction mechanism of the charged species with the active sites on the surface of the particles is important in terms of the application of kaolin in different processes. The surface of kaolin can be modified to make it hydrophobic or organophilic for different applications such as functional fillers in plastics and rubber.

Smectite Group

The smectite group of clay minerals has a three-layer structure formed through the decomposition of volcanic glass. In these minerals, a central octahedral layer of hydrous metal oxide (usually

aluminum, sodium, magnesium, calcium, or lithium) is sandwiched between two other layers of silica tetrahedra. Often, alumina substitution for silica in the tetrahedral sheet and iron and magnesium substitution for aluminum in the octahedral sheet creates a net positive charge imbalance in the 2:1 layer (Murray 2000). This charge deficiency is balanced by exchangeable cations such as sodium, calcium, lithium, and magnesium adsorbed between the unit layers and on the edges. The mineral in the smectite group is sodium montmorillonite (see Figure 8) if the dominant exchangeable cation is sodium, and it is calcium montmorillonite if the exchangeable cation is calcium. The smectite group can be classified as montmorillonite, beidellite, nontronite, and saponite.

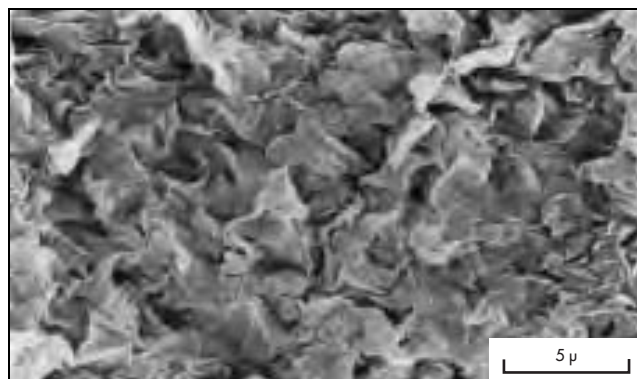
Calcium montmorillonite has very strong adsorptive properties and is widely used in various processes for removing impurities and as an additive sorbent in different products (Konta 1995). Both sodium and calcium montmorillonites are used in binding animal feed into pellets and both act as absorbents for bacteria and certain enzymes. Montmorillonite is also used as a pet waste absorbent, which may be treated with deodorants and bactericides. A variety called "clumping litter" uses a mixture of calcium-bentonite granules and sodium bentonite. The sodium bentonite swells and clumps when the waste moisture contacts the litter, which makes for selective and easy waste removal from the litter box (Murray 2000).

Calcium montmorillonite is largely used to decolorize, deodorize, and remove impurities from vegetable, animal, and mineral oils, and fats and waxes. Acid-activated calcium montmorillonite is used for filtering and decolorizing oils (Murray 2000; Odom 1984). Calcium ions from the surfaces and edges of the layers will be removed when calcium montmorillonite is treated with sulfuric or hydrochloric acid, which increases the overall negative charge. Acid-activated clay is more effective in removing anionic color species from the oil.

A moderately large amount of natural smectite clay is used to remove colloidal impurities from wine. These impurities are positively charged and adsorb on negatively charged smectite clays. In the clarification of wine, beer, vinegar, and fruit juices, sodium montmorillonites having a light or white color with high dispersibility are preferred. A relatively new market for acid-activated clay is in animal feed, where it absorbs mycotoxins (Murray 2000).

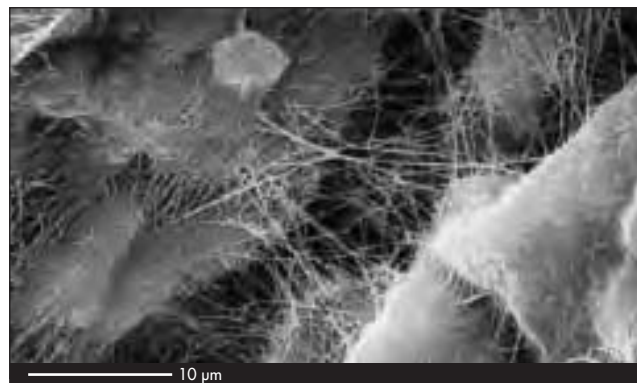
Other adsorbent and desiccant applications of the smectite group, including calcium bentonite, sodium bentonite, acid-activated bentonite, and organophilic bentonite (Murray 2000; Konta 1995), follow. Members of the smectite group are used

- As pillared clays for specific catalyst and absorbent uses
- As a dry detergent for the sorption of impurities
- For the removal of alkaloids and insecticides from vegetable extracts
- As an anti-irritant, and in industrial creams and organic medications in pharmacy
- As a sorbent in soaps, polymers, and construction materials
- For removal of metallic and other ions from water
- For the sorption of sulfur, nicotine, and other impurities from the atmosphere
- As a carrier of substances such as codeine phosphate in pharmacy
- For the removal of oxidation products from lubricating oils
- For water purification
- In different food industries such as in sugar and wine production
- For removal of pigments from fats



Courtesy of H.H. Murray.

Figure 8. SEM image of sodium montmorillonite



Courtesy of H.H. Murray.

Figure 9. SEM image of palygorskite showing elongated particle shape

Palygorskite and Sepiolite

Palygorskite (see Figure 9) and some other clays are termed as fuller's earth because of their sorptive and bleaching properties. Attapulgite, which is a hydrated magnesium silicate mineral with a slight substitution of magnesium by aluminum, is the trade name for palygorskite. Its crystal structure is layer fibrous. The chemical structure of sepiolite is almost the same as palygorskite except it has a slightly larger unit cell (Murray 2000).

Palygorskite and sepiolite are excellent absorbents and are used in many applications that utilize this property (Murray 2000; Konta 1995). The major applications are in the manufacture of pesticides; as floor absorbents; in agricultural carriers; in bedding for small animals; as anticaking agents; for removal of oil and grease; for purification of sugar; for decolorization and purification of petroleum derivatives; in wax and paraffin; in lubricating oils; for purification of oils and animal fats; as environmental absorbents; and as a natural decolorizing agent, particularly for mineral oils (Galan 1996). Another use of these materials is for environmental applications as barrier clays. A mixture of palygorskite and sodium montmorillonite works well to prevent movements of liquids through the barrier and to absorb heavy metals and toxic pollutants from landfills and industrial wastes (Murray 2000).

Attapulgite is another clay mineral that belongs to the palygorskite group and is widely used as an absorbent. Approximately

939,500 t of attapulgite were produced around the world in 1999, with the United States accounting for 75% (725,000 t), valued at \$80 million. The estimated overall global production of fuller's earth, including attapulgite, montmorillonite, and sepiolite, is just over 3.3 Mt. In the United States, attapulgite has an average value of \$110 per t. Global demand for the material is sensitive to oil drilling activity. U.S. producers saw a decline in the sale of attapulgite from 793,000 t in 1998 to 725,000 t in 1999. Major markets for attapulgite are pet waste absorbents, oil and gas absorbents, pesticide carriers, cement fertilizer carriers, drilling mud, gypsum products, animal feeds, and adhesive applications.

An overview of the market for sepiolite shows that Spain was the largest producer with an estimated production of 750,000 tpy in 1998. Other producers are Turkey at a rate of about 15,000 tpy, the United States at a rate of about 40,000 tpy, and China at a capacity of about 15,000 tpy. Sepiolite is mainly used in cat litter, industrial absorbents, animal feed additives, and carriers for insecticides and herbicides. The expected percentage increases for the consumption of sepiolite over 5 years are in technical applications, +17%; in industrial applications, +20%; in cat litter production, +11%; and in animal feed manufacture, +28%. More than 70% of sepiolite output is used to produce pet litter, mainly cat litter. European demand for sepiolite in animal feed applications is expected to grow by more than 15%. Cat litter usage is likely to have lower growth.

OTHER MATERIALS

Other materials used as adsorbents include diatomite, perlite, sand, and gravel. Diatomite and perlite have cell structures that form microscopic voids. As explained previously, diatomite is a siliceous, sedimentary rock consisting of the fossilized skeletal remains of the diatom plant related to algae (Kadey 1983). Perlite is a dense, amorphous, hydrated volcanic glass, generally of rhyolitic composition. In industry, it is processed and thermally expanded as the lightweight aggregate (Kadey 1983). In 1997, the total market for perlite was 1.66 Mt; United States, 773,000 t; China, 250,000 t; former U.S.S.R., 90,000 t; Denmark, 95,000 t; France, 80,000 t; and South Korea, 53,500 t. The mineral is used mainly for filtration and as an absorbent. It is used in the manufacture of beer and wine. Demand in developed countries is relatively flat but is expanding in developing countries. Diatomite is losing market share for brewing applications to ceramic polymerics and carbon membranes, and it is under pressure from bentonite for absorbent applications. Mallina Holdings has opened a new diatomite plant in western Australia. This has a capacity of about 20,000 tpy. A 10-Mt diatomite deposit at Akhaltsikhe, Republic of Georgia, is to be developed by a joint venture between a U.K. company and a local business. Breakdown of diatomite usage in the United States is beer, 7%; wine, 2%; fruit juice, 3%; sugar, 4%; pharmaceuticals, 2%; exports, 36%; and other, 46%.

Sand and gravel consist of separate grains or particles in the size range of $1/16$ to 2 mm in diameter. For absorbent applications, sand consists mainly of pure, rounded quartz, and gravel consists of rock fragments (Davis and Tepordei 1985; Van Kouteren 1994).

PROCESSING AND SPECIFICATIONS

The processing of clays for use in absorbent applications is fairly similar for attapulgite, montmorillonite, specialty clays, and kaolin. Because clay ore contains up to 60% water, the main objective for processing is to remove water and to reduce the material to the appropriate size. Before the crude clay is dried, it must first be passed through shredders to reduce it to fist-sized pieces for feed to a dryer (Moll 1986).

Proper drying techniques are essential for developing and maintaining the open structure in montmorillonite and attapulgite. At temperatures between 100°C and 200°C, water in the interlayer region of montmorillonite or in the tubes of attapulgite begins to evaporate. At higher temperatures, certain tightly bound water molecules in attapulgite begin to evaporate. Between 500°C and 800°C, the hydroxyl ions begin to combine to form water, which leaves the structure (Moll and Goss 1987).

Once the clay is dried, the material is typically crushed in a corrugated roller or hammer mills and passed over large shaking screens. Oversize material goes back to the crushers, and undersized material goes to the next set of smaller sized screens to produce increasingly smaller granule sizes. These smaller products are typically destined for the pet litter and floor absorbents markets (Moll 1986).

The key properties for clays used as floor absorbents are proper granule size, low bulk density, the ability of the product to absorb liquids readily and rapidly, and durability (so that the granules do not break down in normal shipment and use). Floor absorbents, mainly used for oil and grease, are sold in sizes ranging from 4.00 to 0.43 mm. The other key properties typically are a bulk density of about 625 kg/m³ and the ability to absorb about 65% to 100% of their weight in water or oil (Moll 1986).

In cat litter, the pH and size are the important factors that affect the clay's performance. Low pH products are more effective in controlling the fermentation of urea in cat urine. The size of clay granules is important for avoiding dustiness in use and tracking by the cat. A common size range for cat litter products is often 4.75 to 0.60 mm.

Another key property is surface acidity, also known as Lewis acidity. The surface acidity of the clay granules can cause degradation of some chemicals absorbed into the granule. To prevent the degradation, formulators must measure the strength of the Lewis acid sites to determine how much deactivation is required. High surface-acidity clays, measured by the Hammett acidity function unit (pKa), are deactivated with alcohols or glycols to neutralize the acid sites (Moll and Goss 1987). Table 5 presents examples of the important specifications for carrier materials.

TESTING

As is common with most industrial minerals, the testing procedures by which processed minerals and aggregates are evaluated and standardized are designed to quantify an attribute required in the performance of a product (Kadey 1983).

The important characteristics to measure include a clay's ability to absorb liquids easily and quickly, to have a high liquid-holding capacity, to have granules that do not break down during shipment, and to have relatively low bulk densities. Standard tests and techniques to measure a granule's maximum absorption and resistance to attrition are outlined by federal specifications P-A 1050A and P-A 1056A, respectively. In addition, agricultural carriers undergo a liquid-holding capacity test. The Rhone-Poulenc method MP-12 is a test that measures the amount of liquid the granules can absorb without sticking together (Moll 1986).

In filtering and clarifying applications, the final color of the bleached oil is the critical property. Test methods for evaluating montmorillonite and other types of fuller's earth for bleaching edible oils are outlined in the American Oil Chemists' Society (AOCS) official methods Cc 8a-52 and Cc 8b-52. These specifications contain instructions on bench-type tests, including stirring time, heating rates and temperatures, approved equipment, quantities of clay and raw oil required, and other items (Patterson and Murray 1983).

Table 5. Key properties for select specialty clays used as absorbents

Grade	Color	Bulk Density, kg/m ³	Surface Area, m ² /g	Free Moisture, % (110°C)	Base Exchange Capacity	pH
Attapulgite						
RVM	Gray	545	125	7	20	8.0
LVM	Tan	545	125	2	20	8.0
Other†	Cream	275	120	1	NA‡	8.5
Montmorillonite						
Acid activated	NA	640	250	16	NA	3.2§

* Milliequivalents per 100 g.

† Powdered grade.

‡ NA = not applicable.

§ 25 g of product in 75 mL deionized H₂O.

USE OF ABSORBENTS AND DESICCANTS

Industrial minerals and rocks are used in many absorbent and desiccant applications. On a tonnage basis, the majority of the minerals, including sand, diatomite, perlite, attapulgite, and montmorillonite, find such end uses as municipal waters, food products, chemicals, pet litter, oil and grease, and carriers.

The use of specialty clays in the pet litter market has proven very effective in absorbing liquid pet waste and related odors. Specialty clays used for pet litter have the ability to absorb large quantities of liquid cat waste and retard the formation of ammonia, which is created when urea from cat urine ferments (Harris et al. 1989).

Any user of oil and grease or machinery requiring oil and grease may ultimately require specialty clays to absorb and control spills. Slippery films of oil and grease as well as puddles of water and other chemicals often create dangerous conditions on the floors of machinery repair shops, factories, service stations, and numerous large and small industrial facilities (Harris et al. 1989). Specialty clays can absorb up to their own weight in oil, grease, water, and a variety of other chemicals. The clays also are safe, absorb rapidly, and can be cleaned up using a broom or shovel (Moll 1986).

Specialty clays used as mineral carriers have a wide variety of applications in the field of agricultural chemicals. Most pesticides, including herbicides, fungicides, and insecticides, are highly toxic and typically require only a kilogram per hectare (Moll 1986). The primary function of these carriers is therefore to dilute high-potency chemicals to a spreadable field concentration and to apply them to a location where pests can be destroyed while damage to desirable plants, wildlife, and the environment is minimized (Swayer 1983).

The two main types of mineral carriers are absorbent and non-absorbent. The absorbent carriers, which account for the majority of demand, have a highly porous structure that accounts for their high absorptivity and low density. The nonabsorbent types provide only enough surface area to carry the chemicals and typically have high bulk densities, which limits the amount of chemicals they can carry. Montmorillonite, attapulgite, and diatomite comprise the absorbent carriers, and such minerals as ball clay, calcium carbonate, quartz sand, and talc are considered nonabsorbent (Moll and Goss 1987).

In fertilizers, clays are also used as anticaking additives in dry fertilizer mixes. The anticaking function of the clay works by coating fertilizer particles and absorbing solvents or water that may be present. This reduces the formation of crystals that often bind particles and cause caking problems (Harris et al. 1989).

The most significant other absorbent market for specialty clays is desiccants. Clay desiccants are used to adsorb moisture

from the air enclosed in such packaged products as military equipment and electronic components. This helps prevent corrosion of the product and retards the formation of mildew. The desiccants are made up entirely of calcium montmorillonite clays that are oven-dried, crushed, and packaged in bags or canisters. These products are most effective in conditions of moderate relative humidity (15% to 40%) and are generally preferred because of their ability to adsorb more than 20% of their equivalent weight in water without any apparent change in size, shape, or texture. Furthermore, they are also available at a relatively low cost (Harris et al. 1989).

NEW APPLICATIONS, MARKETS, AND FUTURE TRENDS

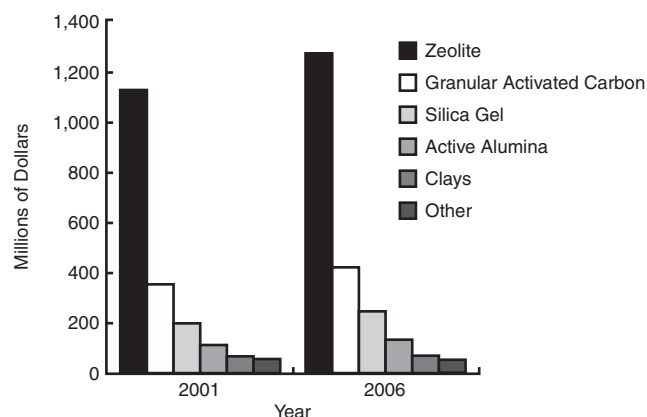
The microporous adsorbents industry is a mature industry with a wide variety of products satisfying the requirements of well-established applications. The expanded scope and applicability of environmental regulations, however, along with improving living standards around the world, are stimulating significant increases in demand for these products. In addition to environmental forcers, newly invented, specialized, microporous adsorbent products are creating novel market opportunities in the electronics manufacturing and biomedical industry sectors.

According to a study released in 2001 by Business Communications Company (BCC) Inc., the market value for inorganic microporous adsorbents was estimated at nearly \$1.78 billion in 2001. This total, which comprises the top five and other types of inorganic microporous adsorbents, is forecast to increase at an average annual growth rate (AAGR) of 3.1% to reach \$2.08 billion by 2006.

Water and air purification applications in the environmental pollution control industry consume the majority of GAC (granular activated carbon) production. GAC constitutes nearly one fifth of the total market size and is projected to grow at an AAGR of 3.8%. Its projected growth rate will be negatively affected by relaxed environmental legislation as well as dumping activity from foreign nations.

As shown in Figure 10 and Table 6, zeolites account for the largest market, with nearly 62% of the total market, and thus heavily influence overall growth rates. Their applications range from detergent builders to high-end catalyst supports in the chemical and petroleum industry. Overcapacity in low-end zeolites and reduced obsolescence of improved high-end products will limit the zeolite market's average yearly growth rate to 2.5% in the next 5 years.

Silica gel adsorbents and activated alumina are expected to have the highest AAGR of 4.8% each, with a projected increase from \$177 million and \$91 million in 2001 to a 2006 value of \$224 and \$115 million, respectively. Silica gels are the most common



Source: Business Communications Company, Inc., and R. Deshpande 2001.

Figure 10. Market value of adsorbents, through 2006, million \$

Table 6. Market value of adsorbents, through 2006, million \$

	2001	2006	AAGR, % 2001–2006
Zeolite	1,100	1,245	2.5
Granular activated carbon	334	402	3.8
Silica gel	177	224	4.8
Active alumina	91	115	4.8
Clays	44	52	3.4
Other	32	37	2.9
Total	1,778	2,075	3.1

Source: Business Communications Company, Inc., and R. Deshpande 2001.

desiccants and drying agents, and their growth rate will be fueled by applications in health care, building materials, and the high-end paper manufacturing industry. Activated alumina adsorbents are used as common catalyst support in the chemical processing industry. Their application in chromatographic separation columns is expected to accelerate in the biochemical sector.

Usage of clays as adsorbents is projected to grow at a rate of 3.4% to a market size of \$52 million in 2006. Clays are often used as adsorbents where purity is not a primary concern. Development of pillared intercalated layered clay may offer a niche commercial opportunity. The adsorbent materials discussed have attained best available technology (BAT) status in many of their prominent applications. Although they have achieved significant penetration in those application segments, innovation activity remains brisk.

SUBSTITUTE MATERIALS

Substitute materials for adsorbent minerals consist of such organic materials as sawdust and ground alfalfa, corncobs, and citrus fruit rinds (Van Kouteren 1994). Although these materials are typically less expensive, they are not as effective as specialty clays. On the other hand, such synthetic materials as molecular sieves, silica gel, precipitated silica, and nonwoven polyethylene fabrics are very effective but are expensive. In more limited cases, other mineral products such as vermiculite, gypsum, lime, sand, and zeolites are used in specific applications where low cost and/or high performance is desired. Other substitutes include diatomite and perlite, especially in the western United States because of the transportation cost advantage that they have over clays (Harris et al. 1989).

Polyethylene fabric has had the largest impact on the demand for mineral absorbents. These nonwoven fabrics have a natural affinity for petroleum-based products and as a result they can absorb up to 20 times their weight of oil and grease. The use of these materials has grown as a result of the classification of spent clay as a hazardous material and the subsequent disposal costs associated with these clays. The big advantage of these nonwoven fabrics is that they can be incinerated with less than 1% ash remaining (Harris et al. 1989).

ENVIRONMENTAL AND HEALTH REGULATIONS

Governmental regulations concerning crystalline silica have had an adverse effect on the demand for diatomite. This trend began in 1988 when the International Agency for Research on Cancer (IARC) classified crystalline silica as a probable carcinogen. The classification triggered regulation of crystalline silica at a threshold concentration of 0.1% in materials under the IARC's Hazard Communication Standard (Miles 1990).

The diatomite and other minerals suppliers responded to this in a number of different ways, including worker and user training programs, product labeling, and dust reduction programs. The diatomite industry also created the International Diatomite Producers Association (IDPA) to study and issue reports on health, safety, and environmental issues related to the use of diatomite. Other mineral and chemical producers formed a Chemstar Crystalline Silica Panel. The panel, formed in 1989 and sponsored by the American Chemistry Council (ACC), works with government agencies to avoid random banning of minerals suspected of being hazardous.

Another governmental regulation that has adversely affected the demand for minerals and rocks used as filters and absorbents was the 1991 Environmental Protection Agency ban on disposing oil-containing wastes in landfills. This ruling caused some consumers of clays for oil and grease absorbents to switch to other products, mainly because organic products could be incinerated instead of placed in landfills. Clay suppliers are currently fighting to have new tests approved for measuring the leaching or leaking of absorbed oil from clay products. Under the current regulations, a toxicity test renders the clays hazardous, but if proposed liquid release tests are accepted, the absorbent minerals may prove to be less of a hazard (Van Kouteren 1994).

SELECTION OF ADSORBENTS AND DESICCANTS

This section briefly reviews the criteria for the selection and design of adsorbents. More detailed information can be found in a recent book on adsorbents by Yang (2003).

The selection of a proper adsorbent for a given application is a complex problem. Adsorbents are designed based on the adsorption isotherms, which are calculated based on interaction potentials and adsorbent structures. There are three basic types of contributions to the adsorbate–adsorbent interactions: dispersions, electrostatics, and chemical bonds. Weak chemical bonds involving π electrons have recently been explored for the design of new and highly selective sorbents. Adsorption occurs when the interaction potential energy is equal to the work done to bring a gas molecule to the adsorbed state. Many researchers have discussed the individual contributions to the total potential energy in detail by (e.g., Barrer 1978; Israelachvili 1992; Masel 1996). Five different types of interactions contribute to the potential: (1) dispersion energy; (2) close-range repulsion energy; (3) induction energy (interaction between electric field and an induced dipole); (4) interaction between electric field and a permanent dipole; and (5) interaction between field gradient and a quadrupole. The first two are nonspecific interactions and nonelectrostatic in nature, and the last three arise from the

charges on the solid state. The most important property that determines nonspecific interactions is the polarizability of the surface and magnetic susceptibility. The van der Waals radii of the interacting pairs is defined as an equilibrium distance at which the sum of nonspecific interactions is equal to zero. Polarizability, electronic charge, and van der Waals radius are the most important parameters that must be considered in designing adsorbents. Alkali and alkaline earth metal atoms have very high polarizabilities and, when present on the surface, can cause high potentials. When these elements are present as cations, the polarizability is significantly reduced (Yang 2003).

The van der Waals radii of the surface atoms and electronic charges determine electrostatic interactions and are crucially important factors when considering ion-exchanged zeolites and molecular sieves as sorbents (Yang 2003).

Other criteria for selection of adsorbents are the pore size and geometry. The interaction potential between a molecule and a flat surface is greater than that between two molecules or atoms because molecules interact with all adjacent atoms on the surface. When a molecule is placed in a pore of a given shape (i.e., cylindrical surface), it interacts with different sides and the potentials are greater because more surface atoms interact with the adsorbate molecules. Rege and Yang (2000) have calculated the threshold pressure for adsorption in different pore sizes and geometries for nitrogen on carbon using the model that was developed by Horvath and Kawazoe (1983). These results (Yang 2003) indicate that attractive forces acting on the adsorbate molecules are strongly affected by the size and shape of the pores.

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Minerals Used in Formulating and Manufacturing Catalysts

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INTRODUCTION

Catalysts are designed or preengineered materials that, by their presence, change the nature of chemical reactions. They speed up or drive a reaction toward a desired product while typically not being consumed in the process. Catalysts are either homogeneous or heterogeneous. The former consists of one uniform, harmonized material whereas the latter is made up of two inseparable components: a *support* that can be inert or active, and an *active agent*, usually a precious or base metal. Some catalysts may contain several components, each designed for a different function.

The field of catalysts and catalysis is often broken into two broad areas: refining and industrial. Refining, of course, refers to catalysts used specifically in converting crude oil and its fractions into transportation fuels and various coproducts such as lubricating oils. This is a large area but relatively easy to define. In contrast, the industrial catalyst sector is a very broad one, encompassing all catalysts used in making chemical products ranging from polymer intermediates to pharmaceuticals.

The concept of catalysis as a method of controlling the rate and direction of a chemical reaction has captured the imagination of scientists and technologists since 1835 when Jöns Jakob Berzelius coordinated a number of disparate observations on chemical transformations by attributing them to a “catalytic force” and coined the term *catalysis* to refer to the “decomposition of bodies” by this force (Stell 2003). The first heterogeneous catalytic process of industrial significance, introduced about 1875, used platinum to oxidize SO_2 to SO_3 , which was then converted to sulfuric acid by absorption in an aqueous solution of the acid (Magee and Dolbear 1998).

Today, catalytic processes, and the chemicals derived from these processes, touch every part of daily life. Many chemicals are produced through industrial-scale application of catalysis. Automobiles run on gasoline fuels produced by fluid catalytic cracking (FCC) catalysts made from processed kaolin clay. Emissions from internal combustion engines are purified by catalytic converters that use precious metals (e.g., platinum, palladium, ruthenium) on a silica-alumina honeycomb structure to burn off residual hydrocarbons. Detergents and soaps are made using copper–chromite catalysts. Hydrogenated vegetable fats and oils are produced or purified by nickel and bleaching-clay catalysts. Zeolites and molecular sieves synthesized from silica, alumina, and titania minerals are used commercially to produce chemicals like cumene or paraxylene that are processed further into plastics used in buildings,

cars, and toys. Even the plastic powder for 2-L beverage containers (e.g., soda pop and drinking water) is first purified with a precious-metal-on-carbon catalyst to remove yellow color bodies and to produce a crystal-clear view of the beverage.

MATERIALS

Careful study of the scientific literature on catalysts reveals that most elements in the periodic table have been used effectively in catalysts. For example, uranium was used in a selective ammoxidation catalyst developed by Standard Oil of Ohio (now BP) in the early 1960s. All the metals and nonmetals used in catalysts are derived from minerals, but almost none of them are used directly as recovered. Three exceptions are:

1. Bauxite, used in the Claus process for converting H_2S to sulfur
2. Kieselguhr (diatomaceous earth), used as a support for precious metals in some hydrogenation catalysts
3. Iron oxide (red) mud, used in older ammonia catalysts

Activated carbon and char coal are used as catalyst supports, generally in hydrogenation catalysts.

Generally, the key attribute for the successful application of these materials is their physical form. Catalysis requires contact between the reacting species and the surface of the catalyst. This contact is enhanced when the surface area of the catalyst is high, especially in materials with an open porous structure, where most of the measurable surface area exists on the walls of pores. The pores must have diameters large enough to accommodate free passage of feed and product molecules; because the majority of the surface area is on the walls of pores, however, an increase in pore diameter has a corresponding decrease in surface area. Over the last century, techniques were developed relying on precipitation: Sol-Gel; calcination; and to some extent, gas-to-solid reactions, such as flame spraying, for making useful materials such as catalysts and catalyst supports.

To be effective in various catalytic processes, solid materials must be formed into powders, balls, pills, “noodles,” and so forth. Because catalysts tend to be used for years at a time, the particles must be physically strong and must maintain their integrity under reaction conditions. For example, powders used in FCC processes have an average particle diameter of about $70\text{ }\mu\text{m}$ and must pass stringent attrition tests. This ensures their retention in the unit while they are circulated between reactor and regenerator five to ten times

per hour for months without decrepitating into fine powders that may be lost into the atmosphere as waste.

REFINING CATALYSTS

In 2004, approximately 85 million bpd (barrels per day; about 14 million st/day) of crude oil were produced worldwide. This quantity is reduced through distillation, but most is processed through refinery conversion units (Stell 2003). Conversion may involve a reduction in molecular weight of the distilled feedstock (as in catalytic cracking or hydrocracking), an increase in molecular weight (as in alkylation and polymerization), or a change in the structure of the feedstock without an appreciable change in molecular weight (as in reforming, isomerization, and hydrotreating). In addition to these conversion processes, refiners use catalysts for environmental purposes (SO_x , NO_x , hydrogen sulfide, and CO emission control) and to manufacture on-site hydrogen (water–gas shift and steam reforming) (Magee and Dolbear 1998).

All of these processes use catalysts that are formulated to contain a wide variety of minerals. The minerals contained are rarely used as-is in catalyst formulations; rather they are variably pre-treated chemically or thermally before they are incorporated into the catalyst formulation. An example of a treated mineral product widely used in petroleum catalysis is alumina. In this case, the mineral is bauxite, which consists of aluminum hydroxide and aluminum oxide hydroxide. In their catalytic use, mineral aluminas are converted to active aluminas through the conversion of either gibbsite (gamma aluminum trihydroxide) or boehmite (aluminum oxide hydroxide) to high-surface-area gamma alumina, or through the conversion of bayerite (alpha aluminum trihydroxide) to high-surface-area eta alumina (Satterfield 1980). The crude oil itself is carbonaceous material containing small (parts per million) levels of vanadium, nickel, copper, iron, and other heavy metals.

Tables 1 and 2 present a summary of catalysts and their mineral components used in the major petroleum conversion processes and other related processes. Some of the processes, especially catalytic cracking, are presented with literally dozens of catalysts for the various requirements of individual refiners. These requirements may depend on the type of feedstock being processed, the product demands of a specific market, or the type of conversion units that the refiner uses (Stell 2003). Thus, in Table 1 the catalyst formulations cited are a more or less generalized average of all the catalyst grades manufactured by the suppliers and available to the refiner. To accommodate this generalization, a range has been given, where possible, for the mineral content. This figure is shown in weight percent (wt %) of the catalyst formulation. Only the most widely produced formulations are given. It must be emphasized that the minerals cited are *rarely* used as-is, and the processing used prior to incorporation in the catalyst formulation will be described in the text devoted to each catalyst type.

Specific Refining Processes

More detailed descriptions of the processes presented in the following subsections are found in Magee and Dolbear (1998).

Catalytic Cracking

It can be argued that the catalytic cracking process is the most important technology to come out of the first half of the 20th century. The process allows oil resources to be converted into the most needed products in high yield: gasoline, diesel, and turbine fuels. FCC is the most flexible process in the refinery.

This flexibility results in part from the development of a surprising variety of catalyst types to meet many requirements. Cracking units are large, typically 40,000 to 100,000 bpd, and a typical

Table 1. Minerals in petroleum refining catalysts

Catalytic Process	Mineral Used	Catalyst Formulation, wt %
Cracking (FCC)*	Rare earth oxide	0.0–2.5
	Silica	2.0–25.0
	Kaolin†	25.0–60.0
	Alumina (bauxite)	90.0–95.0
	Zeolite (faujasite)	10.0–40.0
Octane enhancement‡	Zeolite ZSM-5	5.0–25.0
	Kaolin†	70.0–90.0
	Phosphorous	3.0–10.0
	Silica	1.0–20.0
CO oxidation§	Platinum	0.1–1.0
	Alumina	99+
SO _x reduction§	Magnesia	No data
	Alumina	
	Vanadium	
	Rare earth oxide	
NO _x reduction§	Cobalt	No data
	Lanthanum	
	Alumina	
Gasoline S reduction§	Zinc	No data
	Alumina	
Bottoms cracking§	Silica	No data
	Alumina	
	Rare earth oxide	
Reforming‡	Silica	90.0–98.0
	Alumina	2.0–10.0
	Platinum or precious metal	0.1–1.0
Hydrotreating‡	Alumina	75.0–85.0
	Molybdenum oxide (MoO_3)	15.0–17.0
	Nickel oxide	3.0–4.0
	Cobalt oxide	3.0–4.0
Hydrocracking**	Silica	80.0–98.0
	Alumina	2.0–20.0
	Platinum or precious metal	0.1–1.0
Alkylation**	Aluminum chloride	No data
	Alkali metals	
	Metal oxides	
Isomerization**	Silica	80.0–98.0
	Alumina	2.0–20.0
	Alkali metals	0.1–2.0
	Precious metals	0.1–1.0
Polymerization**	Magnesium–aluminum hydroxyl carbonates	No data

* Usage = >50,000 tpy.

† Mineral used as-is or with minimal pretreatment (i.e., washing, drying, classification).

‡ Usage = 10,000–50,000 tpy.

§ No usage data available.

** Usage = <10,000 tpy.

Table 2. Minerals in petroleum refining catalysts—related refinery processes

Catalytic Process	Minerals Used	Catalyst Formulation, wt %
H ₂ S removal (Claus)*	Alumina	85–95
	Cobalt	No data
	Molybdenum	No data
	Titanium	85+
Hydrogen production (steam reforming)†	Nickel	40
	Alumina	60
	Calcium aluminate	60
Hydrogen production (water–gas shift)‡	Magnetite	High-temperature shift
	Chromium oxide	Low-temperature shift
	Zinc oxide	
	Alumina	
	Copper§	

* Usage = 10,000–50,000 tpy.

† Usage = <10,000 tpy.

‡ No usage data available.

§ Mineral used as is or with minimal pretreatment (i.e., washing, drying, classification).

unit contains 100 to 300 t of catalyst at any one time, an amount referred to as its “circulating inventory.”

The chief function of the FCC unit (FCCU) is to reduce the molecular weight of the feedstock (distillation range of 650°F to 1,000°F) to make lower-boiling-point transportation and heating fuels and valuable light gases high in olefin content. To accomplish this, a wide variety of catalysts are manufactured and a wide variety of feeds are processed. The catalytic sites are strong acids, chemically equivalent to 90% sulfuric acid in their acidity. Catalysts must have the ability to withstand high temperatures under alternating oxidizing and reducing environments and to continue operation with accumulations of several thousand parts per million of nickel, vanadium, iron, and copper coming from the crude oil. Although typically 60 to 100 µm in diameter, they must have the mechanical strength to survive the physical punishment they endure during routine operation, where any given sample passes through the unit up to 10 times per hour.

Manufacturing the wide variety of catalysts needed uses two very different processes: in situ and incorporation.

The in situ process uses high-purity kaolin as the starting material. It is slurried in water, spray-dried to form microspheres, and calcined at temperatures near 1,800°F to form extremely hard particles 70 µm in diameter. The microspheres are basically an incipient mulite at this point and are catalytically inactive. Since an acidic solid surface is necessary for catalytic cracking, the microspheres are processed further with meta-kaolin and concentrated sodium hydroxide to produce an in situ external and internal porous system containing Type Y zeolite (synthetic faujasite) in its sodium form. Simple ammonium exchanges with the sodium, followed by low-temperature drying, yield the active solid-acid cracking catalyst. Alternate exchanges with mixed rare earth chloride solutions can give a variety of activity and stability levels. Special requirements for gasoline octane enhancement, Ni and V tolerance, and heavy molecule cracking are met through a wide variety of preparative changes.

In the incorporation process, components of the catalyst generally are mixed in a high-shear mixing tank and then spray dried. The resulting microsphere at that point contains a binder (usually silica sol, but sometimes alumina sol), the sodium or exchanged

form of zeolite Y (synthetic faujasite), kaolin, and an activated form of bauxite alumina (generally gamma alumina). (Alternatively, the bauxite may have a mineral phase such as boehmite or gibbsite, which is then converted to gamma alumina during operation in the FCCU or by calcination at the manufacturer.)

Both procedures fill the needs of refiners and are actively employed by three main suppliers: Engelhard Corporation (incorporation and in situ), Albemarle (formerly Akzo Nobel; incorporation), and Grace Davison (incorporation). These three companies account for about 95% of the catalyst market, with the remainder supplied by Catalysts & Chemicals Industries Co., Ltd. (CCIC) and Sinopec Corp.

Catalytic Cracking Additives

In the mid-1970s it was discovered that carbon monoxide could be oxidized completely to CO₂ in the regenerator of the FCCU without being emitted into the atmosphere. This is accomplished by simply adding a very small quantity of platinum-on-alumina powder to the circulating inventory of the cracking catalyst. This gave rise to an entire subclass of fluid catalysts called “cracking catalyst additives.” Now, nearly three decades later, additives are available for gasoline octane enhancement, heavy molecule (bottoms) cracking, gasoline sulfur reduction, SO_x emission control, NO_x emission control, and (originally) CO emission control. A recent survey shows that nine companies are involved in supplying additives to the refining industry. All major FCC catalyst suppliers are involved, but specialty producers such as Intercat Inc. and Ambur Chemical Co., Inc., supply major portions of the market (Stell 2003).

Additives are made to be compatible with the fluid cracking catalyst in use in the FCCU. Therefore, each additive is manufactured in the FCC catalyst size range (~60 µm average particle size) and at approximately the same density (~0.7 g/cc). An additive then transports throughout the reactor with similar fluidization properties as the FCC catalyst. In operation, the additive is added to the FCCU with the principal catalyst, or separately in an amount from 1% to 10% until the desired change in product yield is achieved or until the desired reduction in gaseous emissions is obtained.

As shown in Table 1, additives contain some minerals commonly used in FCC catalysts, but also some not found in FCC catalysts. In bottoms cracking and octane enhancement applications, one can expect to find formulations similar to FCC catalysts because the reactions being catalyzed depend on solid-acid surfaces; the mechanism of octane enhancement, however, requires the presence of a shape-selective zeolite (ZSM-5) rather than faujasite.

SO_x reduction is achieved by reversibly reacting SO₂ and SO₃ onto the catalyst in the oxidizing atmosphere of the catalyst regenerator and carrying the sulfur into the reducing environment of the reactor, where it is converted to H₂S and released into the product vapor stream. This takes place on a solid that is essentially a modification of magnesium aluminate, typically promoted with vanadium and ceria. The overall reactions are complex but have been described in Magee and Mitchell (1993).

NO_x reduction depends on the reduction of NO to nitrogen. Again the reactions are complex, but satisfactory catalysts have been discovered that are alumina based (gamma alumina), promoted with cobalt and lanthanum.

Gasoline sulfur reduction additives convert thiophenes and mercaptans (alkyl sulfides) to hydrogen sulfide, which then can be separated from the gasoline fraction and converted to elemental sulfur in a Claus reactor. Again, an alumina base (as gamma alumina) promoted with zinc oxide is being used.

Although none of the previously described formulations represent a major usage of industrial mineral components, their

importance to the petroleum refiner cannot be overemphasized. Incremental changes in yield structure (potentially achieved with octane, bottoms cracking, and gasoline sulfur-reduction additives) can make a substantial difference in refinery profitability. Also, the proper emission controls for CO, NO_x, and SO_x in this era of environmental uncertainty can mean the difference between compliance and noncompliance with U.S. Environmental Protection Agency (EPA) regulations.

For all these reasons, one can expect the additives segment of the petroleum catalysis industry to grow in both size and diversity.

Reforming

The reforming process produces aromatic compounds from naphthenes (cycloparaffins) and alkanes (paraffins) in the same boiling range as gasoline (100° to 440°F). In the process, both dehydrogenation and cyclization occur. Reforming catalysts contain active metals supported on an alumina carrier (usually high-surface-area gamma alumina or eta alumina, which is treated with chlorides to give an acidic surface). The reactions are performed in a high-pressure atmosphere of hydrogen. Catalysts of this type contain an active metal that functions as a hydrogenation–dehydrogenation catalyst and an acidic component that can induce a carbenium reaction to promote cyclization or cracking. These are called “dual function” catalysts.

A variety of reactor configurations are used in reforming, operated at different reaction severities. Many different formulations optimize catalyst performance under specific conditions. This accounts for use of platinum, rhodium, iridium, or tin as the active metal on the alumina support. In some situations, combinations of two or more of the active metals are used. As stated earlier, quantities of mineral-derived components are not large, but the catalysts themselves play an essential role in the overall quality of the gasoline product. Gasoline-range aromatics from the reformer typically exhibit octane numbers of 110 or greater. Reforming catalysts are expensive but may last in operation for years and can then be either reclaimed or, in some processes, regenerated during the operation (Sinfelt 1997). Refiners often use catalysts under “rental” contracts, with precious metals remaining the property of the manufacturer.

Reforming, and many of the other applications discussed here, use catalysts as solid particles (e.g., 1/16 to 3/8 in. in diameter) in what is known as a “fixed-bed mode.” The catalysts are a heterogeneous type made up of a solid support/carrier that typically is coated with an active metal. The active agent also can be blended directly with the support during the manufacturing or forming process. Catalyst particles are loaded into large vessels or tanks, sometimes in quantities of 100 to 500 t. There is a requirement for both strong physical integrity and high activity–selectivity. Usually these two requirements conflict with one another, and so, through an optimization process, a material having the best of these qualities is produced.

Catalyst supports for fixed-bed mode are found in a variety of forms. Among these are granules, tablets, and extrudates, which are the most commonly used form. These come in a vast number of diameters and specialty shapes. Extrudates are made by combining powders and liquid chemicals into a type of semidry paste. Screw-type auger devices then force the paste through dies with tiny holes, creating the desired shape and size. By analogy, spaghetti and other pasta noodles are prepared in much the same way, but catalyst extrudates are quite a bit shorter (e.g., 1/4 to 3/8 in.). Tablets are formed when a mixture of active component, lubricant, and binder powders are compressed by mechanical force into a cylindrical shape. Vitamin and medicinal pills are also made by a similar tableting process.

Active agents are either coated onto the surface of the catalyst support or combined before the forming technique (e.g., extrusion or tableting). Typically, active agents (as liquid chemicals) are sprayed onto the catalyst support while it is tumbling inside industrial mixing equipment. The coated media is dried to remove moisture, and then is usually heat treated at a high temperature (i.e., 950° to 1,300°F) to drive off any residual nitrates, chlorides, etc., that were used to dissolve the active agent.

Hydrotreating

Hydrotreaters in the refinery remove sulfur or nitrogen from any product molecule or from the process feedstocks themselves. Environmental restrictions on emissions dictate that levels of S and N should be low in products that may be released into the atmosphere. For example, diesel fuels for sale in the United States after July 2006 may contain no more than 15 ppm S; native oils often contain more than 5,000 ppm S. Hydrotreating treats more barrels per day than any other catalytic process in the refinery scheme. Not surprisingly, the quantity and variety of hydrotreating catalysts produced are exceeded only by the FCC catalyst demand.

Four main hydrotreating-catalyst formulations are manufactured, all of which use gamma alumina supports: molybdena on alumina promoted with cobalt; molybdena on alumina promoted with nickel; and, to lesser extent, cobalt- and nickel-promoted tungsten on alumina. Cobalt-promoted catalysts are used primarily for sulfur removal, whereas nickel-promoted catalysts are more effective for nitrogen removal. Tungsten–alumina combinations are used in the most severe operations and are significantly more expensive than molybdena–alumina compositions. The actual active catalysts are MoS₂ and tungsten sulfide (WS₂), which usually are formed by sulfiding the catalyst in the hydrotreating unit before introduction of the feed. The cobalt and nickel promoters generally are believed to be incorporated into the layered sulfides, probably along the crystal edges. The catalysts themselves can be operated effectively for years before replacement or regeneration, but they still require a substantial use of cobalt and nickel and, to a larger extent, molybdenum and tungsten (Table 1).

Hydrotreating is expected to grow as a process, providing a source of new or improved catalyst materials. More than 30 million bpd of refinery feeds or products currently are hydrotreated—by far the largest quantity catalytically treated in the refinery. Topsoe, Clausen, and Massoth (1996) wrote a detailed survey of hydrotreating science and technology.

Hydrocracking

As the name suggests, hydrocracking catalysts are dual-function catalysts that (1) reduce the molecular weight of the feed (cracking) and (2) hydrogenate the products while also removing N and S, a notable environmental advantage. As hydrogen is added, the fuel becomes less dense, so that product liquid volumes may be as much as 20% greater than the feed volumes, a distinct economic advantage in an industry where feed and product are bought and sold on a volume basis.

Heavily contaminated crude oils are primary feedstocks to hydrocrackers; the resulting products are motor fuels and high-quality middle distillates (e.g., jet fuel and diesel). Some refiners also apply hydrocracking to make high-quality lubricating oils and specialty mineral oils for the food and cosmetics industries.

At least a dozen catalyst formulations are in commercial use; Table 1 lists the mineral-related components. Zeolite catalysts find widespread application in this area. A formulation commonly used to produce gasoline-range products of low sulfur content contains approximately 0.5% palladium, 35% exchanged and thermally

treated zeolite Y (synthetic faujasite), and 65% alumina (gamma alumina type, derived from gibbsite or boehmite). When the product emphasis is directed toward high-quality diesel-range products, a widely used formulation contains the same zeolite Y content (35 wt %), but in stead of palladium, the hydrogenation function is supplied by 20% WS_2 promoted with nickel (~4% as NiO). The balance of the formulation again is supplied by gamma alumina. Formulations containing MoS_2 for the hydrogenation function and combinations of silica-alumina also are widely used in the hydrocracking process.

Catalysts are supplied under license by UOP LLC, Chevron USA Inc., ExxonMobil Corporation, and IFP Group Technologies, and principal manufacturers Criterion Catalysts and Technologies LP, Albemarle, and Grace Davison. Works by Magee and Dolbear (1998) give more information on the hydrocracking process and catalysts.

Zeolites are used as catalysts for hydrocracking and a variety of other industrial chemical processes. Zeolites are composed predominantly of silica and alumina. Other elements such as gallium, germanium, cobalt, and nickel and the compounds titania and alumina phosphate can be incorporated into the zeolite structure as well. If these other substances are present, the net material is called a *molecular sieve*. Zeolites originally were discovered as natural ore deposits. Minerals such as clinoptilolite and chabazite are mined in large megaton quantities for use in ion exchange, in water softening, and in the removal of radioactive isotopes from wastewater from nuclear power plants.

Essentially all zeolites and molecular sieves used for catalysis are synthesized commercially. Typically, processing equipment consists of stirred-tank reactors placed under high-temperature and pressure conditions. Usually, liquid silica and alumina chemicals are combined with organic templates (e.g., amines, tetra-ethyl ammonium hydroxide) and mixed for long periods ranging from 1 to as long as 6 or more days. During this time a crystallization process takes place that will form the material into a specific molecular shape and particle size. The particles are quite small, typically 13 μm . Under the microscope, they might look like thin rods, flat platelets, cubes, or even rose petals. A particular type of zeolite or molecular sieve is synthesized by following a manufacturing recipe that specifies raw materials, mixing conditions, temperature, pressure, and length of time.

The molecular structure of these materials also is carefully controlled during crystallization. Internally, zeolites consist of a series of microscopic channels or tunnels within walls that are 6-sided, 8-sided, 12-sided, or more. The channels comprise alumina, silica, titania, or other chemical molecules that form a series of cross-linked, reticulated chambers resembling a honeycomb. This structure allows for the passage (or diffusion) of certain chemical functional groups to the catalytic sites while preventing others from entering. Specific chemical reactions will occur on these active sites within the honeycomb-like channels. Conversely, products from the reactions will either diffuse out or be prevented from leaving. Both high activity and selectivity are achieved with zeolite or molecular sieve catalysts, and they can be tailored for high performance for a given chemical reaction.

Alkylation

Reactants in the alkylation process are isobutane and olefins (usually pentenes, butenes, and propylene). Products are valuable, highly isomeric, gasoline-range hydrocarbons of high research and motor octane. Such stocks are also free of sulfur except when produced by units that do an ineffective job of removing sulfuric acid aerosols from the products.

The reactions are catalyzed by strong acids; usually concentrated sulfuric and hydrofluoric acids are used. Process conditions are mild: temperatures at $\sim 10^\circ$ to 100°F , and pressures at 50 to 100 psig. Because of environmental concerns there is a major effort to replace these acids with more environmentally friendly materials. This has resulted in the commercialization of so-called solid alkylation catalysts (SACs). To date, the composition of the catalysts used has remained more or less proprietary, but the following formulations are known: trifluoromethane sulfonic acid on a porous support (Haldor Topsoe A/S); a promoted alumina-zirconium halide (Catalytica Energy Systems, Inc.); an antimony pentafluoride on acid-washed silica (Chevron USA Inc.); and a solid catalyst that resembles traditional hydrocarbon conversion catalysts (UOP LLC).

Although mineral-derived catalyst use is relatively small in tonnage and dollars (catalyst sales per year are <\$90 million), the market will remain strong for the foreseeable future. This is because high-octane gasoline products are not only environmentally friendly but are also excellent performance motor fuels.

Tarry by-products tend to form in the sulfuric acid process, and fresh sulfuric acid is added routinely to replace that which is removed for regeneration. Regeneration is accomplished in sulfuric acid furnaces, making the overall consumption of new sulfuric acid negligible.

Isomerization

Isomerization processes convert normal (straight-chain) pentanes and hexanes, naphthenes (cyclohexane), and benzene into a mixture of highly branched isopentanes and higher molecular weight isomers. They use a dual function catalyst capable of catalyzing hydrogenation (an active transition metal) and carbenium ion (solid acid catalyzed) reactions. The reaction takes place in a high-pressure atmosphere of hydrogen. Products, as in alkylation, are valuable gasoline-range materials.

Acid activity is supplied by either a zeolite (exchanged and thermally modified zeolite Y [synthetic faujasite]) or chlorided gamma alumina, and the hydrogenation function is platinum. Although the amount of isomerization on catalyst produced is relatively small, the product value is high. The process is used where much less valuable normal pentanes and hexanes represent a significant quantity of materials in this boiling range. Also, as shown in Table 1, the amount and type of mineral-derived catalyst components bear a strong resemblance to many of the formulations used in higher catalyst consumption processes.

Polymerization

The polymerization process has been widely used for more than 50 years to produce highly branched, high-octane, gasoline-range olefins from light olefins (mainly propylene and butylene). One of the earliest catalyst formulations consisted of a phosphoric-acid-activated mineral, kieselguhr, which is a form of diatomaceous earth. More recently, a polymerization process developed by ExxonMobil Corporation was used to produce either gasoline-range aromatics or distillates depending on the temperature or pressure of the reactor. In this case, the catalyst contains the molecular sieve ZSM-5 bound with gamma alumina. Although neither process is used very much when compared to the other refinery processes described, the polymerization process provides valuable catalyst products and is used when olefin feedstocks are readily available.

Petroleum Refining Catalysts—Related Refinery Processes

Two processes are necessary for the overall well-being and upkeep of a refinery: (1) hydrogen sulfide removal from all refinery streams

and (2) production of hydrogen gas using the steam-reforming and water–gas shift processes. The two processes are widely used and have high-volume catalyst utilization, but they are not directly connected to making refinery products. Catalyst formulations bear a marked resemblance to many other refining catalysts and are shown in Table 2. The catalyst formulations listed represent an estimated average for each.

Hydrogen Sulfide Removal—the Claus Process

The Claus process (Wagner and Nehb 1997) catalyzes the oxidative conversion of hydrogen sulfide to elemental sulfur using granular bauxite as the catalyst. Until the mid-1960s it was used worldwide. Today the process is used in hundreds of plants with sulfur capacities up to 2,000 tpd of activated alumina- or titania-based catalysts. The most desirable properties of these catalysts are high surface area (200 to 400 m²/g), pore volumes from 0.4 to 1.0 cc/g, and large pore diameters (~75 µm). Cobalt and molybdenum are used as promoters in a number of Claus catalysts. With the current emphasis on environmental issues, the Claus process and catalysts keep refinery operations in compliance by mitigating hydrogen sulfide streams regardless of the source.

Hydrogen Production—Steam Reforming

Although catalytic naphtha reforming produces hydrogen gas in large quantities as well as gasoline-range aromatics, most refiners also rely on steam reforming (Magee and Dolbear 1998) to supply their many hydrogen needs. Steam reforming plants actually rely on several catalytic steps. Most prominent of these is the reaction of steam with light hydrocarbons to make a mixture of hydrogen and carbon monoxide, and then the conversion of this mixture to hydrogen. The process also uses a hydrotreating step to remove any sulfur from the hydrocarbon feed; for adsorption of product H₂S onto zinc oxide; to remove by-product CO₂ from the hydrogen in one of several noncatalytic steps; and for the catalytic reaction of trace CO₂ and hydrogen to make methane as a protection for downstream catalysts.

Metallic nickel supported on alumina (corundum) or calcium aluminate catalyzes the reaction of steam at high temperatures (typically >1,500°F) with a low-molecular-weight hydrocarbon (usually methane) to form hydrogen and carbon monoxide (steam reforming). Nickel content in these catalysts is very high (~40+ wt %), and the process must be operated at very low sulfur levels because of the extreme susceptibility of nickel to sulfur poisoning.

In the water–gas shift reaction, hydrogen and carbon dioxide are produced from the reaction of carbon monoxide and steam using several different catalyst types. So-called high-temperature shift (HTS) reactions (600° to 1,020°F) are catalyzed by magnetite (Fe₃O₄) containing minor amounts of chromia, whereas low-temperature shift (LTS) reactions are catalyzed by copper metal paired with zinc oxide and alumina.

As previously mentioned, both water–gas shift and steam reforming are important processes that help fill the refiner's internal hydrogen needs. Data shown in Table 2 suggest that the quantities of catalysts used for both steam reforming and the related water–gas shift process are not large, but nevertheless the refiner is highly dependent on them for much-needed hydrogen.

CHEMICAL CATALYSTS

An immense variety of catalytic materials is used in manufacturing chemical intermediates and products. Most of these catalysts are low-volume materials, especially when compared with refining catalysts; many of them have operating lives measured in years rather than months. Detailed information about them may be difficult to

obtain because compositions and applications are proprietary to the companies that develop and use them.

This section describes several of these catalysts in general to give the reader a feeling for their variety and importance.

Ethylene Oxide

One of the major uses for ethylene is in making ethylene oxide (EO), a product measured on a scale in tons and used mostly in making ethylene glycol, one of the two intermediates for polyesters. The classic catalyst for this application is silver supported on silica gel. Continuing research has led to many small improvements in this basic formulation to improve selectivity, which is defined here as the oxidation yield to EO rather than CO₂.

Saturated Fats

Natural fats and oils are selectively hydrogenated to make products with higher melting points and other desired properties. Catalysts for this hydrogenation typically are based on nickel, supported on silica, kieselguhr, or some other porous solid, or in the form of Raney nickel alloys. Raney nickel contains nickel and aluminum and is activated by hot water or steam to convert some of the aluminum to hydrous oxides.

Ammonia

Development of the synthetic-iron ammonia catalysts in the early decades of the 20th century led to widespread use of nitrogen fertilizers, which have accelerated the production of food worldwide. A variety of processes were developed around the ammonia, allowing the manufacture of inexpensive nitric acid, ammonium nitrate, urea, and other nitrogen-based chemicals. The key invention in the ammonia catalyst, by Fritz Haber and Karl Bosch, was the addition of small amounts of potassium and aluminum oxides as promoters to the iron oxide catalyst. The iron oxide itself is not the active catalyst, but is converted in the reactor to active metallic iron by reduction with hydrogen. The iron oxide usually is prepared by precipitation of a hydroxide or hydrous oxide, which is dried, calcined, and formed into strong particles. Some commercial catalysts have been made directly from oxide minerals.

The ammonia process also incorporates a long series of additional catalytic steps. The process typically starts with natural gas, which is first desulfurized and then reacted with steam to form a mixture of CO and H₂. This mixture is then passed over a series of water–gas shift catalysts to convert the CO to more hydrogen. Each of these steps is catalytic, using various catalysts made with cobalt, molybdenum, nickel, copper, and chromium. There are also sulfur and CO₂ removal steps. In the sulfur removal step, H₂S formed during desulfurization is adsorbed onto ZnS. The CO₂ removal step uses any of several adsorption technologies; trace CO₂ also may be removed by catalytic hydrogenation to methane.

Selective Oxidation

Many chemical products are made by selective oxidation of some intermediate material. Catalysts for these oxidations often are based on vanadium oxide and often are promoted with lesser amounts of other oxides such as bismuth. Other catalysts used in selective oxidation are those based on manganese, chromium, zirconium, niobium, molybdenum, and even uranium; many catalysts are well-defined mixed oxides such as copper chromite or bismuth molybdate. Research has shown that such materials generally operate by supplying oxygen from the oxide matrix, which is then replenished by reaction with oxygen fed with the organic starting materials. Selectivity often is controlled by precipitating the precursor hydroxides in such a way that specific crystalline faces are

avored; much of this technology is proprietary to the companies that developed these catalysts.

Terephthalic Acid

Terephthalic acid is a high-volume intermediate used for the manufacture of polyesters. It is made by selective oxidation of very pure para-xylene with air or oxygen. The classic process for this conversion, the Midcentury Process, uses manganese or cobalt salts dissolved in glacial acetic acid. Bromine is used as a co-catalyst. Many variants and improvements have been made to this process in the nearly 50 years since its introduction. These technologies, coupled with the proper product isolation steps, result in a polymer intermediate material with levels of total impurities less than 25 ppm, essentially pharmaceutically pure products.

Automotive Exhaust Control

The introduction of catalysts to reduce carbon monoxide, hydrocarbons, and nitrogen oxides dramatically improved urban air quality. The original catalysts were introduced in the 1970s, and a series of dramatic improvements over the ensuing 30 years have significantly reduced the pollutants emitted by the modern automobile. Modern catalysts rely on a combination of precious metals, with platinum or palladium mixed with iridium, rhodium, and others. These catalysts are used in the form of thin coatings on monolithic honeycomb materials based on high-temperature ceramics.

SUMMARY

A survey of compositions for petroleum refining and chemical process catalysts presented in this chapter shows an extremely wide range of mineral-derived components currently in use. Noble metals, rare earths, transition metals, acids, zeolites, silicas, and aluminas are part of the myriad systems available to petroleum refiners and chemical manufacturers. Characteristic of most catalyst compositions available is the presence of bauxite-derived alumina. Alumina invariably is converted to an active phase—gamma or eta—and is an essential ingredient of many petroleum and chemical cata-

lysts. Many of the conversion processes call for strong acids that require some degree of uniform structure. In these cases—catalytic cracking is a prime example—zeolites such as Type Y (synthetic faujasite) are needed. Cobalt, nickel, molybdenum, and tungsten supported on alumina are the principal ingredients in the most used process in the refinery—hydrotreating. Noble metals and zeolites are used for hydrocracking with noble metals supported on modified aluminas handling catalytic reforming.

Although the quantity of mineral-derived catalyst components may not be large compared to other industrial uses, it is apparent that extraordinary contributions come from minerals used in petroleum refining and chemical catalysts.

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Adobe and Earthen Construction

George S. Austin and David A. Holmes

INTRODUCTION

Soil is the ultimate sustainable building material, meaning that it has little effect on the environment, and that building with it expends little or none of the earth's finite resources, such as fossil fuels. Its "embodied costs," which means the cost to individuals and society overall in its creation, storage, distribution, use, and maintenance, are very low. The cost of housing is a critical factor for the future survival and well-being of the earth's population.

Mud or earthen material is one of the oldest building materials used by humans. Today, close to 40% of the world's population lives in earthen buildings. If the world's population doubles by 2060 as projected, that proportion probably will stay about the same, greatly increasing the number of earthen-construction dwellers. Not all of these people are members of primitive societies or live in developing countries. Some European, African, Asian, and North and South American countries, in addition to Australia, are home to a significant number of such structures. In the United States, the American Southwest in particular is known for earthen construction (Austin 1994).

Some of the earliest remains of adobe brick were discovered in the ruins of Neolithic farming villages in Mesopotamia dating as far back as 7,000 BCE (before the Common Era; Steen 1972). The Spanish conquest of the New World spread the use of wooden molds used to prepare a standard adobe brick. The word *adobe* is Spanish for "mud brick," or for the clay soil from which the brick is made. The term has its roots in Egyptian hieroglyphs (Lumpkins 1977). The Arabic word for mud brick is *ah-tob* or *al-tob* (sun-dried brick), which traveled with the Arab migration westward from the Middle East and Egypt to Spain, as the root word of adobe. Today adobe is used in the United States and Latin America to describe not only the sun-dried adobe brick but also puddled adobe structures, mud-plastered logs or branches (jacal or wattle-and-daub), pressed-earth blocks, and rammed-earth walls, or *pisé* (Ferm 1985; Smith and Austin 1996). The rest of the world uses variations of the terms "earth or earthen construction" to describe all types of construction using mud or soil raw materials.

Modern mud construction is used in many countries around the world. In North America, the southwestern states from Texas to California are best known for earthen construction, and New Mexico has the dominant reputation for adobe brick construction. Indeed, in New Mexico, the Santa Fe style (Figure 1) has made adobe not only acceptable but preferred.



Courtesy of Edward W. Smith.

Figure 1. Modern solar adobe home in Santa Fe, New Mexico

RAW MATERIALS

Geologic Settings

Virtually all earthen or adobe materials are recovered from soils or soft alluvial sediments on the surface of the earth. Although medium- to coarse-sized sand is the most important structural component, clay is the most important fine, binding component. Gravel-size particles add strength to earthen walls but are generally kept to less than 10% as they tend to pop out. Silt and fine sand contribute the least strength to earthen structures and act more as filler material. The best earthen construction raw materials are generally Recent stream or river sediments or residual soils containing a wide range of particle sizes. The two great original areas of earthen construction in ancient Egypt and Mesopotamia depended on the sediments of the broad Nile and Tigris/Euphrates River valleys, respectively, as raw materials. Soils used by current and past adobe producers in the Americas are mostly sandy loam (50% clay and silt), although clayey silts are used in some areas (Coffman et al. 1990). In New Mexico, the best adobe soils are those developed on stream deposits, particularly Recent terrace deposits and loosely compacted Tertiary formations, such as the Santa Fe Group in the Rio Grande Valley. Soils of windblown origin are not commonly suitable for earthen

construction unless other surface materials are added. Wind action concentrates surface sediments by particle size. Coarse sand and light gravel are generally missing altogether, and the clay fraction was blown much farther away at the time of deposition. Some modern adobe producers use a mixture of materials from the screened fines of aggregate operations and mud dredged from irrigation ditches in river valleys, combined with varying amounts of sand, to produce proper blends.

Mineralogy

X-ray diffraction analyses of whole-rock samples show that the major constituents of New Mexican adobe soils are quartz and feldspar, with lesser amounts (in decreasing order of abundance) of calcite, clay minerals, and gypsum. The quartz, feldspar, most of the clay minerals, and some calcite are derived from the mechanical/chemical breakdown of older rocks. Some clay minerals, much of the calcite, and all the gypsum are precipitated from evaporating water.

Clay Properties

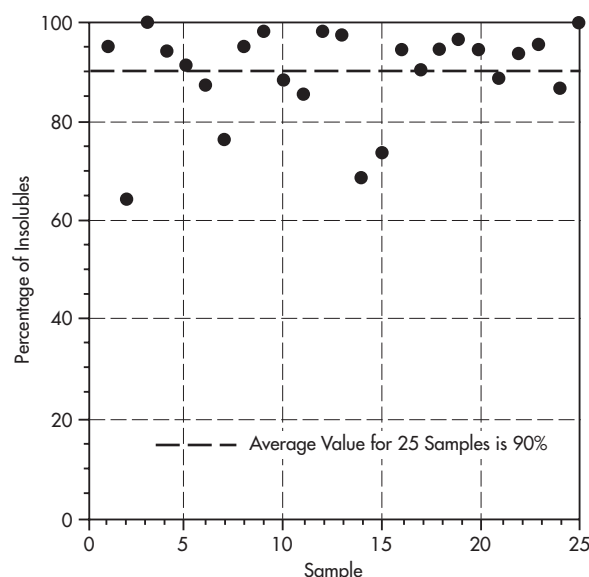
Clay-size particles, although the smallest in percentage of size in earthen construction material from New Mexico, are the most compositionally variable in commercial adobe soils. Clay minerals are dominant, but nonclay minerals also are present. In this size fraction, clay mineral groups consist of about equal parts of expandable clay minerals (smectite and mixed-layer illite/smectite, or I/S) and nonexpandable clay minerals (kaolinite, illite, and chlorite), with minor constituents of quartz, calcite, and feldspar (Smith and Austin 1989, 1996; Austin 1990). The smectite is universally calcium-rich, and the I/S is disordered, randomly interstratified smectite and illite. Only 2 of the 42 samples taken as part of the study by Smith and Austin (1989) contained chlorite; vermiculite, sepiolite, and palygorskite were not found. Although commonly found in minor amounts, clay-sized calcite was present in nearly every adobe soil sample.

Expandable clay minerals tend to be more “sticky” than nonexpandable varieties and thus are more effective in binding silt and sand particles together. Expandable clay minerals also form colloidal suspensions with water. As a result, moisture, whether from rainfall or groundwater, has its greatest effect on adobe soils with large proportions of smectite and I/S.

For past and present adobe producers in New Mexico, expandable clay minerals have sometimes proved problematic. Cracking of adobe bricks while drying is most probably caused by a large proportion of smectite and I/S in the adobe soil; soils with higher clay content but relatively lower smectite and I/S content are less likely to crack. Although cracking is extreme on windy days when the shrinking of clay occurs more rapidly, drying slowly over many calm days allows multiple layers of finely crystalline calcite (and some gypsum) to form on a clay-size scale, strengthening the bricks and preventing cracks. If the adobe bricks do not contain too much clay material and are properly cured, the resulting adobe wall can resist torrential late-summer rains for many years.

Chemical Properties

Soils in the arid New Mexican climate are typically alkaline. Groundwater near the Rio Grande Valley, where most of the adobe brick in New Mexico is produced, is generally hard to extremely hard, containing total dissolved solids (TDS) ranging from about one hundred to several thousand parts per million (Wilkins 1986; Anderholm 1987; Austin 1994). Soluble salts, notably calcium carbonate and calcium sulfate, precipitate as this water evaporates. At the surface of seasonal marshy areas of the state, white crusts of



Source: Austin 1990.

Figure 2. Summary of leaching analysis of 25 commercial New Mexico adobe soils

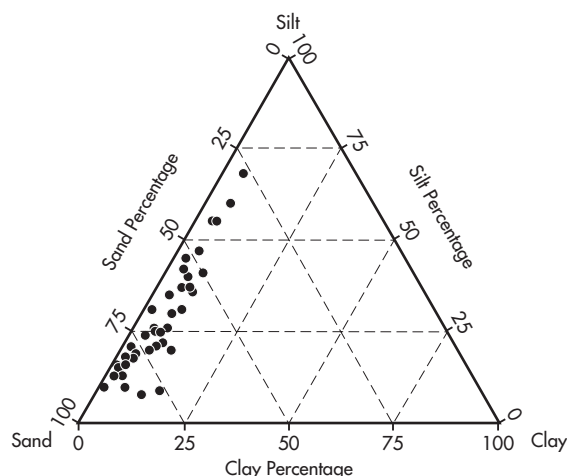
these salts commonly appear during drier times of the year. The desert surfaces are stabilized by precipitation of calcium carbonate from groundwater, initially producing calcium-rich soils, followed by impermeable pedogenic calcite layers, called *caliche*, just above the groundwater table (Gile, Hawley, and Grossman 1981).

Adobe walls in New Mexico are remarkably durable in the dry desert climate. With proper care, walls may last for hundreds of years. Great care is taken to keep the interior walls dry. In Native American pueblos, the inhabitants re-cover exterior adobe walls with a natural plaster each year as part of community service. The natural plaster has about the same mineral and chemical composition as the walls themselves but is slightly finer grained. It is expected to erode off slowly during the year and is then replaced during the next year's replastering. The slow weathering of the plaster apparently results from calcite and gypsum precipitation from water used in mixing the plaster. This precipitation forms a caliche-like bond between grains as the mud plaster slowly dries.

Leaching tests with EDTA (ethylenedinitrilotetraacetic acid) on 25 commercial New Mexican adobe soils (Figure 2) suggest that commercial soils contain an average of about 90% insoluble and 10% soluble material; the latter is dominantly calcite with some gypsum (Austin 1990). In that study, the soluble material ranged from 36 wt % to essentially zero. Adobe soils with the smallest amount of soluble material were also the highest in sand and larger-size particles.

Physical Properties

Particle-Size Distribution. The common statement by New Mexican adobe producers is that their soil mix is usually one half sand and one half clay or fines (silt and clay), although commercial adobe soils range from 85 to 99 wt % nonclay-size particles (Smith and Austin 1989, 1996). Tests of commercially produced adobe show that the soil material contains 27 to 89 wt % sand-and-larger grain size, 8 to 68 wt % silt-size grains, and 1 to 15 wt % clay-size grains (Figure 3). The average grain-size composition was 67 wt % sand and larger, 27 wt % silt, and 6 wt % clay. The wide variation of



Source: Austin 1990.

Figure 3. Plot of sand-and-larger-, silt-, and clay-size fractions of 42 production adobe soils used in New Mexico. The diagram shows the dominance of larger particles as compared to clay-size material.

particle sizes, particularly in the sand-and-larger- and silt-size grains, affects the penetration of paint or stabilizer sprayed or painted on walls. The smaller the average grain size, the more surface area is involved, and the more preservative is needed to create an impermeable layer to a given depth in the wall. Adobe walls with high clay- or silt-size content would need the largest amount of preservative. An abundance of clay-size particles in adobe soils causes excessive cracks as blocks dry in an adobe yard. To combat this, producers add straw, additional sand, or both, to the mud mixture.

In New Mexico, large-scale commercial adobe producers use adobe soils with less clay-size material than do small-scale commercial and noncommercial adobe producers. Some of the former use soils as low as about 1 wt % clay, whereas many of the latter use soils between 8 and 15 wt % (Smith and Austin 1989, 1996). In part, this is because large-scale commercial adobe producers use stabilizers that not only protect blocks from rain damage but aid in consolidation of the drying soil mix as well.

Thermal Properties

Traditionally, materials are evaluated for the thermal properties based on measurements known as *R-values* and *U-factors*. An indicator of the ability of a wall to insulate effectively, the *R-value* is calculated by dividing the thickness of the wall by the wall's thermal conductivity (the amount of heat per unit area in a given time), flowing from the hotter side to the cooler side of the wall. The units for *R-value* are per square meter/degrees Kelvin/hour/watt (square foot/degrees Fahrenheit/hour/British thermal unit). The inverse of the *R-value*, the *U-factor* reflects the rate at which heat is conducted through a material. The total *R-value* may be calculated for a given wall by adding up the values of the individual components of a wall structure, including all insulation, interior sheathing, framing, airspace resistance, and masonry. Adobe walls have very low *R-values* because they commonly consist of 26-cm (10-in.) or 36-cm (14-in.) blocks covered with a thin stucco on the outside and thin gypsum plaster on the inside.

R-values and *U-factors* do not tell the full story in determining what is a high-quality, thermally efficient wall (Fine 1976). Both these values reflect the rate at which heat passes through a wall only after the steady state of heat flow (the constant rate of heat energy

passing uninterrupted from one side of the wall to the other) has been achieved. What is not considered, although of critical importance in masonry-mass walls such as adobe, is the heat storage capacity of the wall, which determines the length of time that passes before a steady state of heat flow is achieved. The higher the heat storage capacity of the wall, the longer it will take for heat flow to reach a steady state. In real situations external temperatures, in particular, change constantly, so that a true steady-state condition is rarely achieved. Because diurnal changes in the arid Southwest are typically 15° to 28° C (27° to 50° F), a "fly-wheel effect" (in this case, the damping of interior temperature fluctuations resulting from the massive adobe construction) will keep daytime temperatures of adobe buildings cool in the summer and warm in the winter.

Resistance of Sound. Thick massive walls of adobe are well-known absorbers of sound, making these homes remarkably quiet. Windows in older adobe buildings are normally small, adding further to the sound deadening. Newer solar adobe homes take advantage of the many sunny days in arid climates with larger windows that are thermally designed, but also retain much of the sound-deadening characteristics of adobe dwellings.

Other Physical Properties. Other physical properties that make adobe construction advantageous are its water resistance, nonflammable and termite-proof character, and energy efficiency. The sun-dried method of production, rather than the use of high heat to produce masonry brick or cement, contributes to the energy efficiency. Wright (1978) stated that it takes more than 300 times as much energy to produce a commercial concrete block than a sun-dried adobe block of the same volume.

An unusual test on adobe in Nicaragua determined that adobes were resistant to penetration by bullets (Lola 1981). Five shots from a machine gun at an adobe wall at 20-m (61-ft) distance penetrated only 4 to 5 cm (1.6 to 2.0 in.).

INDUSTRY STRUCTURE

Traditional/Old World Sector

Earthen construction, principally adobe bricks, evolved throughout Asia, the Middle East, Africa, and parts of Europe over millennia. Civilizations gradually developed their unique sources of materials and architecture for residential, agricultural, and commercial construction. Building materials and techniques, however, stayed ubiquitously simple, relying on straight walls, simple infill foundations, and too often earthen materials for roofs or multistory structures. The greatest threat to traditional earthen construction is its vulnerability to massive earthquakes, which can result in death and destruction.

Contemporary Construction Sector

In the United States, most adobe artisans come from generations of *adoberos* (adobe makers) who learned their techniques from family traditions locally or in Latin America. The recent heavy wave of migration from Mexico and other Central American countries has brought a large number of workers knowledgeable in adobe construction into the United States. In addition, contractors hiring *adoberos* now commonly recruit workers, as they are needed, from Mexico. Local trade associations, minor academic attention, and a great deal of Internet communication have kept interest in adobe technology alive. Some educational institutions in the Southwest offer formal or noncredit courses in adobe construction. In association with the International Institute for Conservation of Historic and Artistic Works, the Getty Conservation Institute (GCI) of Los Angeles, California, directs attention to the preservation of adobe construction, particularly in the American Southwest. Creation of the Adobe Association of the Southwest is a recent attempt to organize adobe contractors,



Courtesy of Edward W. Smith.

Figure 4. After 2 to 3 days of drying time, adobe is released from a 10-brick ladder form at a commercial adobe yard in New Mexico. The adobe is trimmed by hand, turned on edge, and dried for an additional 2 weeks. Blocks then are stacked in the yard ready for sale.

researchers, architects, and students to promote the adobe industry. Older industry groups, such as the El Paso Solar Energy Association, have active programs promoting solar and alternative energy research along with Southwest trends in adobe architecture and design.

International Research Centers

In the interests of improving earthen architecture, a number of international research and academic study groups sprang up during the 20th century. These groups were principally aligned with United Nations relief groups in Europe, but came to show more interest in the North American market. The University of New Mexico's Department of Architecture has offered courses in earthen architecture in both Spanish and English for more than 2 decades. Other branches of the university have been leaders in advancing adobe studies for U.S. applications. Smaller organizations such as Southwest Solar Adobe (SWSA) function today as commercial or educational groups that spread knowledge regionally to the construction industry and interested builders. The International Centre for Earth Construction (CRATerre-EAG, typically abbreviated to "CRATerre"), affiliated with the Ecole d'Architecture in Grenoble, France, trains students in earthen architecture and construction and sponsors conferences and research on earthen technology. CRATerre also contracts with government agencies, particularly in developing countries, to train students and build large housing projects on site. Another typical international research project trained experts at the Regional Seismology Center for South America (CERESIS; El Centro Regional de Sismología para América del Sur) in assessing different methods for strengthening existing earthen homes. The project involved 6 years of research and was funded by the German Cooperation for Development Programme (Deutsche Gesellschaft für Technische Zusammenarbeit GmbH [G TZ]). Considerable progress has been made using structural steel, wire mesh, and selective roof strengthening to reduce deaths related to earthquake destruction. The International Center for the Preservation and the Restoration of Cultural Property (ICCROM; *Centre international d'études pour la conservation et la restauration des biens culturels*) focuses worldwide attention on adobe by holding international meetings on the preservation of earthen construction.

TECHNOLOGY

Several varieties and sizes of earthen brick are produced throughout the American Southwest, including traditional adobe, semistabilized and stabilized adobe, New Mexican *terrones* (cut-soad brick), *quemados* (burnt adobe), and machine-pressed-earth block; in addition, rammed-earth walls are constructed without brick (McHenry 1984; Smith and Austin 1989, 1996). The two major types of adobe brick currently produced in New Mexico are the traditional adobe brick and the semistabilized adobe brick.

Production Techniques

Traditional (Untreated) Adobe Bricks

Often called *untreated* or *sun-dried* adobe brick, traditional adobe is made with soil composed of sand with some larger particles, and of silt and clay (Figure 4). Straw is sometimes added for strength and to prevent excessive cracking during drying. The moistened soil mixture commonly is packed into a brick-like mold, released, and allowed to dry and cure for several weeks before use.

Stabilized Adobe Bricks

The New Mexico Building Code defines fully stabilized adobe brick as water-resistant and made of soil with certain admixtures that limit the brick's 7-day water absorption to less than 4 wt %. A fully stabilized adobe brick usually is made with 6 to 12 wt % of asphalt emulsion (California Research Corporation 1963; Scheuch and Busch 1988). Exterior walls constructed with stabilized mud mortar and brick require no additional protection and can be left exposed without stucco. The production of fully stabilized adobe brick is very low because most walls are stuccoed with water-resistant plaster, and the additional waterproofing agent adds extra cost.

Semistabilized Adobe Bricks

Semistabilized adobe brick was developed by major adobe producers in New Mexico and is classified as a water-resistant brick because of the addition of 3 to 5 wt % of stabilizer or water-proofing agent (California Research Corporation 1963; Scheuch and Busch 1988). The stabilizer protects the brick from rainstorm damage during the curing process. Asphalt emulsion is the primary stabilizer because of the ease of use and the low cost, but 5 to 10 wt % portland cement produces the same result. Semistabilized adobe is made the same way as traditional adobe, except the stabilizer is mixed into the adobe soil prior to packing it into a form.

Pressed-Earth Blocks

Pressed-earth blocks currently make up a small portion of earth brick used in New Mexico (Smith and Austin 1989, 1996). Although the CINVA-Ram hand-operated press, developed by a Chilean engineer in the 1950s, has been used in New Mexico, most pressed-earth blocks in the state are made by gasoline- or diesel-powered machines (Figure 5). Several have been designed and used in the past in New Mexico to press the adobe soil mixture into a form, minimizing the amount of time required between forming the block and placing it into the wall. Portland cement or asphalt emulsion has been used to partly or fully stabilize pressed-earth blocks. Most producers are small volume and/or part-time, or noncommercial.

Rammed-Earth Walls. Rammed-earth homes commonly have much thicker walls than most other earthen dwellings, up to 0.9 m (3 ft) thick. Wooden or metal concrete-type forms are put in place on stone or concrete footings, and layers of moistened soil (15 to 20 cm [6 to 8 in.] thick) are deposited between the walls of the forms. Hand or hydraulic tampers are used to pound the soil into the shape of the form, compacting and reducing the volume of

the mixture by 25% to 30% (McHenry 1984; Middleton 1987). Once the layers of tamped soil reach the desired height, the forms are removed and the wall is allowed to dry (Figure 6). Portland cement is the common stabilizer used. Producers say rammed-earth walls continue to harden, or cure, during the first year after construction. From 2002 to 2005, there were approximately 28 buildings constructed by New Mexico's five rammed-earth construction firms, with 10 built during the spring and summer of 2005.

Specifications

Specifications for adobe or mud construction are not widely used in the United States. The state with the most adobe construction, New Mexico, probably has the most complete approach. The New Mexico code for unburned mud construction is Section 2412 of the New Mexico Building Code. A summary of the most significant rules governing adobe blocks follows (the code uses standard units rather than metric units):

- Compressive strength: The units shall have an average compressive strength of 300 lb/in² when tested.
- Modulus of rupture: The units shall have a 50 lb/in² in modulus of rupture when tested according to the specified procedures.
- Moisture content: The moisture content of untreated units shall be 4%.
- Adsorption: A dried cube cut from a sample shall adsorb 4% moisture by weight when placed upon a constantly water-saturated porous surface for 7 days. An adobe unit that meets this specification shall be considered stabilized.
- Shrinkage cracks: No unit shall contain more than three shrinkage cracks, and no shrinkage crack shall exceed 2 in. in length or 1/8 in. width.

Architectural Advances

Major advances are being made in architectural improvements, principally in the rammed-earth and cast-earth sectors in Australia and Texas. Although the Santa Fe style of adobe design is still the most popular in the Southwest, new design changes are gaining support for using earthen construction in multistory buildings, high-ceiling homes and buildings, and for novel approaches with large glass surfaces, passive solar additions, and functional flooring materials such as tiles and cut stone. In Australia, new architectural designs incorporate brick and concrete work as well as wood ceiling beams and internal structural features such as staircases, all in conjunction with the earthen portion. This not only allows greater beauty in the building, but also contributes to greater building strength from a seismic point of view.

Construction Technique Advances

New construction techniques will produce stronger adobe walls in the future, including (1) the use of rebar and steel wire mesh in adobe walls, (2) building walls that taper from wide at the base to thinner at the top, and (3) experimental additions of new starches and resins to adobe mixes to achieve stabilization with less additive materials. Although traditional adobe-making and building methods will still prevail in remote rural areas, urban areas offer more variety in artisan skills and construction materials that may result in new building techniques.

Research on Product Strength and Longevity

Project TERRA is a research umbrella group formed by CRATerre, GCI, ICCROM, and several other international earthen study organizations, known as the TERRA Partners, to develop worldwide



Figure 5. A mixer with a conveyor-belt system feeds a large-size commercial pressed-earth-block machine operation at the Ridge Adobe production yard in Santa Fe, New Mexico.



Figure 6. Exterior rammed-earth wall of a home under construction. The wall is 0.6-m (2-ft) thick. Note the layering produced by tamping and the concrete bond beam topped by the wooden frame at the top of the wall.

conservation of earthen architectural heritage. This research effort is also developing new information on ways to improve the strength and longevity of future earthen buildings. On May 14, 2000, the TERRA Partners, in cooperation with the English Heritage group, hosted a meeting in Torquay, England, to begin compiling world knowledge on earthen construction and its restoration, and to establish research priorities for the partners. This was the first international attempt to unravel the physical and chemical attributes of adobe and earthen construction on a very high scientific level. In the meeting, the following themes emerged for channeling future studies most effectively:

- Classification, binding, and unbinding
- Nonstructural decay or evolution
- Structural decay
- Chemical interventions
- Physical interventions
- Continued use



Courtesy of Edward W. Smith.

Figure 7. The 1,000-year-old Taos Pueblo originally was built of puddled adobe. Residents replaster the pueblo with mud each year to maintain the structure.

USE AND DISTRIBUTION

United States

Examples of early mud construction are present in many parts of the United States. Perhaps the most famous is the still-occupied, 1,000-year-old Taos Pueblo in New Mexico (Figure 7). Large earthen mounds built by North American aboriginal people, known as mound builders, are present in many parts of the eastern United States as well (Emerson and Woods 1990). The common building method in these pre-Columbian structures was puddled-clay or clay-lump construction, which preceded the adobe mold introduced by the Spanish in the 16th century. Similar construction was used in several sections of the country into the 19th century, as in western New York state (Dassler 1990). During the same period, sod was the principal building material of many immigrants on the treeless Great Plains. As modes of transportation broadened and the cost of moving building materials fell, earthen construction declined in most areas of the country.

An earlier improvement in adobe construction occurred in the 1880s when the railroads reached New Mexico. Local inhabitants soon learned how sloped roofs, covered by corrugated iron sheets brought from the east, were far more effective than the flat, dirt-covered roofs used prior to that time. Modern improvements, such as the use of soil stabilizers, further improved earth blocks' ability to withstand moisture damage.

The American Southwest has long had a love affair with adobe, and the landscapes of Arizona, California, New Mexico, and Texas contain many examples of enduring adobe homes. Old military forts, churches, and commercial buildings also attest to its popularity. New Mexico, both historically and today, is the largest domestic producer and user of adobes. During the past several decades, 3 to 4 million adobe bricks and pressed-earth blocks have been produced in New Mexico each year by as many as 50 commercial manufacturers (Smith and Austin 1989, 1996).

More than 59,000 adobe buildings, representing one third of the adobe dwellings in the United States, are in New Mexico (Gerbrandt and May 1986). Although less than 3% of new homes built each year in the state are constructed with adobe, the number usually averages between 500 and 600 dwellings. From examination of building permits in New Mexico and discussions with local architects, realtors, and planners throughout the Southwest, it appears

that most of new adobe dwellings are built for high-income customers. The houses usually contain above-average square footage with the addition of extensive southwestern architectural details and style. In some areas, particularly in parts of rural northern New Mexico, many backyard adobe producers build their own homes (McHenry 1985). This is often done on a part-time basis, and the house is completed without extensive debt or long-term mortgage payments.

Before 1970, most adobe buildings were built with traditional adobes. A breakdown of New Mexican adobe-brick production in 1987 shows that 27% were traditional (untreated) bricks, 68% were semistabilized bricks, and 5% were stabilized bricks (Smith and Austin 1989). Since the 1980s the percentage of semistabilized bricks has increased at the expense of traditional adobes.

Today, most builders purchase adobe bricks from commercial yards located throughout New Mexico. The principal, standard-size adobe brick produced and used in New Mexico measures approximately 10 × 25 × 36 cm and weighs approximately 13.6 kg (Smith and Austin 1989, 1996).

Latin America

Earthen and stone construction has been the dominant building style throughout Latin America, except in areas where timber and wood products are also available. In Central America today, rural people commonly tend to build adobe houses and structures rather than use readily available wood products. Urban areas in Latin America are heavily inclined to concrete construction and stick (wood-frame) housing, but rural areas still rely on a mix of stone, concrete, and earthen construction, depending on the availability and cost of materials. It is estimated that 35 million people live in earthen housing in the Andean region. Although the low cost of such housing greatly benefits the residents, the buildings are vulnerable to earthquake damage, with the associated mass deaths.

Australia

During the last two centuries, brick, stone, and, more recently, concrete construction has dominated urban areas of Australia. Rural construction has been mostly wood frame housing and earthen construction. Corrugated iron roofing is common throughout the country. Enough Australian forests have been largely cut down that the remaining forest lands are being preserved as national parks and recreational reserves. Because of this, most lumber and other forest products are now imported into the country from Indonesia and the island nations (e.g., Papua New Guinea) immediately to the north. As a result, rammed-earth construction is rapidly becoming a style of choice in both rural and suburban areas. Schools, churches, wineries, and much new housing in Western Australia are being built with rammed earth.

North Africa and Middle East

Stone and earthen construction have dominated North African and Middle Eastern construction since the dawn of civilization, supplemented only in the past century by abundant concrete construction. There are no other construction material alternatives in these countries. Rural areas in particular have mostly earthen construction, which is also desirable in countries where air conditioning is prohibitively expensive. Multistory earthen construction is common in some of the emirate cities around the Persian Gulf, dating back many centuries.

South Asia

South Asia, including India, Pakistan, Afghanistan, and a few adjoining countries, relies heavily on earthen and stone construction.

Urbanized areas with long distances to natural earth materials have shifted more to concrete, which is used to build high-rise buildings, major highway systems, and huge residential areas. Earthen building, however, is traditionally important to the Indian and Pakistani cultures. With their combined populations making them the second most populous countries after China, the future holds enormous potential for locally centered earthen building.

China and Interior Asia

Earthen construction is still very common throughout China, particularly in rural and lower-income urban areas. Concrete dominates urban construction and China is the world's top producer and exporter of cement, partly a result of the decimation of China's forests for fuel over many centuries. Interior Asia, which includes Tibet, Mongolia, and various "stan" countries, relies heavily on stone and earthen construction, using concrete only for the small number of highways, institutional buildings, airports, and such. Choice of construction materials is primarily determined by the pattern of their availability over time. An exception in Mongolia and other countries, but still related to traditional use, are yurts and other animal-skin tent housing.

Europe

There is a long history of earthen construction across Europe, and today it is thriving in such countries as Hungary, Bulgaria, and Poland where raw materials are readily available and people cannot afford expensive housing. Europeans have long preferred stone and brick construction in housing, but the reality of high-cost construction material is forcing them more and more to alternate materials. Only in northern lands, where wood is still readily available, does housing employ a greater amount of wood.

Sub-Saharan Africa

As the most economically disadvantaged location in the world, Sub-Saharan Africa depends on whatever materials are available for building. In many rural areas this is adobe construction, commonly complemented by thatched roofs, woven sticks, corrugated iron roofs, and other nonearthen alternatives. When adobe structures are constructed with these alternatives, the relatively few earthquakes that occur in seismically active areas in this region do not automatically result in mass collapse of walls and roofs. Judging by the grim economic future of this area, earthen construction will remain a dominant rural building style in the future.

ECONOMIC FACTORS

Cost

In New Mexico, adobe brick production varies from a labor-intensive, traditional technique using a hoe, shovel, and wheelbarrow to a mechanical large-scale operation producing 5,000 to 20,000 bricks per day. The production of adobe bricks is seasonal and is usually limited by the number of frost-free days for a particular adobe yard. In New Mexico, the production season lasts from 5 to 9 months, depending on local climate and weather conditions.

Smith and Austin (1989, 1996) reported that producers using the handcraft technique for traditional (untreated) adobe marketed their products at 21 to 40 cents per brick at their yards. One-person commercial yards produced 100 to 300 bricks per day. Semimechanized adobe yards with 8 to 10 employees can produce 5,000 to 6,000 semistabilized bricks per day that are sold for 30 to 35 cents per brick at the adobe yard (Figure 8).

In 2004, the largest mechanized adobe yard in New Mexico (the Adobe Factory in Velarde), which has 3 to 6 employees, produced up to 24,000 semistabilized adobes per day, which sold for



Figure 8. An adobe lay-down machine at an adobe yard in northern New Mexico. A front-end loader places the adobe mud in the hopper, which moves over the form, filling the spaces. The form is then retracted and the machine moves on.

72 cents each at the adobe yard. The same producer also sells traditional adobe for 72 cents each, but fully stabilized adobe is sold at 90 cents. Other producers say that the stabilizers (asphalt emulsion and portland cement) add between 15 and 20 cents to the price of an adobe brick. Pressed-earth blocks in a production yard are sold for comparable prices, but some producers take their machine to the job site and use local soil for their blocks at a slightly reduced price. These producers are the contractors as well and build the desired walls.

Markets in the American Southwest

Tradition is the most important factor in determining markets for adobe materials. In areas that have a strong history of mud construction, adobe is a appealing and even preferred. In other areas where the population is not familiar with adobe or considers it "lower class" to live in such buildings, new adobe buildings will not replace the old ones that disappear. Santa Fe is an example of a traditional adobe area, where the "Santa Fe style" of construction is adobe pueblo and territorial style (Smith and Austin 1989, 1996). Adobe buildings are preferred by many wealthy landowners and contractors who use other types of construction to mimic the adobe styles.

In nearly all other parts of the United States, mud construction is not popular and there is virtually no new construction with this method. In Great Britain, France, and Germany, countries with long histories of earthen construction, mud construction is no longer used, even though excellent examples of multistoried rammed-earth buildings still exist.

Transportation

Although adobe may be made on the construction site, it is now more likely to be made in adobe yards and transported to building sites on flatbed trucks (Figure 9). Larger flatbed trucks carry about 5,000 palletized or stacked adobes. Although transport to distant construction sites is uncommon, some producers ship adobes several hundred miles. The reason for the long transport of adobe blocks is not because of the lack of the raw, native materials, but because contractors in some areas of the country have neither the training nor the talent for this type of construction.

Rammed-earth construction methods require that the walls be made at the building site. Consequently, the typical method of



Courtesy of Edward W. Smith.

Figure 9. A truckload of adobe bricks on pallets ready for delivery in northern New Mexico

construction is to use local materials or materials that have not been transported far.

ALTERNATIVE AND COMPLEMENTARY MATERIALS

The most commonly used alternative material is concrete block. Even in the American Southwest, many adobe-style homes are constructed of stucco-clad concrete block. Although smaller and lighter than adobe and easy to use, concrete block walls do not have the physical properties of thicker adobe walls and must be carefully insulated to achieve consistent temperature and sound-deadening properties similar to those of adobe.

Complementary materials also can be used to make adobe blocks. These materials include "off-spec" aggregate plant products, ditch dredgings, fly ash, shredded tires, reject clays, and other fine-particle products and similar "waste" products that would otherwise have a disposal cost. Such materials are already commonly used in concrete manufacturing, so there is an established practice in such by-product use. Using complementary materials in adobe or earthen construction has a threefold advantage:

1. They are inexpensive as aggregates and filler materials.
2. They may contribute physical advantages to the finished product (e.g., pozzolanic effects, and greater tensile strength).
3. They resolve another producer's disposal problems and may solve environmental problems in the process.

In underdeveloped countries, sometimes the lack of availability and the higher cost of cement can make adobe the preferred type of construction. The use of available native materials can be a strong incentive in countries where builders are short of funds to buy cement or construct cement plants.

GOVERNMENTAL CONSIDERATIONS

In the U.S. regions where adobe is widely used in construction, locally adopted amendments to the Uniform Building Code establish building specifications. In the New Mexico code for adobe, which was last completely modified in 1988, acceptable earthen construction materials and products and the tests necessary for their use are listed and explained. Earthen construction specifications have been similarly codified in other states.

Health and Safety Regulations

Seismic Activity

The greatest potential problem with adobe/earthen buildings is their vulnerability to earthquakes when they are in seismically active areas. Improved building techniques and materials, better architecture and roof design, and better building sites may alleviate most or all of the perceived problems. In the past, the same issues raised for fired brick, cut stone, concrete block, and concrete buildings were resolved. Solving most of the seismic-related concerns with earth and stone construction could have a big impact in alleviating massive death and destruction in cities heavily dependent on earthen construction, including those in developing countries such as Chile, China, Iran, Nepal, and Peru.

Adobe buildings in the United States are commonly constructed on concrete slab foundations and have one or two stories. Designing the slab to resist cracking both during normal life of the structure and possible earthquakes is prudent in seismic areas. Work in California suggests that a combination of techniques can serve to reduce hazards related to earthquakes—proper slab construction; walls reinforced with rebar; wire mesh beneath the plaster and stucco both inside and outside the building; interconnected bond beams and roof beams at the top of walls; and buttresses (Tibbets 1986).

Radon

The identification of radon gas as a health hazard has caused owners to be concerned about the safety of their adobe structures. Radon is a colorless, odorless, heavier-than-air radioactive gas derived from the breakdown of radioactive elements in soil and rock in some parts of the world. The most stable radon isotope, ^{222}Rn , has a half-life of 3.8 days (Wilkening 1980). Radon enters buildings through cracks and accumulates in low spots such as cellars, crawl spaces, and poorly ventilated zones, particularly when they are closed and have a negative air pressure, as is common during the winter months. This problem is not unique to adobe-type structures but commonly occurs in soils overlying granite, black shale, light-colored volcanic rock, sedimentary rock with phosphate, and similar geologic settings. Although adobe buildings have not been shown to have significantly more radon than other types of construction, good ventilation and positive interior air pressure are the easiest ways to alleviate a buildup of radon. Modest changes in construction and care commonly will prevent problems in all but the most severe cases (Smith and Austin 1989, 1996).

Building Codes

The building code for earthen construction in the United States focuses on safety for the inhabitants. In New Mexico and California, two states with numerous adobe structures and substantial seismic activity, the building code specifically addresses the need for adobe structures to endure considerable movement during seismic events (Smith and Austin 1989, 1996). The New Mexico code forbids the construction of adobe structures exceeding two stories in height, and all load-bearing walls must be topped with a continuous belt course or tie beam. The belt course is commonly reinforced concrete, and a tie beam is solid wood and at least 15.24 cm (6 in.) thick. The California building code requires that walls have internal reinforcement with rebar, as well. Following these codes, adobe structures fare about as well in earthquakes as buildings constructed with more conventional materials.

In summary, although adjustments must be made for such problems as possible damage during earthquakes, insulating properties, and radon gas accumulation, these modifications are neither

costly nor difficult to make. In addition, on a worldwide basis, earthen construction offers the considerable advantage of housing a rapidly expanding population with a maximum amount of local building material and a minimal use of expensive energy resources. Earthen construction is indeed the champion sustainable construction material.

Critical Importance in Middle Eastern Countries

Iran, Iraq, Kuwait, Pakistan, and other countries clustered around the Persian Gulf and Arabian Sea are all heavily oriented toward earthen construction. They are also in a region of intense earthquake activity. These countries have much to gain by adopting new building technology, which will cost residents nothing more than the time for instruction.

Because much of Iraq's residential and other construction consists of earthen construction, ongoing rehabilitation of that country after the second Gulf War could benefit greatly from new construction techniques and architecture. The easy availability and low cost of earthen raw materials could significantly ease the expense and time required to bring the country back to its feet. As pointed out earlier, adobe houses are fairly bulletproof and resistant to shell fragments.

FUTURE TRENDS AND INNOVATIONS

Adobe and other types of earthen construction are gaining respectability worldwide, especially as advances in architecture produce better and more livable designs and structures. In addition, improvements such as electricity, air-conditioning, heating, solar heat, and electronics can make a humble earthen structure comfortable and support a high standard of living. Advanced architectural and structural designs in rammed-earth and cast-earthen construction in Australia, South Africa, and selected Latin American countries will encourage more countries with limited construction material supplies to pursue a greater proportion of earthen building.

In the American Southwest, earthen construction will continue to account for about 5% of new residential building. The Santa Fe style of earthen construction continues to be the most popular and will be the preferred type of construction of both low- and high-income groups. The availability of local materials, and the fact that individuals can build the structures themselves, has appeal for low-income groups. Adobe is a preferred type of construction for the wealthy because a superior home can be constructed that is in vogue and is in harmony with nature.

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Aggregates

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INTRODUCTION

Construction aggregates are sand and gravel and crushed stone used in various types of construction-related applications. They are a high-volume, low-cost, bulk minable commodity. By volume they are the primary ingredient in portland cement concrete (PCC) and asphalt concrete (AC), often referred to as simply concrete and asphalt, respectively. They are generally crushed and processed to a size and gradation suitable for different specific construction applications.

Aggregates have been used since humans first started constructing buildings, cities, and roadways. In early history most permanent construction included stone, but more than 2,000 years ago the Romans were using a form of lime-concrete incorporating broken stone and sand for many of their buildings. The construction aggregate industry, as we know it today in the United States, developed primarily from the need to improve roads. Boston, Massachusetts, is reported to have had the first paved streets by the mid-17th century. Most roads in the 19th century were unpaved, although some city roads were paved with wood planks, gravel, cobblestone, brick, or crushed stone referred to as macadam. In the early 1800s, the government appropriated money for the first national highway, which eventually extended from the Atlantic seaboard to as far as Illinois and was mostly constructed with broken stone. The railroads then dominated aggregate production in the mid-1800s with their need for railroad ballast (Langer 1997).

By the late 1800s road improvement was finally recognized as important, and the industry as we know it today was born. After the automobile was introduced in the early 20th century and became mass produced (putting a theretofore largely immobile populace on the road), the necessity for road improvements and new construction skyrocketed and has yet to subside. The automobile, along with other industrial advancements, changed the lives of ordinary people and increased their standard of living.

The construction aggregate industry in the United States today is the largest nonfuel mineral industry in the country, producing and consuming approximately 2.6 billion t (2.9 billion st) of mined sand and gravel or crushed stone annually, or approximately 10 t per capita. Every population center in every state, from large cities to small towns, requires construction aggregates for growth, infrastructure maintenance, and literally any type of construction. Aggregate production over the last few years has represented the highest production levels ever recorded in the United States, consistently

increasing over the past decade, reflecting the vitality of the country's economy.

This chapter on aggregate markets and uses briefly acquaints the reader with the aggregate industry; its specifications, marketing, and end uses; how construction aggregates are used in our modern world; and why they are important. It discusses aggregate once it has been processed and stockpiled, usually at the site where it is mined. This chapter does not describe in detail how aggregate occurs from a geologic perspective, how it is evaluated and tested, how it is mined and processed, what is involved in developing and permitting a new resource, and what the major environmental and social impacts are of mining aggregates in the modern world. These issues are covered in detail in the Construction Sand and Gravel and Crushed Stone chapters in this volume.

Aggregates are primarily strong, hard, durable, and so und sand and gravel or stone deposits generally mined near where they are consumed. They are mined locally because they are a high-tonnage, low-cost commodity that cannot economically be hauled for long distances without significantly increasing construction costs. After mining, processing consists of crushing, screening, and washing. Aggregates are used primarily in PCC, in AC, and as base material, but there are numerous other specialty uses as well. Strict specifications govern the finished aggregate product to ensure a long-lasting and quality end product.

Many challenges face the construction aggregate industry because of social, environmental, and economic factors. Competing land uses, environmental regulations, negative attitudes toward mining, and the NIMBY (not in my backyard) syndrome are all adversely affecting the industry. Yet there will be a continuing need for an adequate supply of local aggregate because increased transportation costs can negatively affect reasonable consumer costs. So industry must educate the public on the need for aggregates and the realization of industry's commitment to mine responsibly with an emphasis on adequate reclamation or post-mine land use. Gone are the days of leaving a water-filled, steep-sided open pit as a legacy.

Aggregate Types

"Construction aggregates" can be a broad term, including everything from the highest quality crushed rock or sand and gravel used in high-strength concrete applications to ordinary borrow suitable only as general construction fill. This chapter does not discuss ordinary borrow material, and, for the most part, the discussion is confined to

applications for higher-quality construction aggregates, which are hard, durable, and chemically inert. The primary sources of good-quality construction aggregates are either sand and gravel deposits or quarried and underground bedrock sources.

Sand and Gravel

Sand and gravel deposits are found along rivers and streams and their floodplains, in alluvial fans, in glacial and beach deposits, and as paleosediments. Sand and gravel result from erosion of other rock units and redeposition of clasts of these previous rock units in new environments, primarily by the action of running water but occasionally by glaciers, waves, or mass wasting. Size distribution ranges from enormous boulders to rock flour and reflects the distance the individual grains have traveled and the forces involved in transportation. Deposits rich in sand are the result of lower-energy environments where gravels have previously dropped out and only sand particles can be held in suspension. Deposits typically consist of various rock types, reflecting the varied distribution of the parent geology from which the sand and gravel were derived. Quality of the sand and gravel is likewise determined by the qualities of the original parent rocks, the distance the material has traveled, the dynamics of the depositional environment, subsequent weathering that may have occurred, and the age of the deposit. This is vividly illustrated by the lack of gravel deposits along the U.S. Gulf Coast. Here the flat terrain and the scarcity of nearby hard-rock units to serve as a gravel source combined to create an unfavorable, slow-moving depositional environment without gravels.

For higher-quality construction aggregate uses, sand and gravel deposits must contain individual clasts that are hard, durable, and chemically inert. In addition, the deposit should contain sufficient reserves to sustain a mining operation for a suitable length of time.

Crushed Stone

Crushed stone deposits are found where appropriate bedrock exists. Suitable bedrock can occur in sedimentary, igneous, and metamorphic terrains. The primary sedimentary rock deposits are the carbonates, limestone and dolostone. Igneous rocks include plutonic rocks ranging from granites to gabbros and volcanic rocks ranging from basalts to rhyolites. Metamorphic rocks generally include gneiss, marble, quartzite, and argillite. "Trap rock," a common term in the aggregate industry, refers to dark-colored, fine-grained, igneous rocks ranging from diabase in the eastern portion of the country to Recent basalts in the West. Bedrock occurs where tectonic forces and subsequent erosion have exposed the older, indurated hard-rock units and should be free of deleterious constituents and relatively unweathered. As in sand and gravel, suitable bedrock sources must be hard, durable, chemically suitable, and large enough to sustain an extended mining operation.

Other Materials Used as Aggregate

Slag. Slag is a by-product of the iron and steel refining industry. Approximately 20% of the raw material going into the furnaces to produce iron and steel remains behind as slag. It is composed primarily of alumina silicates and is hard and durable. Slag is sometimes an important local source of aggregate in communities close to iron and steel mills. Total slag used as aggregate is relatively small, being less than 0.5% of total aggregate production.

Lightweight Aggregate. The concrete industry uses both natural lightweight aggregate (i.e., pumice and volcanic cinder) and manufactured lightweight aggregate (i.e., expanded clays and shales, perlite, and vermiculite), primarily in concrete masonry units, to reduce weight of individual units. These aggregates are also used in

structural concrete to reduce weight, especially in high-rise buildings. Perlite and vermiculite are typically used for their insulation properties. For a detailed discussion of lightweight aggregates, refer to the *Lightweight Aggregates* chapter of this volume.

Recycled Materials. Recycling of concrete and asphalt has become more prevalent, reflecting the increasing economic advantage of using these materials. Approximately 15 Mt of concrete and asphalt are recycled yearly in the United States (Bolen 2002; Tepordei 2002). As transportation costs, energy costs, and environmental concerns increase, recycling makes better economic sense.

Concrete from demolition and from general construction debris is often collected, crushed, sized, and processed into aggregate base (AB). It is generally not used as an ingredient in new concrete applications because of quality concerns.

Recycling is sometimes used on asphalt roads: existing worn-out surfaces are ground and reincorporated, at a limited percentage, into new hot-mix asphalt surfaces. These recycled asphalt products are referred to as RAP. Lengthy "trains" can often be seen on road construction projects milling and reincorporating the grindings into an on-the-road mixing plant, where it is blended with new hot-mix material, then relaid as a new asphalt surface. In addition, RAP can be used in AB or as road surfacing on unpaved secondary roads to prevent dust and improve performance.

Recycling is most prominent in the larger metropolitan areas where aggregates command a premium price because of associated transportation costs from distant deposits. Also, waste construction materials require disposal, and often it is more cost-effective to recycle than to pay for transportation to remote landfills, which may charge for disposal. Recycling is entirely an economic decision unless mandated by local or federal regulation on some projects.

Other Materials. Occasionally, other materials have been used in concrete and asphalt products for specialty applications. Shredded rubber tires in asphalt, barite in concrete used in radiation shielding, organic waste and wood chips for lightweight applications, broken glass or cullet in AB, and burned coal cinders in cinder blocks.

Production and Consumption Statistics

Construction aggregates are the largest nonfuel mineral industry in the country. As detailed in the two chapters on construction sand and gravel and crushed stone in the *Commodities* section of this volume, approximately 2.6 billion t (2.9 billion st) of aggregate, consisting of both sand and gravel and crushed stone, were produced in 2003, which equates to approximately 10 st for every person in the United States. On a per-capita basis, consumption and production are the standard gauge of measuring and forecasting aggregate. The U.S. Geological Survey (USGS) indicated that 1,260 companies operating 3,300 active quarries in 49 states produced \$8.6 billion worth of crushed stone in 2003, or 1.49 billion t (Tepordei 2003). And 1.13 billion t of sand and gravel, valued at \$5.8 billion, was produced by an estimated 4,000 companies operating at 6,400 locations in 50 states (Bolen 2003). The USGS conducts annual surveys and compiles statistics on aggregates throughout the country. These results, published yearly, are considered the best available statistical analysis for the aggregate industry in the country and are the source of the statistics presented in this chapter.*

* These estimates are based on voluntary responses from producers. Not all producers respond; therefore certain assumptions and adjustments are made to arrive at the final figures. In addition, crushed stone production includes stone used to manufacture cement and lime, which are also considered to be construction materials but, strictly speaking, are not construction aggregates.

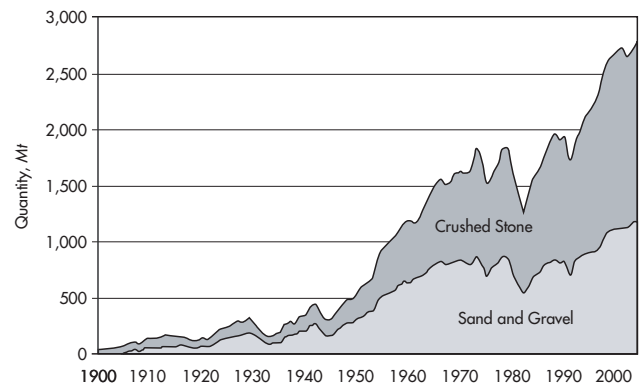
The United States imports small quantities (approximately 18 million t) of construction aggregate, mostly crushed stone, from Canada, Mexico, and the Bahamas. At one time, there were imports from Scotland, but closer sources now predominate. Imports are increasing, however. Although imports are a small portion of total aggregate production, they can be a significant portion of the market in those coastal areas where the imports arrive. Imports make up a significant percentage of total aggregate consumption in some areas of the West, East, and Gulf coasts.

Figure 1 graphs aggregate production since 1900, which reflects the industrialization and increased standard of living enjoyed by the U.S. population. It especially reflects the effects of the nation's transportation system as it went from horse-drawn wagons to "horsepower" when it entered the age of automobiles and airplanes. More than one half the aggregate production in the last century was produced in the past 25 years. The construction of the nation's transportation system consumes a good part of the aggregate resources mined and produced. The figure is broken down by sand and gravel and crushed stone; and, as can be seen in the stacked graph, crushed stone production exceeded sand and gravel starting in 1972. This is attributable to the decline of sand and gravel resources through attrition and the exhaustion of resources, but, more important, to the increased conflict of land uses along flatter, lower-lying lands where sand and gravel naturally occur. These lands, especially near metropolitan areas, are becoming more valuable for other uses besides mining as development encroaches on close, available flat lands. In addition, environmental considerations and social pressures (NIMBY attitudes) are driving resource exploitation farther from the cities and from readily visible flat terrain along major drainages where sand and gravel resources are generally located. Aggregate operations are moving to areas in bedrock where visibility is limited and where impacts to groundwater and the environment are more controllable.

Figure 2 displays how aggregate operations are a high-volume, low-cost commodity, located relatively close to the market. Though this figure was compiled with data from the late 1990s, it well illustrates the point at hand: nearly every county in every state in the union has an aggregate source, either sand and gravel or crushed stone or both, supplying local needs. Aggregates are the only mining commodity nationwide that are readily visible to a large proportion of the population: Commuters within our major metropolitan areas often drive by aggregate operations daily. Aggregate mining operations are, by far, the most visible segment of the mining industry in the country with nearly 10,000 quarries and pits, most concentrated near population centers. Therefore, aggregate mining is the most recognizable form of mining to most of the populace.

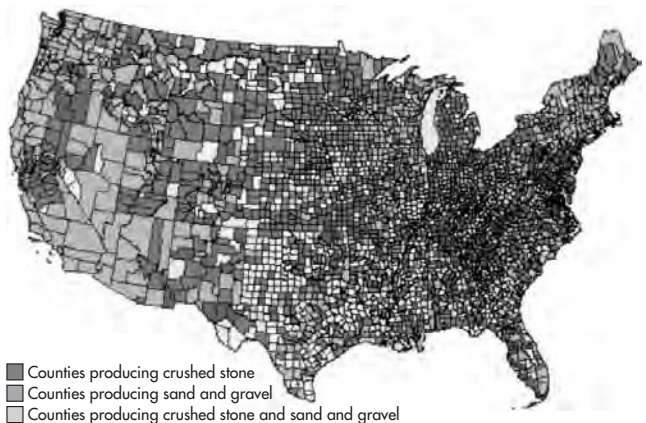
Figure 3 shows the distribution of aggregate production in the United States. It is evident that production mirrors population density. Again, the figure was compiled with data from the late 1990s, but the situation remains the same: The more rural states, most having abundant aggregate reserves, produce only those amounts necessary for consumption in the local area. Another characteristic shown is the production distribution of sand and gravel versus crushed stone. Those states where crushed stone dominates are those where sand and gravel reserves are limited. The eastern portion of the country reflects the increased trend toward crushed stone, and, as can be seen, the majority of aggregate production is in the eastern portion of the country and on the West Coast, where the majority of the population is located.

Table 1 shows aggregate production statistics: tonnages produced, total values, and average unit values. The five leading states for sand and gravel production are California, Texas, Michigan,



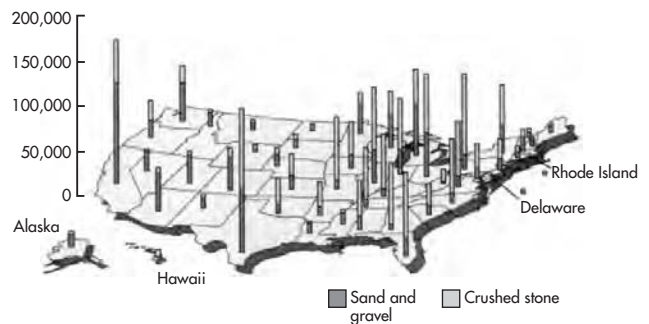
Adapted from Kelly et al. 2005.

Figure 1. Aggregate production in the United States from 1900 to 2004



Source: Tepordei 1997.

Figure 2. U.S. counties producing natural aggregate



Source: Tepordei 1997.

Figure 3. Distribution of natural aggregate in the United States, by state

Arizona, and Ohio. The five leading states for crushed stone are Texas, Pennsylvania, Florida, Illinois, and Missouri.

Prices

Despite having one of the lowest average-per-ton values of all mineral commodities, the constant dollar price of crushed stone has

Table 1. Natural aggregate production by state, t

State	Sand and Gravel	Crushed Stone	Total Aggregates
Alabama	12,500	43,400	55,900
Alaska	16,300	2,810	19,110
Arizona	53,800	8,450	62,250
Arkansas	8,810	30,600	39,410
California	151,000	67,400	218,400
Colorado	40,700	15,000	55,700
Connecticut	8,140	10,200	18,340
Delaware	2,190	0	2,190
Florida	26,400	97,700	124,100
Georgia	6,600	70,500	77,100
Hawaii	610	6,380	6,990
Idaho	15,700	3,420	19,120
Illinois	32,000	75,200	107,200
Indiana	27,600	55,500	83,100
Iowa	14,600	35,900	50,500
Kansas	9,560	21,300	30,860
Kentucky	9,530	50,600	60,130
Louisiana	17,900	W*	na†
Maine	9,680	4,010	13,690
Maryland	12,200	22,300	34,500
Massachusetts	12,200	13,800	26,000
Michigan	77,300	41,100	118,400
Minnesota	43,700	9,960	53,660
Mississippi	13,600	2,620	16,220
Missouri	10,000	73,200	83,200
Montana	16,700	2,370	19,070
Nebraska	12,900	7,220	20,120
Nevada	35,400	8,010	43,410
New Hampshire	8,640	4,810	13,450
New Jersey	16,000	20,500	36,500
New Mexico	12,800	3,680	16,480
New York	29,800	56,500	86,300
North Carolina	10,000	62,900	72,900
North Dakota	10,700	W	na
Ohio	48,700	72,000	120,700
Oklahoma	10,200	45,000	55,200
Oregon	19,500	19,800	39,300
Pennsylvania	18,100	102,000	120,100
Rhode Island	1,760	1,780	3,540
South Carolina	10,300	25,700	36,000
South Dakota	11,900	6,780	18,680
Tennessee	9,220	54,900	64,120
Texas	82,600	109,000	191,600
Utah	27,600	7,640	35,240
Vermont	4,990	4,360	9,350
Virginia	10,500	58,900	69,400
Washington	43,200	13,700	56,900
West Virginia	1,700	14,400	16,100
Wisconsin	39,000	36,200	75,200
Wyoming	7,710	4,450	12,160

Source: Bolen 2002; Tepordei 2002.

* W = withheld to avoid disclosing proprietary data.

† na = not available.

Table 2. Aggregate and related construction product price increases, 1994–2003

Commodity	Price Change	Percent Change
Gravel for concrete (f.o.b. plant)	\$9.12–\$10.31	13
Crushed stone (f.o.b. plant) per short ton:		
Aggregate base	\$6.09–\$7.96	31
Concrete aggregate	\$6.77–\$8.27	22
Sand for concrete	\$6.12–\$7.44	22
Ready mix concrete (delivered; standard 3,000-psi mix)	\$50.57–\$76.16	51

Adapted from ENR 1994–2004.

changed relatively little over the past 33 years. As a result of rising costs of labor, energy, and mining and processing equipment, the average unit price of crushed stone, based on USGS statistics, increased from \$1.58/t, free on board (f.o.b.) plant, in 1970 to \$5.78/t in 2003. This, however, parallels or slightly exceeds inflation. Increased productivity achieved through increased use of automation and more efficient equipment was mainly responsible for maintaining the prices at this level. During the 10-year period from 1994 through 2003, the average price of crushed stone for all uses rose from \$5.39 to \$5.78/t, a 7.2% increase. For crushed rock used in concrete, it rose from \$5.58 to \$7.27/t, a 30.3% increase. Prices for sand and gravel during that same period rose from \$4.20 to \$5.14/t for all uses, a 22.4% increase, whereas for concrete sand and gravel, prices rose from \$4.67 to \$5.80/t, a 24.2% increase. *Engineering News Record* (ENR 1994–2004) also tracks published prices for aggregates and related construction products monthly. Table 2, compiled with data from ENR, lists a average price increases for aggregate and related construction products from 1994 to 2003.

These figures for aggregates are averages for the country based on ENR's method of survey (prices in 20 cities throughout the country). Individual commodity prices vary widely from city to city. ENR's typical prices at the end of 2003 for concrete sand ranged from \$4.40 to \$10.95 in the 20-city survey.

In California, the leading producer and consumer of aggregate, the average cost of concrete aggregate was between \$8.00 and \$10.00/st in 2002. In certain large metropolitan areas such as San Francisco, where sand is imported from British Columbia, prices can be as high as \$20/st. This high cost reflects the lack of permitted aggregate resources in the San Francisco Area (Kohler 2002).

The 51% average price increase for ready mix concrete in Table 2 exceeds the aggregate increase. Even though ready mix is approximately 75% aggregate, cement costs over the 10-year period rose more sharply, partially reflecting the higher price for ready mix concrete.

INDUSTRY STRUCTURE

The basic precept of the aggregate industry is making little rocks out of big rocks. The aggregate industry has undergone a dramatic change over the last century. Once confined to small localized deposits, the industry took off with the rise in popularity of the automobile and the government's construction of highways to accommodate those automobiles. By the 1950s hundreds of thousands of roads had been built on the continent, giving birth to the interstate highway system, which had added more limited-access, higher-speed freeways. This increased the trend to larger deposits, bigger companies, and more quarries and pits owned by individual companies. In the 1980s the mergers and buy-ups began. The majority of the "mom-and-pop" operators were bought by larger

Table 3. The 25 leading U.S. companies ranked by total output of aggregates, 2004

Rank	Company	Rank	Company
1	Vulcan Materials Co.	14	General Dynamics Corporation
2	Martin Marietta Aggregates	15	RMC Industries Corporation
3	Hanson Aggregates	16	TXI Operations
4	Oldcastle Materials Group	17	A. Teichert & Son, Inc.
5	Rinker Materials Corporation	18	National Lime & Stone Company
6	LaFarge North America, Inc.	19	New Enterprise Stone & Lime
7	Cemex, Inc.	20	Minnesota Mining & Manufacturing
8	Florida Rock Industries, Inc.	21	Dolese Bros. Co.
9	Aggregate Industries, Inc.	22	Vecellio & Grogan, Inc.
10	MDU Resources/Knife River	23	Robertson Ready Mix, Inc.
11	Rogers Group, Inc.	24	Oglebay Norton Co.
12	Ashland, Inc./APAC, Inc.	25	Irving Materials, Inc.
13	Luck Stone Corporation		

Source: USGS 2005.

companies or even international corporations that wanted to broaden their market share and produce additional profits. This trend continues, with major companies expanding throughout the country.

The industry is highly competitive, characterized by thousands of operations selling into regional and local markets. Production costs are mainly determined by the costs of equipment, energy, labor, and compliance with local, state, and federal regulations. These costs vary greatly depending on type and size of deposit, number of products produced, and variability of regulation requirements from state to state and city to city.

Table 3 lists the 25 largest aggregate producers in the country as compiled by the USGS. These companies produce approximately 66% of all aggregate, both sand and gravel and crushed stone, that is used. Many of the companies not only are large by American aggregate industry standards but also are leaders in the mining and processing of aggregate worldwide. Five of the top ten aggregate producers are owned by foreign companies. The combined production of the top ten companies was 43% of the national total for crushed stone as reported for 2002 and 48% for sand and gravel as reported for 2002.

A distinction between sand and gravel and crushed stone producers is not necessarily significant because both commodities are essentially interchangeable when used as construction material, and most if not all the major companies produce both products. The USGS and this volume differentiate the two, however, treating them as separate commodities. They are certainly separate commodities, but the aggregate industry itself seldom differentiates. Both can be used for PCC, AB, and AC as well as other construction applications.

Many companies are vertically integrated, not only mining the raw aggregate material but also using that aggregate in the end product (i.e., concrete, asphalt, and AB). In some instances they are major contractors, specializing in highway and site construction and paving. In this instance they control the aggregate from mining until it is incorporated into finished roadways or associated construction projects.

As companies become larger and more sophisticated in the marketplace, they must become more productive and technical in the modern competitive world. What were once small, local operations now employ more geologists, engineers, and other technical

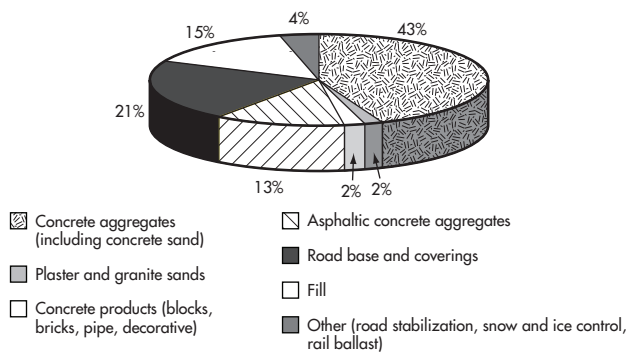
personnel to run their operation more efficiently. In addition, the structure and corporate cultures of large companies in the aggregate industry have changed over time, reflecting the current social and business environment.

FINISHED PRODUCTS AND SPECIFICATIONS (USES)

Most construction aggregate is used in PCC, AC, and AB. Other specialized uses are railroad ballast, plaster and mortar products, concrete masonry units, filter and drain rock, decorative rock, and others. The aggregate used in these various applications must meet certain specifications because the aggregate influences the physical characteristics of the end product, primarily strength and durability. The aggregate is essentially a filler in PCC and AC applications. Every aggregate deposit must be thoroughly tested to determine if the material meets specifications for these individual products. Often, individual deposits meet some specifications but not others. Aggregate specifications have been developed to ensure the manufacture of durable, strong, chemically resistant end products that can withstand prolonged use and the effects of weathering.

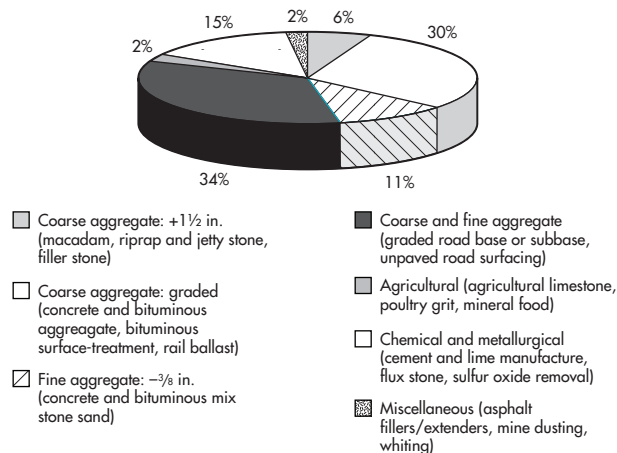
Figure 4a shows end product uses for aggregate derived from sand and gravel, and Figure 4b shows uses for aggregate derived from crushed stone. About half the aggregate (for both crushed stone and sand and gravel) produced in the United States is used in government-funded projects. Of the 1.16 billion t of construction sand and gravel produced in 2003, it is estimated that about 43% was used as concrete aggregates; 21% for road base and coverings and road stabilization; 13% as AC aggregates and other bituminous mixtures; 15% as construction fill; 2% for concrete products such as blocks, bricks, and pipes; 2% for plaster and gunite sands; and the remainder for snow and ice control, railroad ballast, roofing granules, filtration, and other miscellaneous uses (Bolen 2003).

Several entities, both governmental and private, have developed specifications for the various aggregate uses. The American Society for Testing and Materials (ASTM) and the American Association of State Highway and Transportation Officials (AASHTO) are the two most important agencies that developed specifications for all construction materials, including aggregates. ASTM is most commonly used in the private sector, whereas AASHTO is used by the individual state departments of transportation and city and county public works departments. AASHTO aggregate specifications are often



Adapted from Bolen 2003.

Figure 4a. End-product uses for aggregate—construction sand and gravel



Adapted from Tepordei 2003.

Figure 4b. End-product uses for aggregate—crushed stone

adopted from ASTM. Sometimes certain government agencies tighten these specifications even further to improve aggregate performance. For instance, Caltrans (California Department of Transportation) has a more-stringent specification for aggregate used on Interstate 80 over the Sierra crest in northern California. The harsh weather environment coupled with the need for heavy trucks to use tire chains during snowstorms dictated the need for more durable concrete to increase the life of the roadway.

Federal agencies such as the U.S. Bureau of Reclamation, Federal Highway Administration, Federal Aviation Administration, and the U.S. Army Corps of Engineers also have their own specifications for certain construction materials, primarily the end products such as PCC and AC.

In the construction aggregate industry, the definitions of fine and coarse aggregate, whether it is from natural sand and gravel deposits or manufactured from crushed stone sources, can generally be characterized as follows:

- **Fine Aggregate** (natural sand or crushed or manufactured sand)—Granular material passing the 3/8-in. (9.5-mm) sieve, almost entirely passing the No. 4 (0.187-in. [4.75-mm]) sieve, and predominantly retained on the No. 200 (75-μm) sieve (ASTM C125).
- **Coarse Aggregate** (natural gravel or crushed stone)—Granular material predominantly retained on the No. 4 (0.187-in.

[4.75-mm]) sieve (ASTM C125). Construction industry usage commonly restricts gravel size between 1 1/2 in. and 3/8 in. (3.8 mm and 0.95 mm, respectively).

It should also be understood that most oversize material in natural gravel deposits, plus 1 1/2-in. (3.8-mm) material (cobbles and boulders), is crushed to produce both fine and coarse aggregate.

As previously described, construction-fill applications are often cited as a use for construction aggregates, but because fill can be considered ordinary borrow with limited physical requirements, it is not considered here to be a construction aggregate. Construction aggregate implies a unique material that must meet certain physical requirements. Often, ordinary borrow or fill can be satisfied with most any material excavated, whether it be good-quality aggregate or ordinary dirt. Often the overburden and waste from existing aggregate pits and quarries are sold as ordinary fill.

Commodities that use the higher-quality construction aggregates are described in the following subsections.

Portland Cement Concrete Applications

PCC is one of the most common construction products. It is used in virtually every type of construction, from individual homes to high-rise office buildings, from structures along county roads to pavements for multiple freeways, and a part of private, commercial, and public works projects.

Aggregate makes up between 70% and 80% of concrete by volume, or from 75% to 85% by weight. Laypeople often incorrectly use the words *cement* and *concrete* interchangeably. Portland cement is the “glue” that binds the aggregate together to form PCC. The cement is referred to as “portland” because of its unique chemical composition, first developed in England in the late 1890s, in which the resultant concrete had the appearance of a natural limestone near Portland in southern England that was used for building stone. Portland cement is a manufactured product derived from calcining limestone with lesser amounts of alumina, silica, and iron. The resulting clinker is then ground to a fine powder and mixed with a minor amount of gypsum to form portland cement. A detailed discussion of cement is found in the Cement and Cement Raw Materials chapter in this book.

PCC is a mixture of hydrated portland cement, coarse and fine aggregate, water, and air. Hydration of the cement takes place when water is added to the mixture. The water reacts with the cement, hydrating the calcium silicate paste, which quickly solidifies (hardens), binding the aggregate together and forming the finished concrete.

Concrete mixes are variable depending on the application. Strength is determined by the amount of cement in the mix and the water:cement ratio—the lower the ratio, the higher the strength. In general, cement contents in a typical cubic yard of concrete (the general method of measurement) ranges from 4.5 to 7.0 sacks per cubic yard of concrete, which equates to between 423 and 658 lb (192 kg and 298 kg, respectively) of cement per cubic yard of concrete. In addition, a certain optimum amount of water is required for placement to allow the concrete to flow into the forms. Aggregate in the mix must be combined properly to make for a dense mixture where void space is at a minimum and the cement paste fills all the voids. This is accomplished by blending two or more aggregate sizes in predetermined percentages. At least one size of coarse aggregate is blended with a fine aggregate. Admixtures can be incorporated in the mix to reduce water demand, to increase strength, to retard or accelerate setting time, to reduce heat of hydration, to decrease permeability and shrinkage, to make the concrete more durable and frost resistant, and for color. High-strength concretes, >6,000 psi, can be achieved only by using admixtures. A

detailed discussion of PCC concrete is beyond the scope of this article and for further information the reader should contact organizations such as the American Concrete Institute (ACI) and the Portland Cement Association (PCA).

Aggregate properties important to PCC are hardness, durability, soundness, absorption, specific gravity, surface texture, particle shape, cleanliness, size and grading, and chemical inertness. Meininger (1994) gives an excellent discussion of the effect of aggregate properties on concrete.

In general, the most widely accepted specification for concrete aggregates is ASTM C33-03, *Standard Specification for Concrete Aggregates*, summarized in Tables 4 and 5.

Several different types of applications use aggregates in combination with portland cement; these are discussed in the following subsections.

Ready Mix Concrete

Ready mix concrete is batched at a centrally located plant and generally transported by mixer truck fitted with a rotating drum, with internal mixing fins, to a jobsite where it is poured wet into forms. The mixer truck is one of the most recognizable vehicles on our highways. Generally, these trucks carry between 8 and 10 yd³ (6.1 to 7.6 m³) of concrete (up to 20 st). Most concrete is placed in this fashion. Specifications generally require the concrete to be placed within 90 minutes of batching because hydration is progressing. For large jobs, the mixing plant may be located on the jobsite with the plant batching directly in to open trucks that deliver the concrete to the job quickly.

Precast/Prestressed Concrete

Precast concrete is batched and placed into forms in a precast yard making certain structural components, which are better controlled and more economically manufactured at a centralized plant. Examples of precast concrete are pipe, septic tanks, utility vaults, structural concrete beams, and so forth. Generally, precast concrete is structurally reinforced with rebar or post-tensioned or prestressed to impart better tensional or flexural strengths.

Concrete Masonry Units

Concrete masonry units, commonly referred to as block, are a drier concrete consisting of sand, fine coarse aggregate, and water, which are batched, mixed, and then consolidated in molds in block machines. (*Cinder block* is an older term commonly used by laypersons and reflects the fact that cinder was often the aggregate used in block manufacture.) The most standard size block is the 8-8-16 (referring to its dimension in inches) with hollow cores. The masonry units are palletized and delivered to the jobsite on flatbed trucks. They are mortared together in horizontal rows. Masonry units can build structures ranging from ordinary privacy fences separating residential lots to high-rise structural buildings. For structural applications, the hollow cores are then reinforced with rebar and grouted solid with a fine-aggregate concrete mix.

Because masonry units require skilled hand labor for placement, their weight becomes important. A mason can lay more 25-lb (11.3-kg) block in a day than 35-lb (15.9-kg) block. The lightness of the block is therefore a consideration, and often block are manufactured using either natural or manufactured lightweight aggregate. Lightweight aggregates are covered as a separate chapter in this volume.

Mortars, Plasters, and Stucco

Mortars, plasters, and stucco are similar in that they comprise cement and sand mixtures. In addition, they may contain lime,

Table 4. General specification for fine aggregates (natural sand, manufactured sand, or a combination thereof) for use in concrete

Grading	
Sieve Size	Percent Passing
3/8 in. (9.5 mm)	100
0.187 in. (4.75 mm; No. 4)	95–100
0.0937 in. (2.36 mm; No. 8)	80–100
0.0469 in. (1.18 mm; No. 16)	50–85
600 µm (No. 30)	25–60
300 µm (No. 50)	5–30
150 µm (No. 100)	0–10
Limits for Deleterious Substances	
Item	Percent of Total Sample, Maximum
Clay lumps and friable particles	3
Material finer than 75-µm (No. 200) sieve:	
Concrete subject to abrasion	3
All other concrete	5

Adapted from ASTM C33-03.

NOTES:

- The fine aggregate shall have not more than 45% passing any sieve and retained on the next consecutive sieve of those shown in the above table, and its fineness modulus shall not be <2.3 nor >3.1. (Fineness modulus is a factor obtained by adding the total percentages, cumulative, of an aggregate sample retained on each of a specified series of sieves and dividing the sum by 100. The sieves are No. 100, No. 50, No. 30, No. 16, No. 8, No. 4, and 3/8 in. (0.95 mm).
- In the case of manufactured sand, if the material finer than No. 200 sieve consists of the dust of fracture, essentially free of clay or shale, the limits on material finer than No. 200 are permitted to be increased to 5%, for concrete subject to abrasion, and 7% for all other concrete.
- Fine aggregate shall be free of injurious amounts of organic impurities.
- Fine aggregate for use in concrete that will be subject to wetting, extended exposure to humid atmosphere, or contact with moist ground shall not contain any materials that are deleteriously reactive with the alkalis in the cement in an amount sufficient to cause excessive expansion of mortar or concrete, except that if such materials are present in injurious amounts, use of the fine aggregate is permitted with a cement containing less than 0.60% alkalis, or with the addition of a material that has been shown to prevent harmful expansion resulting from the alkali-aggregate reaction.
- Fine aggregates subjected to five cycles of the soundness test (ASTM C88-05) shall have a weighted average loss not greater than 10% when sodium sulfate is used or 15% when magnesium sulfate is used.

which enhances workability. Since they are used in smaller amounts, mortars are usually packaged in bags for easier handling. Mortar is placed by trowel and used to cement block or natural stone together. Plaster and stucco is hand or pneumatically placed onto surfaces for final finishes or to make distinctive textures.

Shotcrete/Gunite

Shotcrete and gunite are specialty concrete products that are pneumatically applied to a surface in contrast to normal concrete, which is placed in forms. Shotcrete, a wet, premixed concrete, is pumped to a nozzle and sprayed. *Gunite* is a trade name for a dry-gunned concrete where the water is added at the nozzle. Common applications are concrete liners in mines and tunnels, slope stabilization structures, swimming pools, and like applications.

Asphalt Concrete Applications

AC, also referred to as hot-mix asphalt (HMA) and most often as just asphalt, is the most common road pavement in the country. It is a flexible pavement compared to the rigid structure of a PCC pavement. Unlike PCC, AC is used only in pavements on grade (i.e., highways, airports, secondary roads, driveways, parking lots, pond

Table 5. General specification for coarse aggregates (gravel, crushed gravel, crushed stone, air-cooled blast furnace slag, crushed hydraulic-cement concrete, or a combination thereof) for use in concrete

Sieve Size	Grading		
	Percent Passing (most commonly used gradations)		
	1 1/2 in. to 3/4 in. (37.5 to 19.0 mm)	1 in. to No. 4 (25.0 to 4.75 mm)	3/4 in. to No. 4 (19.0 to 4.75 mm)
2 in. (50.0 mm)	100		
1 1/2 in. (37.5 mm)	90–100	100	
1 in. (25.0 mm)	20–55	95–100	100
3/4 in. (19.0 mm)	0–15		90–100
1/2 in. (12.5 mm)		25–60	
3/8 in. (9.5 mm)	0–5		20–55
0.187 in. (4.75 mm; No. 4)		0–10	0–10
0.0937 in. (2.36 mm; No. 8)		0–5	0–5
Limits for Deleterious Substances			
Item	Maximum Allowable for the Following Weathering Regions, %		
	Severe	Moderate	Negligible
Clay lumps and friable particles	3.0	5.0	5.0
Chert	5.0	5.0	
Sum of clay lumps, friable particles, and chert	5.0	7.0	
Material finer than 75- μ m (No. 200) sieve	1.0	1.0	1.0
Coal and lignite	0.5	0.5	0.5
Abrasion (ASTM C131-03)	50	50	50
Magnesium sulfate soundness (ASTM C88-05) or when sodium sulfate is used	18 (12)	18 (12)	

Adapted from ASTM C33-03.

NOTES:

- For the sake of brevity, the deleterious substance limit presented here is for concrete exposed to the weather and subject to frequent wetting such as pavements, bridge decks, driveways and curbs, walks, patios, exposed floors and porches, or waterfront structures. Severe weathering refers to a cold climate where concrete is exposed to deicing chemicals or where concrete may become saturated prior to freezing. Negligible refers to a climate where concrete is rarely exposed to freezing in the presence of moisture.
- Coarse aggregate for use in concrete that will be subject to wetting, extended exposure to humid atmosphere, or contact with moist ground shall not contain any materials that are deleteriously reactive with the alkalis in the cement in an amount sufficient to cause excessive expansion of mortar or concrete, except that if such materials are present in injurious amounts, use of the coarse aggregate is permitted with a cement containing less than 0.60% alkalis, or with the addition of a material that has been shown to prevent harmful expansion resulting from the alkali-aggregate reaction.

* Blanks in this table indicate no specification given for this size range.

liners, paths, floors, etc.). AC pavement is generally less expensive than PCC pavement and provides a smoother, quieter ride. (PCC pavements have a hard, rough surface and closely spaced joints.) AC pavements are sometimes referred to as blacktop, as opposed to the light-colored surface of a PCC pavement.

Aggregate makes up between 75% and 85% of HMA by volume, or 90% to 95% by weight. The glue that holds the aggregate together in HMA is asphalt cement, often referred to as *bitumen* or *oil binder*. This “black sticky stuff” comes from oil refining and is the bottom oil left after the lighter oils are cracked or separated out for use as gasoline and other grades of fuels. AC and aggregate are heated together and mixed in what are referred to as HMA plants, which have large burners as components. AC comes out of the plant hot and, for most applications, must be placed hot to obtain the required compaction, strength, stability, and durability. These properties are also dependent on an optimal oil content that is generally dictated by the gradation, absorption, and particle shape of the aggregate. Most asphalt mixes have oil contents between 3.0% and 7.0%. HMA is placed by paving machines in thin lifts and compacted using a heavy roller to achieve the desired end product. Some mixes are described based on their gradation and their utilization for different applications and are referred to by names such as open-graded, dense-graded, and so forth.

Aggregate properties important to HMA are hardness, durability, soundness, absorption, surface texture, particle shape, clean-

liness, size and grading, and affinity for asphalt (stripping). *The Asphalt Handbook* (Asphalt Institute 2004) contains an excellent discussion on the effect of aggregate properties on asphalt. Of special significance is the difference between concrete and asphalt aggregates is that in asphalt, because it is a flexural pavement, the aggregates must be crushed. Crushing produces angular particles with a rough surface texture that better holds the oil and that allows the particles to interlock with one another, giving the pavement better flexural strength and stability. In addition, absorption characteristics of an aggregate are critical. The higher the absorption, the more oil binder required to make a suitable mix, which adds costs because it increases oil demand.

Other asphalt mixes are thin seals or topcoats of asphalt or emulsion mixed with chips or sand to improve and extend the life of existing road surfaces and to mitigate raveling or surface deterioration of existing pavements.

State departments of transportation generally produce specifications for AC aggregates. Table 6 is a typical asphalt aggregate specification.

Aggregate Base Applications

AB is a crushed and screened end product meeting certain gradation requirements. It is not mixed with a binding agent but rather consists entirely of raw processed aggregate. AB is used under asphalt and concrete pavements and other structures for support and drainage.

Table 6. Typical specification for asphalt concrete aggregate*†‡

Sieve Size	Grading Requirements (Percent Passing)			
	3/8 in. (0.95 mm)	1/2 in. (1.3 mm)	3/4 in. (1.9 mm)	1 in. (2.5 mm)
1.5 in. (38.1 mm)				100
1.0 in. (25.4 mm)			100	90–100
0.75 in. (19.05 mm)		100	90–100	90 maximum
0.50 in. (12.7 mm)	100	90–100	90 maximum	
0.375 in. (9.525 mm)	90–100	90 maximum		
0.187 in. (4.75 mm; No. 4)	90 maximum			
0.0937 in. (2.36 mm; No. 8)	32–67	28–58	23–49	19–45
75 µm (No. 200)	2.0–7.0	2.0–7.0	2.0–7.0	1.0–7.0

Source: Washington Department of Transportation 2004.

* Aggregates for hot mix asphalt shall be manufactured from ledge rock, talus, or gravel.

† Los Angeles Abrasion; 500 revolutions; 30% maximum loss; degradation factor, wearing course, 30 minimum; sand equivalent 45 minimum.

‡ Blanks in this table indicate no specification given for this size range.

NOTES: Specifications for aggregates used in asphalt concrete vary from state to state. Other requirements may also include limits on the following based on anticipated weather conditions and traffic loads, end-product application, material type, and availability of suitable material to make aggregate (taken from typical Nevada and California specifications):

Fractured faces, 25% to 90% minimum

Los Angeles Abrasion, 35% to 50% maximum

Plasticity index, nonplastic to 10 maximum, depending on fines content

Soundness of fine and coarse aggregate, 10% to 18% maximum

Absorption, 4% to 6% maximum

Other requirements may include limits on stripping, durability, specific gravity, organic impurities and liquid limit.

Table 7. Typical specification for aggregate base*†

Sieve Size	Weight Percent Passing			
	Washington (Crushed Surfacing)	California (Class 2)	Arkansas (Class 7)	Nevada (Type 1, Class A)
2 in. (50.0 mm)		100		
1 1/2 in. (37.5 mm)	100	90–100	100	100
1 in. (25.0 mm)	80–100			80–100
3/4 in. (19.0 mm)		50–85	50–90	
5/8 in. (15.8 mm)	50–80			
0.187 in. (4.75 mm; No. 4)	25–45	25–45	25–55	30–65
0.0394 in. (1.18 mm; No. 16)				15–40
600 µm (No. 30)		10–25		
425 µm (No. 40)	3–18		10–30	
75 µm (No. 200)	7.5 max†	2–9	3–10	2–12
% fracture	75 min§		90 min	35 min
Sand equivalent	40 min	25 min		
Degradation factor	15 min			
Durability index		35 min		
R-value		78 min		70 min
Plasticity index			6 max	3–15 max
Los Angeles Abrasion	35 max		45 max	45 max

* Aggregate base shall be manufactured from ledge rock, talus, or gravel and be free from organic matter and other deleterious substances and shall be of such nature that it can be compacted readily under watering and rolling to form a firm, stable base.

† Blanks in this table indicate no specification given for this size range.

‡ max = maximum.

§ min = minimum.

AB, and sometimes coarser material, is used on soft, wet, or clayey soils for stabilization and to provide a hard usable surface or for a base for other structures. It is usually a 1-in. or 1 1/2-in. minus crushed product. Crushing produces characteristic interlocking particles that add stability and resistance to deformation. Table 7 provides typical specification for AB. The table highlights the great

ranges in gradation and qualifying test methods between various states and is a compilation of typical AB specifications from four specific states. It should be noted that most state highway departments design aggregate base specifications to fit available materials in their respective states for their particular climatic and physical conditions. These specifications show the great ranges in gradation

and qualifying test methods among various states. For more complete explanations of test methods and for other maximum sizes or classes of aggregate bases, the individual state departments of transportation have jurisdiction.

Other Products

Filter/Drain Rock

Filter rock and drain rock are generally free-draining coarse-particle combinations containing little or no fine material that would inhibit free flow of liquids. They are usually 1½ in. (38 mm) maximum for such applications as septic system leach fields or drainage control around foundations. Sand filters are common in wastewater plants.

Riprap/Armor

Riprap is coarse angular cobbles or boulders used as a slope stabilizer to prevent erosion and for slope stabilization. The large particles are generally a quarried product captured at the gizzly before entering the crusher. The angularity helps the interlocking of particles, adding to the intercollective stability. Boulders are sometimes used along coastal area jetties and as armor to combat wave action.

Decorative Rock

Decorative rock can be either sand or gravel or a crushed, quarried rock. It is used as ground cover and for decorative and architectural applications. Usually, it is coarse aggregate particles measuring from less than an inch to many inches across. Decorative boulders used in landscaping often weigh several tons and demand premium prices.

Deicing Sand

Deicing sand, or antiskid material, is unique to those more-northern or higher-elevation environments where winter snow and freezing temperatures create ice and related safety concerns on pavements and roads. The sand, sometimes mixed with salt or other chemicals to help melt ice, is mechanically spread during or after storms to increase traction. Often this sand is limited in the amount of very fine particles allowed, thereby mitigating later fugitive dust emissions when the pavement dries.

Miscellaneous Minor Products

Minor products sometimes produced by construction aggregate operations are pea gravel, golf course sand, septic system sand, ball-field sand, roofing and flooring materials, and many others.

MARKETING AND DISTRIBUTION

General Marketing Considerations

Aggregates are generally marketed to those who use them in the end product, the concrete and asphalt producers. Often these end-product producers are also the same companies who mine the aggregate, a common occurrence referred to as vertical integration. Little aggregate is marketed directly to individuals.

AB is an exception, because it can be marketed to anyone doing construction work, from large construction companies involved in multimillion-dollar projects to homeowners improving a driveway.

Aggregates are a component of all construction products and the major component of some such as highways. Concrete and asphalt suppliers are often subcontractors and must market their products to prime contractors, often through a bidding process. These suppliers, if they do not have their own aggregate source, generally go for the cheapest aggregate price available in the area. Often the decision on which aggregate to use, assuming it meets all applicable specifications, depends on the transportation costs of obtaining that aggregate.

Aggregates are a low-cost, high-volume commodity and therefore very sensitive to transportation costs. For economic reasons, construction aggregates are generally crushed and processed at the mine site. The price of a construction aggregate at the mine site, without transportation, is referred to as the f.o.b. cost. Waste material such as fines, generated as part of the mining process or the result of processing the material into the finished product, costs money to transport. It is more economical to leave the waste on site and transport only the finished product. The ultimate sale price of aggregate products reflects the transportation costs. A 30-mi (48-km) haul can often double the price of an aggregate product's f.o.b. cost. Location of the aggregate source is therefore very important in ensuring a reasonable price for the material. The cheaper the transportation, the cheaper the end-product concrete and asphalt as well. The trend is for aggregate deposits to move farther from the urban centers where those products are most in demand. This is the major factor in the rising cost of aggregate materials.

There are several scenarios on what happens to the finished product once in the stockpile at the mine site. In many cases, concrete and asphalt plants are also at the same location as the mine and processing plant. The aggregate in these instances goes directly from the stockpiles into the concrete or asphalt batch plants. The fresh asphalt or concrete is then hauled to the local, nearby market. It is important to have the batch plants close to the market for several reasons. First, aggregate can be hauled in larger containers than the end-product concrete or asphalt. The finished products must be delivered in manageable sizes so they can be properly placed. The end products are more valuable than the aggregate on a unit basis. The time involved in delivering the finished product (concrete or asphalt) must be considered. When batched, concrete has a limited time before it begins to hydrate and set. Asphalt must maintain a certain temperature for proper placement. If necessary, the aggregate can be hauled hundreds of miles, but not the batched end product.

When there are no local sources, the aggregate has to be brought in from remote locations. It has to be hauled to the concrete and asphalt plants that are located near the urban market. In these instances, the aggregate can be hauled by truck, rail, barge, or ship, depending on economics.

AB is another matter, however, and because it is an end product in itself and is not time-placement sensitive, it can be used directly from the stockpiles at the mine or processing site and hauled long distances before placement.

Transportation

The United States has an extensive network of federal, state, and local highways and roads, an extensive railroad grid, and both inland and coastal waterways. The choice between these three transport methods involves tradeoffs between capital investment and operating expense, extensive roadway systems versus more limited rail and water transport, and high-volume versus limited tonnage shipments. Aggregate inventory stored in stockpiles becomes expensive, and the amount of land available for that storage may be limited. Conversely, when a customer wants an aggregate product, it usually requires timely delivery.

The basic modes of transporting aggregate are described in the following subsections.

Truck

Hauling aggregate by truck is usually the preferred, most flexible, and only method in most locations where the aggregate deposits are within 30 to 50 mi (48 to 80 km) of the market. The advantage of using trucks is that they can go almost anywhere where there is a

road. The disadvantage of truck transport is the cost over longer distances. Obviously, the haul costs per ton go down as the volume of material in a given load goes up. Most truck haulage is by tractor-trailer rig ("eighteen-wheelers"). Most states regulate the trucking industry to a large extent, limiting the allowable loads for a given size and weight vehicle or number of axles. In most states, this limits the trucks to a maximum of 20 to 25 st per load which is, generally, a single or double trailer. In some of the less populous states triple trailers are allowed; these can haul approximately 38 to 40 st per load.

During 2003, approximately 78% of aggregate produced was transported by truck (Bolen 2003; Tepordei 2003). Trucks can usually easily access the finished product within aggregate operations and be loaded using various techniques. They can then deliver their payload via existing roads and can empty their loads relatively easily without specialized equipment. Trucking usually can adjust the timing of delivery to meet customers' needs. Trucking generally requires less initial capital outlay than fixed systems but commonly incurs higher operating costs.

Freight rates for trucks are variable depending on the location, the time it takes to deliver the product, and the size of the truck. In rural areas, and on freeways where a higher speed can be maintained, freight rates can range between \$0.08 and \$0.15 per short ton-mile. In urban areas where traffic is slow and congested, it can be as high as \$0.20 per short ton-mile. Price often reflects the cost of living in certain metropolitan areas.

Rail

Rail transport is important in some of the more urbanized areas of the country where the distances from the aggregate source to the metropolitan areas are more than approximately 50 mi (80 km). Individual rail cars haul approximately 100 to 112 st. Unit trains consisting of 50 to 100 cars can deliver up to 10,000 st of aggregate at one time. Rail rates are less costly than truck rates over long distances; there are, however, disadvantages as well.

The United States has about 149,000 mi (240,000 km) of main-line railroad routes, and during 2003, approximately 2.6% of aggregate production was transported by rail (Bolen 2003; Tepordei 2003). This is a fixed-route system that required considerable capital investment. Rail transport is economical when moving large volumes of aggregate distances not economical for trucks. In rail transport, however, there must be access to the plant, a means to load and unload the rail cars at their destination, and, if the aggregate is not used at their destination, a means for further distribution. Rail access to an aggregate operation potentially expands that aggregate's market area. The distribution of rail lines, however, is far more limited than roads. Railroad schedules and extraneous conditions such as elevation climb, scheduling, and track usage volume also help determine whether rail is the preferred transport method or not.

Rail rates can range between \$0.02 to more than \$0.05 per short ton-mile, depending on the above-outlined conditions and circumstances.

Water

The United States has about 41,000 km of navigable inland channels, exclusive of the Great Lakes. In 2003, about 4.0% of aggregate production was transported by barge (Bolen 2003; Tepordei 2003). Like railroads, this is also a fixed-route system that requires a substantial capital investment in ships or barges and also requires loading and off-loading facilities and equipment. Water transport can be the most economical way to ship aggregate on a per-tonnage basis if the market demands the material and if other sources and methods of transport are not available.

Barges are used for long-distance haulage, i.e., distances generally greater than 100 mi (160 km). Barges and ships are used along both coasts, in the Great Lakes, and along interior navigable waterways such as the Ohio and Mississippi rivers and their tributaries. Inland barges ply the interior rivers of the country and carry aggregate from sources located along rivers in rural areas and to urban areas also located along the rivers. These barges commonly hold 1,500 st and can be grouped into tows of 30 to 40 barges, depending on the width and depth of the waterway and the size of the towboat. Larger oceangoing barges can haul along the coasts. The disadvantages of using barges are that they are limited to navigable waterways and loading and unloading is much more time-consuming than with trucking.

Ship transport is primarily along the East and West coasts, where transporting material hundreds of miles is the norm, primarily from sources outside the United States. On the West Coast, aggregate is shipped in from British Columbia. These ships are 60,000- to 70,000-st self-unloading ships and are relatively new to hauling aggregates. They have a series of bins and belts that can readily unload their aggregate cargo without using shore-based equipment. On the East Coast, aggregate comes in on similar ships from Nova Scotia, and in the Gulf of Mexico region they come from the Yucatan Peninsula. These self-unloading ships are approximately half the price of a barge on a per-short-ton-mile basis.

Imports

The imports briefly mentioned under ship transport are driven by economics, the cheapest aggregate based on the cheapest transportation. For instance, aggregate coming into the San Francisco area from British Columbia travels approximately 1,000 mi (1,609 km) in 70,000-st ships. This material is more economical to use than California aggregate mined in the Sacramento area, which is less than 100 mi (160 km) away. The Seattle, San Francisco Bay, and Los Angeles areas along the West Coast are seeing increased imports from British Columbia and Mexico as locally permitted aggregate resources are exhausted and not replaced. At one time, aggregate came from Scotland by ship to select East and Gulf Coast cities; this has been supplanted by exports from both Nova Scotia and Yucatan.

GOVERNMENT, ENVIRONMENTAL, AND HEALTH CONSIDERATIONS

Mining, including aggregates, is facing many challenges. Issues involving the finished product are noise and dust from trucks and plants, crystalline silica in the aggregate, truck traffic leading to increased congestion and safety issues, and others. Permitting of plants and industrial zoning are as contentious as permitting a new mining operation. Reclamation plans may be applicable to the PCC and AC plants that are part of the mining operation.

The aggregate industry is a highly regulated industry. At the mine, health and safety is regulated by the Federal Mine Safety and Health Act of 1977 and policed by the Mine Safety and Health Administration (MSHA). Section 30 of the Code of Federal Regulations (30 CFR) contains the rules under which the mine operates. At the batch plant, the industry is regulated by the Occupational Safety and Health Administration (OSHA).

A more in-depth discussion of government, environmental, and health considerations for aggregate mining operations under the Construction Sand and Gravel and Crushed Stone chapters in this volume.

INDUSTRY TRENDS AND OPPORTUNITIES

Aggregate resources in the United States are inexhaustible from a purely geological standpoint, and despite environmental, zoning,

and regulatory restrictions no shortages on a large scale are expected in the future. Certain markets will have to import materials, however, and others will find many limitations on mining. The National Stone, Sand & Gravel Association (NSSGA), in their announcement for issues to be discussed at their 2004 Annual Convention (NSSGA 2004), indicated that the state of the American aggregate industry at the dawn of the 21st century is faced with the following challenges:

- Complying with the ever-changing rules and regulations of 10 federal agencies and their state counterparts, plus dealing with local governments and their zoning and permitting processes
- Battling antigrowth, anticonstruction factions who enjoy the benefits of aggregates but do not approve of the process necessary to derive them
- Striving to ramp up efforts so that workers have safe and healthful environments in which to do their jobs
- Training the workforce to operate safely and productively
- Facing how the federal and state governments will continue to fund transportation infrastructure projects so critical to commerce, jobs, and everyday life in our country
- Succeeding in business during a time of national economic volatility

As land-use conflicts, NIMBY attitudes, and environmental pressures increase (resulting in the constantly changing regulatory climate), the ability to mine aggregate is becoming more difficult in the United States, and in most of the developed world as well. Competition fuels technological advancements, managerial evolution, and other economical changes to improve productivity. Government and job requirements demand better quality. Local and regional government entities are recognizing the need for available construction aggregate. Combined, these pressures have and are changing the industry. Some of these changes and adjustments are as follows:

- *Crushed-rock sources predominate.* Crushed rock has become the primary source for aggregate since the early 1970s because sand and gravel is generally found in terrain more suitable for other uses (e.g., flat lands for development, scenic river corridors, wildlife habitat protection).
- *Industry is consolidating.* The aggregate industry continues to consolidate. The small operators are being acquired by the larger operators.
- *Operations are farther removed from their markets.* Aggregate deposits move farther from their markets, necessitating transportation cost increases. Existing aggregate resources in urban areas are closing as permitted reserves are depleted and new resources in urban areas are difficult, if not impossible, to zone properly and permit. Robinson (2004), in a recent article on the availability of aggregate, points out that the number of aggregate operations declined since 1975, implying that transportation distances therefore increased.

Those aggregate operations moving farther from their markets also have the following characteristics:

- They are large operations, sometimes referred to as mega-quarries (10 Mstpy). These large operations economize in scale. By increasing production, they serve a larger market, resulting in fewer quarries.
- They are located along major transportation arteries, whether that is freeway, rail, or waterway.
- They limit their visibility. New quarries want to be out of sight as much as possible to limit visual impact to a generally uninformed and unsympathetic public.

- These outlying pits and quarries often have sales yards closer to the market where the aggregate is off-loaded and redistributed as either raw material or final product.
- *Imports are expanding.* Imports from off-shore deposits are likely to continue to expand as land-use conflicts along the coasts intensify. Water transport allows large tonnages to be shipped long distances. It should be realized, however, that land use, social, and environmental issues are not isolated to the United States. Recent environmental and social issues in Mexico curtailed sand imports into the San Diego area, and recent newspaper articles have highlighted some of the negative aspects of coastal aggregate mining in British Columbia that exports material to the United States.
- *Underground operations are more common.* Underground operations in urban areas are becoming more common, especially in the central and eastern portion of the country where there is an abundance of limestone. The USGS reported 83 underground mines in 17 states in 2002, producing 60 Mtpy (Tepordei 2002). The advantages of going underground are becoming more apparent to producers. Problems that are usually ubiquitous to surface mining such as environmental impacts and community negativity are significantly reduced by going underground.
- *Public awareness and outreach are important.* The industry is becoming more aware of the need for public outreach and of informing the general public about what aggregates are and how important they are in the local community. The distinction between operation of a quarry and operation of a ready mix or asphalt plant sometimes does not matter, because often the plants are in the aggregate pits that furnish the raw material. Unlike most mined commodities, aggregate operations tend to be closer to the urban environment and much more visible than most other commodities mined. The denser the population, the more aggregate pits and related plants necessary to provide materials for a growing lifestyle.
- *Specifications are tightening.* Specifications continue to be tightened in the quest for better roads and more durable concrete and asphalt products. Changing technologies are leading to new types of concrete such as roller-compacted concrete (RCC) and "Superpave" designs for asphalt concrete. Most specification trends tend to be for better gradation control and fewer fines.
- *Plant designs are improving.* Production plants are improving by using more efficient equipment, instrumentation, and computerization to better control production and increase automation. Producers are going to larger plants for economy of size. Information technology will lead to remote monitoring and better asset management systems. Additional emphasis is on preventive maintenance, better equipment utilization, and the use of the Internet for sales and purchases.
- *Mining equipment is changing.* Mining equipment is getting larger for economy of size. The mobile equipment trend is toward satellite global positioning systems (GPS) in real time, which would include optimizing production by using earth-moving system capabilities to replace conventional surveying.
- *Mining is changing.* Using 10–20% of the mined material in some aspect of the product is becoming more important for better profits. An increased effort to ward mine design and planning will add to future efficiency, increased reserves, and longer mine life. Improved blasting techniques will increase productivity.

- *Research is ongoing.* Research has intensified how aggregates influence the end products. Using fines, usually considered a waste product, has become a goal.
- *Local, state, and federal governing bodies must be involved in resource identification and zoning.* An other goal is getting local, state, and federal agencies to recognize the necessity of construction aggregate resource availability into the future and, therefore, to recognize the need for setting aside potential resource areas or zoning that recognizes aggregate extraction as an acceptable use. Requiring covenants with future developers in these areas that include recognizing the necessity for and acceptance of future resource development in these zones is important.

California was in the forefront of recognizing the need to plan for future aggregate resource availability. It is the nation's leading producer and consumer of construction aggregates. The California Surface Mining and Reclamation Act of 1975 required the state to classify land based on its known or inferred mineral resource potential. The primary goal of the land classification was to ensure that the mineral resource potential of land is recognized and considered in the land-use planning process. This land classification has been going on for nearly three decades, with more than 30 individual reports throughout the state, usually in urban areas. The result has been positive in many respects but has not led to adequate resources for the future. The California Geological Survey (Kohler 2002) recently published a map and report on the availability of aggregate in California. The main focus was a comparison of projected aggregate demand for the next 50 years with currently permitted aggregate resources. The results of the study indicated that, of an identified 34 aggregate consumption areas in 2001:

- Seven areas have less than 10 years of permitted resources remaining.
- Five areas have less than 25% of permitted resources to meet the 50-year demand.
- Seven areas have 25% to 50% of permitted resources to meet the 50-year demand.

This information was prepared to assist land-use planners and future decision makers.

- *Concrete industry trends are vital.* The ready mix concrete industry is dependent on aggregates because they make up to 85% of the concrete mix. Trends in the concrete industry include higher strengths, different admixtures addressing end properties, and increased automation and computing. Trucks will be GPS guided with more sophisticated computer control and monitored loading to increase quality control. RCC technology changes are leading to more applications.
- *Asphalt industry trends are important.* The asphalt industry is slowly changing to emphasize *Perpetual Pavement*, or longer lasting, more durable pavements. Recent research, referred to as *Superpave* design, is modifying aggregate specifications, mainly gradation and lower fines content, to improve the life of pavements.
- *Creative mining techniques are available.* Creative mining techniques can allow mining where otherwise it would not have been permitted. Such techniques include the following:
 - Going underground, as previously discussed, where there is less surface disturbance, visibility, and dust. In some cases, permitting is easier, especially if the end product is to be warehouse space and mining is essentially a waste product of building that space.

- Reclamation enhancements with variable slopes with more natural slope breaks and more natural looking obstructions.
- Using the site for something beneficial at the end of the mine life (i.e., parks, lakes with surrounding residential development, stormwater basins, golf courses, or industrial sites). Never leave a big hole.
- Permitting as part of a development. Partnering with a government or private developer to improve the site for construction.
- *Recycling will increase.* Recycling will continue to increase, not only because of environmental pressures but also because of economic stimulation. In urban areas it makes economic sense to recycle rather than landfill inert construction waste. Recycled, or by-product glass, can be used locally rather than shipping it to a distant glass manufacturer at a high transportation cost. Glass cullet, where available, and other recognized industrial wastes can go into AB without negatively affecting performance (McCoy and Kerwit 1999). Also, shingles and scrap tires can be used as lightweight fill in roads or in hot mixed AC in residential paving.
- *Sustainability must be clearly defined.* Sustainable development is a recent and evolving concept encompassing how society might look at the future, guaranteeing a healthy economy yet preserving quality of life, respecting the ecosystem, and recognizing the Earth's environmental limits. Its main premise is that today's actions, although providing for our own future, must not diminish the assets, resources, and capabilities available to our descendants. With reference to aggregates, and other types of mining for that matter, defining sustainability is elusive. Surely recycling and mine reclamation are a part of sustainability, but the development of new resources bends the paradigm. Certainly there would be a threat to the economy if mining were to cease, yet some say there is a threat to the environment if it does not cease. Continued and new resources will be needed if our standard of living is to remain high and continue to improve. Because sustainability implies preserving our way of life and the environment, true sustainability could mean that aggregate (recognized as always being a high-volume commodity necessary for daily life) should continue to be developed as close as possible to its end use to mitigate unnecessary fuel consumption, traffic, and highway wear and tear. It also means we should strive to use higher-quality aggregates that will impart longer life to the end products, concrete and asphalt, so their most-efficient-use life can be realized. The country's infrastructure is aging, and there is a question of whether it is being replaced at a satisfactory pace. Infrastructure includes roads, bridges, airports, seaports, waste-disposal facilities, water systems, and so forth. A tremendous amount of aggregate will have to be mined to rebuild these facilities.
- Recycling and the identification of other potential waste products that could be substituted for natural mined aggregates should be considered. Essentially the bottom line is that aggregates and other mined materials will continue to be a necessary part of life on Earth. Sustainability will evolve to recognize this fact and the industry will evolve to mitigate adverse impacts by creative mining techniques, recycling, and substitution of possible other waste products for aggregate usage.
- *Health and safety issues are important.* Crystal line silica is probably the most important health and safety issue that the

aggregate industry will face in the near future. Crystalline silica has been demonstrated to be a carcinogen, yet silica is ubiquitous in the aggregate industry. The effect of future regulations is unknown.

- *The future of aggregate worldwide is strong.* Worldwide demand for construction aggregates is projected to rise nearly 5% annually through 2007 to near 22 billion t, valued at \$128 billion. China, which is already the largest national market, will record some of the strongest increases, with its rising demand for aggregates reaching 6 billion t in 2007, accounting for nearly one quarter the global total.

ADDITIONAL SOURCES OF INFORMATION

Extensive references exist regarding natural aggregate. *The Aggregate Handbook*, published by the National Stone Association (Barksdale 1991), is a comprehensive discussion of the aggregate industry and is generally considered to be the most complete guide available. The NSGA, which resulted from the merger of the National Aggregates Association and the National Stone Association in 2001, is the principal nationwide trade organization representing the construction aggregate industry in the United States. The association's roughly 900 members represent approximately 80% of the sand and gravel and crushed stone producers in the country. The association conducts workshops, training courses, seminars, and meetings for its members on the entire spectrum of the construction aggregate business.

The USGS compiles and annually publishes comprehensive data on production and consumption of construction aggregate in the United States. They differentiate between sand and gravel and crushed stone. USGS annual publications include *Mineral Industry Surveys*, *Commodity Summaries*, and the *Minerals Yearbooks*. USGS also created the National Atlas of the United States, which shows, under minerals, the locations and certain information on construction aggregate producers in the country. USGS directories list crushed stone and sand and gravel producers and their rankings nationally. *Natural Aggregates of the Conterminous United States* (Langer 1988) discusses the geologic aspects of aggregate resources. The USGS *Minerals Yearbooks* contain comprehensive statistics about aggregate resource production.

Four comprehensive collections of individual papers offer case histories of global issues related to aggregate resources:

1. *Aggregate Resources—A Global Perspective* (Bobrowsky 1998)
2. *Aggregates—Raw Materials Giant* (Lüttig 1994)
3. *Proceedings from the International Symposium on Aggregates* (International Association of Engineering Geology 1984)
4. *Natural Resources in the Geological Environment* (Kelk 1992)

A study of reports in these volumes not only will provide an understanding of the many different environmental impacts related to aggregate mining, but, because of a nearly 15-year time span, will also give a historical perspective of the issues. *Aggregates* (Smith and Collis 1993, 2001) and the chapter on "Coarse Aggregate" in *Geology of Construction Materials* (Prentice 1990), and *Aggregates* (Primel and Tourenq 2000), describe the industry from the European viewpoint.

The geology of aggregates is also occasionally covered in a variety of journals, including the individual state geological surveys and other nationally recognized journals such as those put out by the Society for Mining, Metallurgy, and Exploration (SME), the Association of Engineering Geologists (AEG), and the Industrial

Minerals Forum (IMF). No journal is dedicated specifically to the geology of aggregates or construction materials.

Trade magazines concerned primarily with the aggregate industry are *Rock Products*; *Pit and Quarry*; *Stone*, *Sand*, and *Gravel Review*; and *Aggregate Manager*.

The International Center for Aggregates Research (ICAR), located at the University of Texas, is known for its research into the properties of aggregates, primarily as they relate to end products. ICAR publishes results of their many research programs.

Most of the more populous states have aggregate associations representing the business concerns of their aggregate industry. Sometimes these associations are also part of a wider group of business interests who use aggregate, such as the road builders and concrete producers.

Each state has a department of transportation that often conducts aggregate and end-product research with regard to specific issues in their individual states.

There are other organizations which publish research on aggregates but who are more focused on the end product such as PCC or A.C. The PCA, the ACI, and the National Ready Mixed Concrete Association stress PCC. The Asphalt Institute and the National Asphalt Pavement Association (NAPA) focus on AC. The ASTM covers many different construction materials, including aggregate.

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Cement and Cement Raw Materials

John D. Macfadyen

INTRODUCTION

This chapter uses the term *cement* in its historical meaning of gray and white portland cement, a crystalline compound of calcium silicates and other calcium compounds having hydraulic properties. Several other hydraulic cements of similar chemical form exist and are produced in similar manner, but they have limited and specialized markets. Much of this chapter applies to these cements as well, although they are not directly discussed. Portland cement is produced by intergrinding cement clinker and gypsum in an approximate ratio of 95:5. Cement clinker is a fused product consisting of principally dicalcium silicate, tricalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite formed by high-temperature reaction in a rotary kiln of carefully proportioned and blended ratios of lime, silica, alumina, and iron oxide. The lime fraction is derived from limestone in the calcining phase of production. White clinker is extremely low in iron oxide, which requires purer raw materials. Table 1 summarizes typical percentages of clinker compounds for the most common portland cement, Type I.

MARKET

A few large companies dominate the marketing and production of cement. Widely distributed plants minimize transportation costs to customers. Although the volume of cement to be sold in the marketplace can be considered inelastic in the short run, a company's sales effort makes a difference. In any given market, although cement sold by competitors must meet certain basic specifications to be considered, other factors dominate, including delivered cost, quality, prod-

uct consistency, technical assistance, and sales relationships with the user companies. Sales relationships ensure the cement company of consideration in the first place, they allow the settlement of questions surrounding the sale, and they offer the selling company a last "look" before sales commitments are made. Sales relationships are based on positive past relations, trust, and friendship.

In the long run, several factors drive the consumption of cement in the marketplace, including economic growth, private and governmental capital investment, and population growth. Influencing decision makers by promoting the architectural, economic, and durability advantages of concrete also drives the market, as does financial or other assistance to concrete suppliers.

Cement companies often evaluate sales success as their continued penetration of the local or regional market expressed as market share. Sometimes this devotion to market share evades the real corporate target of profitability.

In the 1960s the federal highway program was a chief reason for cement plant expansion, along with the nation's continued economic and population growth. At the same time, a new trend established distribution terminals to sell cement to greater geographical markets accessible via water transportation or favorable rail rates. This trend increased competition and held down profits. From 1957 to 1969 the inflation-adjusted price of cement declined significantly. In the 1970s, real prices began to increase but profits were diverted to meet new environmental requirements rather than creating greater efficiency and capital. With a surge in building in coastal markets in the late 1970s, imports began to be a factor. When cement companies did not make the investment to increase capacity or import cement to

Table 1. Probable clinker compounds in Type I portland cement

Compound	Abbreviation	Common Abbreviation	Oxide Composition	Stoichiometric Composition	Approximate Content in Type I Portland Cement, %
Tricalcium silicate (alite)	3CS	C ₃ S	(CaO) ₃ SiO ₂	Ca ₃ SiO ₅	45
Dicalcium silicate (belite)	2CS	C ₂ S	(CaO) ₂ SiO ₂	Ca ₂ SiO ₄	27
Tricalcium aluminate	3CA	C ₃ A	(CaO) ₃ Al ₂ O ₃	Ca ₃ Al ₂ O ₆	11
Tetracalcium-aluminoferrite†	4CAF	C ₄ AF	(CaO) ₄ (Al ₂ O ₃)(Fe ₂ O ₃)	Ca ₄ Al ₂ Fe ₂ O ₁₀	8

Adapted from Clausen 1960.

* Commercial cements contain 4%–6% gypsum or anhydrite (for regulation of the "setting time" of the concrete), approximately 0.5% each of alkali oxides (Na₂O and K₂O) and uncombined CaO, plus a few percent impurities, largely MgO.

† This composition of the iron-containing phase is an approximation and may range from (CaO)₂Fe₂O₃ to (CaO)₆(Al₂O₃)₂(Fe₂O₃).

meet construction needs, outside entrepreneurs did. These importers were not needed during the recession of the early 1980s, and when sales went down, prices often went down and several left the market. Soon local cement producers took over most of the import terminals owned by those “outsiders.” In the surge of the late 1980s and through today, most imported cement has been sold by the producing companies and basically used to meet peak demands of the market and allow U.S. producers to maintain higher utilization of production facilities even in low-demand times.

Imports of clinker and finished cement peaked at 29.351 Mt in 1999, and 24.756 Mt of that was finished cement. Although clinker imports dropped in 2001 as new capacity came on stream, finished cement imports remained between 24 and 25 Mt. The drop in clinker imports reflected new capacity of domestic U.S. cement producers. Countries with the greatest exports to the United States in the peak year of 1999 were Canada, Thailand, China, Greece, and Venezuela. In 1999, New Orleans was the largest port of entry for cement and clinker, followed by Houston and Detroit. The United States is not a significant exporter of cement. Over the next few years, as new capacity comes on stream aided by the higher cost of imported cement, imports are expected to be flat or drop slightly, but not because of the increased production capacity. This anomaly is due to the regional nature of the market, the high cost of truck and rail transportation, and imbalance between production capacity and demand in any given market. In 1997, with the Asian financial crisis, imports from Asian sources began to increase dramatically. In 2003, with Asian markets improving and ocean freight rates escalating rapidly, import sources to the U.S. market began to shift to South America and the Mediterranean region as ocean freight rates became a greater cost component. U.S.-levied “dumping duties” curtailed imports from Japan, Mexico, and Venezuela.

Within the United States, California, Texas, and Pennsylvania have the greatest cement grinding capacity, and Texas, California, and Florida are the top consuming states. Compound growth rates for cement consumption between 1971 and 2001 show Nevada to be the greatest growth state at 5.6% per year, followed by Utah at 3.6% and Arizona at 3.3%.

The ready-mixed concrete industry dominates U.S. cement consumption, accounting for nearly 75% of all cement consumed. Concrete products account for another 12% to 13%, followed by direct sales of 6% to 8% to contractors on major projects. Building materials firms, which are the key sellers of sack cement, account for another 3% to 4%. Sales to governments, mining companies, waste handlers, and oil-well cementers normally fall in a range of 1% to 2% of all cement consumed. Types I and II account for 88% to 90% of cement sold with a rising amount of Type V of 5% being sold in the last 3 years as Type V becomes required on many California projects. Blended cements run approximately 1% to 2% of sales in the United States. Table 2 lists the American Society for Testing and Materials (ASTM) and the American Association of State Highway and Transportation Officials (AASHTO) standards for the various types of cement.

Table 3 summarizes production, shipments, and imports from 1991 to 2003. The U.S. Geological Survey (USGS) maintains the monthly shipments and import statistics (arithmetic mean) of the industry and also publishes an annual review. Not all importers report their shipments to customers to the USGS; therefore, the USGS monthly production and shipments reports and the import statistics leave a gap of about 2%.

PRODUCTS AND STANDARDS

Table 2 lists the five types of portland cement and their standards for use in the United States. Although the principal standards are

the ASTM values, portland cement for highway construction is held to the AASHTO standards. Masonry cement and various market-driven specialized forms of masonry cement produced in certain markets are typically not held to any standard specifications. Pozzolanic cements and blended cements also must meet ASTM standards, as must blast furnace slag as a portland cement substitute. Blast furnace slag producers are able to demonstrate good 28-day strengths comparable to portland cement standards in addition to alkali reactivity benefits. Where consumers do not stipulate concrete strength requirements, ready-mix producers sometimes substitute fly ash for some of the portland cement.

RAW MATERIALS

Market competition, ongoing pressure on cement prices, and the resultant lower costs of production have changed the framework for locating new cement plants and the types of raw materials for producing cements at new and existing plants. Although the fundamental chemical constituents to produce portland cement have not changed, the choices of raw materials as sources of these chemical compounds have changed and are expected to continue changing. Abundant limestone and argillaceous reserves exist throughout most of North America and many parts of the world, but accessibility, quality, cost of extraction, and transportation increasingly affect cement production economics and therefore the ability to extract these minerals. The increasing demand by governments to recycle materials and the changed economic structure of recycling are having a major impact on the cement industry. Additionally, the effect of more stringent environmental regulations and market forces on quality of cement, and modern preheater and pre-calciner production processes, have forced changes in what raw materials are required for producing cement clinker and cement. The production of cement, however, is a chemical process requiring an accurate and consistent blend of the four key inorganic oxides and the limitation of several undesirable oxides and elements.

Minerals Required

The fundamental chemical compounds for producing cement clinker—lime (CaO), silica (SiO_2), alumina (Al_2O_3), and iron oxide (Fe_2O_3)—are now joined by the increasing need to reduce undesirable chemical compounds such as sodium oxide (Na_2O), potassium oxide (K_2O), sulfur, chlorine, carbon, and organics. Additionally, the increasing use of additives with cement clinker to produce different types of cement has affected the use of other materials such as fly ash, gypsum, synthetic gypsum, anhydrite, blast furnace and metallurgical slags, silica fume, limestone, volcanic ash, etc. Lime is not found in nature; it is created from calcium carbonate (CaCO_3) in the production process or obtained from recycled materials. The other key chemical compounds are found naturally and are also present in many recycled and waste materials. Table 4 summarizes the raw materials used in the production of cement clinker.

Calcium Carbonate Resources and Mining Practices

Limestone continues to be the principal source of CaCO_3 . A common mineral on the earth's surface, CaCO_3 is principally found in nature as sedimentary deposits of marine origin. It is also found as marble (a metamorphosed form of limestone), chalk, marl, coral, aragonite, oyster and clam shells, travertine, tuff, and some other forms. In the United States, environmental regulations have essentially eliminated the use of aragonite and oyster and clam shells, and travertine and tuff deposits are rare sources of CaCO_3 . Low-grade sources of CaCO_3 such as siliceous feldspars and argillaceous limestone, which are upgraded by flotation, are also rare and not processed by North American plants.

Table 2. Comparison of ASTM and AASHTO requirements*

Item	Type of Cement															
	Type I		Type IA		Type II		Type IIIA		Type III		Type IIIA		Type IV		Type V	
	ASTM	AASHTO	ASTM	AASHTO	ASTM	AASHTO	ASTM	AASHTO	ASTM	AASHTO	ASTM	AASHTO	ASTM	AASHTO	ASTM	AASHTO
Standard Chemical Requirements																
Silicon dioxide (SiO ₂), min %	—	—	—	—	20.0	20.0	—	—	—	—	—	—	—	—	—	—
Aluminum oxide (Al ₂ O ₃), max %	—	—	—	—	6.0	6.0	—	—	—	—	—	—	—	—	—	—
Ferric oxide (Fe ₂ O ₃), max %	—	—	—	—	6.0	6.0	—	—	—	—	—	—	6.5	6.5	—	—
Magnesium oxide (MgO), max %	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Sulfur trioxide (SO ₃), † when:																
3CaO•Al ₂ O ₃ † 8% or less, max %	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.5	3.5	3.5	3.5	2.3	2.3	2.3	2.3
3CaO•Al ₂ O ₃ 8% or more, max %	3.5	3.5	3.5	3.5	NA	NA	NA	NA	4.5	4.5	4.5	4.5	NA	NA	NA	NA
Loss on ignition, max %	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	2.5	2.5	3.0	3.0
Insoluble residue, max %	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75
Tricalcium silicate [3CaO•SiO ₂], max %	—	—	—	—	—	58	—	—	—	—	—	—	35	35	—	—
Dicalcium silicate [2CaO•SiO ₂], min %	—	—	—	—	—	—	—	—	—	—	—	—	40	40	—	—
Tricalcium aluminate [3CaO•Al ₂ O ₃], max %	—	—	—	—	8	8	8	8	15	15	15	15	7	7	5	5
Tetracalcium aluminoferrite + twice the tricalcium aluminate [4CaO•Al ₂ O ₃ •Fe ₂ O ₃] + 2[3CaO•Al ₂ O ₃] or solid solution [4CaO•Al ₂ O ₃ •Fe ₂ O ₃ + 2CaO Fe ₂ O ₃] applicable, max %	—	—	—	—	—	—	—	—	—	—	—	—	—	—	25§	25§
Optional Chemical Requirements (Note: These optional requirements apply only when specifically requested.)																
Tricalcium aluminate [3CaO•Al ₂ O ₃] for moderate sulfate resistance, max %	—	—	—	—	—	—	—	—	8	8	8	8	—	—	—	—
Tricalcium aluminate [3CaO•Al ₂ O ₃] for high sulfate resistance, max %	—	—	—	—	—	—	—	—	5	5	5	5	—	—	—	—
Sum of tricalcium silicate and tricalcium aluminate, max %	—	—	—	—	58	58	58	58	—	—	—	—	—	—	—	—
Alkalies†† (Na ₂ O + 0.658 K ₂ O), max %	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60
Standard Physical Requirements																
Air content of mortar, ‡ volume max %	12	12	22	22	12	12	22	22	12	12	22	22	12	12	12	12
Fineness, §§ specific surface, m ² /kg*** min %	—	—	16	16	—	—	16	16	—	—	16	16	—	—	—	—
Turbidimeter test:																
Average value, min	160	160	160	160	160	160	160	160	—	—	—	—	160	160	160	160
Min. value, any one sample	—	150	—	150	—	150	—	150	—	—	—	—	—	150	—	150
Average value, max	—	220	—	220	—	220	—	220	—	—	—	—	—	220	—	220
Max. value, any one sample	—	230	—	230	—	230	—	230	—	—	—	—	—	230	—	230
Air permeability test:																
Average value, min	280	280	280	280	280	280	280	280	—	—	—	—	280	280	280	280
Min. value, any one sample	—	260	—	260	—	260	—	260	—	—	—	—	—	260	—	260
Average value, max	—	400	—	400	—	400	—	400	—	—	—	—	—	400	—	400
Max. value, any one sample	—	420	—	420	—	420	—	420	—	—	—	—	—	420	—	420
Soundness, autoclave expansion, max %	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Time of setting, ††† alternate methods																
Gillmore test:																
Initial set, minutes, not less than	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60	60
Final set, minutes, not more than	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600	600

(Table continued next page)

Table 2. Comparison of ASTM and AASHTO requirements* (continued)

Item	Type of Cement											
	Type I		Type IA		Type II		Type IIA		Type III		Type IIIA	
	ASTM	AASHTO	ASTM	AASHTO	ASTM	AASHTO	ASTM	AASHTO	ASTM	AASHTO	ASTM	AASHTO
Vicat test:												
Initial set, minutes, not less than	45	45	45	45	45	45	45	45	45	45	45	45
Final set, minutes, not more than	375	375	375	375	375	375	375	375	375	375	375	375
Strength, not less than the values shown for the ages indicated below:†††												
Compressive strength, MPa (psi)												
1 ay d	—	—	—	—	—	—	—	—	12	12	10	10
3 days	12	12	10	10	10	10	8	8	24	24	19	19
	(1740)	(1740)	(1450)	(1450)	(1450)	(1450)	(1160)	(1160)	(3500)	(3500)	(2760)	(2760)
7 days	19	19	16	16	17	17	14	14	—	—	—	—
	(2760)	(2760)	(2320)	(2320)	(2470)	(2470)	(2030)	(2030)	—	—	—	—
28 days d	—	—	—	—	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—
Optional Physical Requirements (Note: These optional requirements apply only when specifically requested.)												
Heat of hydration, kJ/kg (cal/g)												
7 days, max	—	—	—	—	290	290	290	290	—	—	—	—
	—	—	—	—	(70)****	(70)****	(70)****	(70)****	—	—	250 (60)	250 (60)
28 days, max	—	—	—	—	335	335	—	335	—	—	—	—
	—	—	—	—	(80)****	(80)****	—	(80)****	—	—	290 (70)	290 (70)
False set, final penetration, min %	50	50	50	50	50	50	50	50	50	50	50	50
Strength, not less than the values shown												
Compressive strength, MPa (psi)												
28 days	28	28	22	22	28	28	22	22	—	—	—	—
	(4060)	(4060)	(3190)	(3190)	(4060)	(4060)	(3190)	(3190)	—	—	—	—
Sulfate expansion, †††† 14 days, max %	—	—	—	—	—	—	—	—	—	—	—	—
	—	—	—	—	—	—	—	—	—	—	—	—

* AASHTO 2004; ASTM 2004. Dashes indicate that no standard applies.

† ASTM specifications state that there are cases where optimum SO₃ for a particular cement exceeds the limit in this specification. Where it has been demonstrated by Method C563 that this condition exists, an additional amount of SO₃ in no case more than 0.5 by weight percent of cement, is permissible, provided that when the cement with the additional calcium sulfate is tested by Method C265, the calcium sulfate in the hydrated mortar at 24 ± ¼ hr expressed as SO₃ does not exceed 0.5 g/L. When the manufacturer supplies cement under this provision, supporting data will be provided, on request, to the purchaser.

‡ Expressing chemical limitations by calculated assumed compounds does not necessarily mean that the oxides are actually or entirely present as such compounds.

§ Does not apply when the sulfate expansion limit under Optional Physical Requirements is specified.

** This limit applies when moderate heat of hydration is required and tests for heat of hydration are not requested.

†† This limit may be specified when the cement is to be used in concrete with aggregates that may be deleteriously reactive. Reference should be made to ASTM Specification C33 for suitable criteria of deleterious reactivity.

‡‡ Compliance with the requirement of this specification does not necessarily ensure that the desired air content will be obtained in concrete.

§§ Either of two alternative fineness methods may be used at the option of the testing laboratory. When the sample fails to meet the requirements of the air permeability test, however, the turbidimeter test shall be used and the requirements for the turbidimetric method shall govern.

*** These values were revised in ASTM specifications because of the change in unit from cm²/g to m²/kg.

††† The purchaser should specify the type of setting time test required. If not specified, the requirements of the Vicat test only shall govern.

†††† The strength at any specified age shall not be less than that attained at any previous test age.

§§§ When the optional heat of hydration or the chemical limit on the sum of the tricalcium silicate and tricalcium aluminate is specified.

**** When the heat of hydration requirements are specified, the sum of the tricalcium silicate and tricalcium aluminate shall not be specified. These strength requirements apply when either heat of hydration requirements or the sum of tricalcium silicate is specified.

††††† When the sulfate expansion is specified, it shall be instead of the limits of C₃A and C₄A_F + 2C₃A listed under Standard Chemical Requirements.

Table 3. Annual production, shipments, and capacity of the cement industry of the United States and Puerto Rico, and average prices for cement sold in the United States, kt

Year	Shipments [†]	Production [*]	Imports [‡]	Exports	No. of Active Portland Cement Plants	Capacity		Prices [§] Average Mill, US\$/t
						Finish Grinding Capacity	Clinker Capacity	
1991	68,999	67,193	7,893	633	119	90,194	74,342	55.54
1992	69,203	69,585	6,166	746	119	90,752	75,062	54.61
1993	74,079	73,807	7,060	625	118	90,301	75,091	56.36
1994	85,934	77,948	9,072	633	118	91,228	75,413	61.88
1995	86,561	76,906	11,473	759	118	91,499	76,335	68.46
1996	92,600	78,600	10,700	750	118	91,980	76,000	70.00
1997	96,801	82,582	14,523	791	118	95,678	76,652	73.49
1998	103,696	85,931	19,878	743	116	97,295	77,914	76.46
1999	110,673	87,777	29,351	694	119	100,458	80,162	76.45
2000	111,711	89,510	28,683	738	119	107,455	84,052	78.56
2001	115,002	90,450	25,861	746	117	113,491	89,245	76.50
2002	110,661	91,266	24,169	834	116	111,000	82,959	76.00
2003	114,786	95,833	23,741	483	117	113,754	90,360	76.00

Adapted from USGS Mineral Surveys (to adjust for unreported shipments) and PCA 2000–2002.

* Portland and masonry cement, and cement produced from imported clinker, for the 50 states and Puerto Rico.

† Includes portland cement shipped by domestic producers and distributors.

‡ Includes dinker.

§ Annual prices are based on an average per-ton value of cement sales, f.o.b. plant, reported by producers to the USGS.

In the cement industry, lime stone is a generic term that includes calcium carbonate, magnesium carbonate (MgCO_3), and dolomite ($\text{CaMg}(\text{CO}_3)_2$). The geological definition of limestone is a sedimentary rock mostly containing calcite (CaCO_3). Dolostone is a sedimentary rock mostly consisting of dolomite. Magnesite (MgO), derived in the clinker production process from MgCO_3 , is highly undesirable in the formation of cement clinker compounds. Many limestone deposits are unusable for portland cement clinker because of MgCO_3 content. Normally, the upper limit in the limestone is 3%, although this can be less depending on magnesia content in the other required raw materials. The many classifications of limestone are of little concern to a cement producer because the principal factor in selecting a suitable limestone is the CaCO_3 content and the minimization of the undesirable minerals. The ideal “cement rock”—77% to 78% CaCO_3 , 14% SiO_2 , 2.5% Al_2O_3 , and 1.75% Fe_2O_3 , coupled with <3% MgCO_3 , <0.4% Na_2O , and 0.3% K_2O —is rarely found but highly desirable. Limestone with lower levels of CaCO_3 and higher levels of alkalis and magnesia requires blending with high-grade limestone. Limestone normally has to be blended with argillaceous material to adjust the chemistry of silica, alumina, and iron oxide. Limestone that is high in CaCO_3 presents cost and operating challenges to the cement producer because it requires large quantities of argillaceous minerals such as clay, which are usually more difficult to convey, store, and feed.

Sedimentary limestone deposits, the predominant source of CaCO_3 for cement, are principally extracted by bench mining, in which 150-mm to 300-mm holes are drilled in 3- to 4-m patterns to depths of 10 to 25 m, charged with ammonium nitrate and fuel oil (ANFO) explosive and blasted. Typical drill patterns and blasting techniques will fracture the rock to <300-mm size. The rock is excavated with front-end loaders, often of 10-m³ capacity, and loaded into 70- to 90-t haul trucks and transported to the primary crusher. Marl and chalk deposits are increasingly extracted with modern mining machines because they normally do not require drilling and blasting. The typical modern mining machine includes the excavator, primary crusher, and a feeder that deposits the excavated and

Table 4. Summary of raw material used in the manufacture of portland cement clinker in the United States

Types of Raw Materials	
Sources of calcium carbonate	Limestone, marl, chalk
Sources of argillaceous materials	Clay, shale, sand, iron ore, mill scale, bauxite, diaspore, diatomite, staurolite, loess, silt, sandstone, volcanic ash
Waste material substitutes	Fly ash, bottom ash, foundry sand, metallurgical slags

crushed marl or chalk onto moveable belt conveyors for transport to storage and preblending facilities. A trend in the extraction process is to use in-pit, moveable, impactor-type primary crushers and belt conveyors to transport the rock to a fixed secondary crusher and screening plants, thereby reducing the number of trucks and haulage distance. Load-haul-dump practices with front-end loaders are also employed with these in-pit moveable crushers.

The increased emphasis on chemical uniformity and quality in the subsequent processing of the raw materials into cement clinker has caused the proliferation of various techniques of quality control in extracting the limestone and other raw materials. A common practice is sampling and x-ray fluorescence (XRF) analysis of blast-hole drill cuttings to establish rock grade, quality, and alkali levels. Increasingly, plants are installing online prompt gamma neutron activation analyzers (PGNAAs) immediately after the crushing circuits to analyze the quarry run material and control subsequent blending operations to produce kiln feed. There is also an increasing use of x-ray diffraction (XRD) in quality control of kiln feed and the produced clinker. XRF analysis has been the dominant method for the past 40 years.

Underground mining of limestone deposits is not typical of the cement industry, although in coming years this is expected to increase as economically accessible surface or near-surface sedimentary deposits play out, particularly at established plants constricted by urban encroachment. Currently, one U.S. plant obtains its limestone

Table 5. Raw materials used in producing clinker and cement in the United States*

Raw Materials	Volumes Reported, kt					
	2000		2001		2002	
	Clinker	Cement	Clinker	Cement	Clinker	Cement
Calcareous						
Limestone (includes aragonite, marble, chalk, coral)	93,947	1,263	95,600	1,600	107,000	1,330
Cement rock (includes marl)	21,820	133	21,900	100	16,200	39
Cement kiln dust	351	155	600	100	688	164
Lime	19	49	300	40	196	34
Other	21	225	20	20	5	18
Aluminous						
Clay	4,205	8	4,500	10	4,770	NR†
Shale	3,743	3	3,200	10	3,230	9
Other (includes staurolite, bauxite, aluminum dross, alumina, and other)	400	NR	500	NR	540	NR
Ferrous: iron ore, pyrites, millscale, other	1,310	NR	1,500	NR	1,260	NR
Siliceous						
Sand and calcium silicate	3,142	NR	3,500	NR	2,960	NR
Sandstone, quartzite soils, other	925	NR	500	NR	692	NR
Fly ash	1,679	88	1,600	70	1,960	64
Other ash, including bottom ash	930	NR	800	NR	990	NR
Granulated blast furnace slag	NR	303	NR	300	60	369
Other blast furnace slag	43	NR	200	NR	162	NR
Steel slag	805	NR	500	NR	481	NR
Other slag	12	10	50	5	67	4
Natural rock pozzolans	NR	40	NR	50	NR	28
Other pozzolans	38	8	100	9	165	7
Other						
Gypsum and anhydrite	NR	4,655	NR	4,800	NR	4,740
Clinker imported	NR	4,573	NR	5,030	NR	5,230
Other, not elsewhere classified	NR	46	40	50	21	52
Total	133,400	11,600	135,400	12,200	141,400	12,100

Adapted from *USGS Mineral Surveys* (to adjust for unreported shipments) and PCA 2000–2002.

* Includes Puerto Rico.

† NR = not reported.

from underground operations using the room-and-pillar mining method. Those plants located on navigable waterways may have the option of extracting limestone from surface deposits some distance from the plant and transporting the limestone by barge or ship. Currently one U.S. cement plant obtains its limestone from the Dominican Republic and two others receive limestone from Canada. Several U.S. and Canadian plants receive their limestone and other raw materials by barge or ship from quarries separated from the plant. An increasing number of plants have installed overland belt conveyors to transport limestone to the plant over distances of more than 5 km. In several plants, such as those in Great Britain and Trinidad (but none in the United States), marl or chalk or limestone is ground and slurried and then pumped to the distant plant. Several wet-process plants have been replaced with flash-dryer-equipped, preheater calciner systems that accept the slurried raw material transported by pipeline. This method has allowed extraction of limestone deposits heretofore inaccessible or allowed continuation of production at plants that otherwise would have shut down.

Argillaceous Mineral Resources and Mining Practices

The typical practice is to use clay or shale and sand for the silica and alumina, and a source of iron oxide such as mill scale or iron

ore to adjust the chemistry to the desired composition, in addition to the ash in the coal used to fire the kilns. Other natural sources of silica and alumina, such as loess, silt, sandstone, volcanic ash, diaspore, diatomite, fuller's earth and bauxite, are used based on economics and cement quality. Many plants are using waste or recycled materials for this purpose and sometimes are paid to take this material. Although the industry has used power plant fly ash and bottom ash for decades, alkali levels often limit the use of these materials. The variety of recycled and waste materials containing silica, alumina, and iron oxide precludes a complete listing. The principal factor in the selection of the argillaceous component is economic. Often plants have to invest in additional materials handling, feeding, and proportioning facilities to be able to use waste materials, thus reducing the economic benefits. As a result of the economic pressures on the North American cement industry, many plants are using some waste materials in place of natural minerals. Table 5 summarizes the quantities of raw materials used in the production of cement.

The typical methods of extracting clays, shales, and sand have changed little. These raw materials are typically surface deposits, often overburden of the limestone beds. Clay and shale are normally extracted using front-end loaders and loaded into haul trucks.

In some cases, the deposits are first ripped with large bulldozers. When the raw materials are present as overburden, a common practice is to contract for the removal and stockpiling of the overburden to expose sufficient limestone to run the plant for several months. The clay or shale is then reclaimed as required for the process over ensuing months. Increasingly, older plants must remove larger amounts of overburden to expose the underlying limestone. The clays and shales not used in the process are often reused as fill and reclamation material in mined-out areas of the quarry because plants are required to return the mined-out land to a reusable state.

Because most cement production facilities use the dry process, slurring clay in wash mills at the plant is rarely practiced. More typical is the conventional crushing of the clay or shale in crushers designed for these materials and their characteristics. In some plants the clay is dried in a rotary dryer, a crusher-dryer, or a semi-autogenous mill before mixing it with limestone for further processing.

Waste Materials as Substitutes

Beginning in the early 1980s, environmental regulations and political factors in the United States combined with economics of cement production have created a significant incentive to use wastes containing silica, alumina, and iron oxides as raw materials. Some of these wastes contain minor fuel values, such as carbon in fly ash and coal in tailings, which potentially make them more valuable. Stack emission limits in some cases prevent or limit their use, but many plants now use these wastes. Only those plants permitted to use so-called hazardous wastes can use soils contaminated with organic wastes or other hazardous materials as raw materials and then only as part of the fuel to the kiln. The subject of alternate fuels is discussed in the section on Fuel Firing Systems in this chapter. Substituting waste containing lime, silica, alumina, and iron oxide is a practice that is expected to grow and become prevalent throughout the cement industry as environmental regulations spread and economic factors make such use attractive.

Geology of Calcium Carbonates and Argillaceous Minerals

Calcium carbonate originates from the biological deposition of shells and skeletons of plants and animals to form beds of limestone. Some of the beds or formations within a bed were formed by natural precipitation of calcium carbonate taken into solution by carbon dioxide in water, forming calcium bicarbonate. The precipitation process occurs as a result of evaporation or temperature changes resulting in a saturated solution; this genesis, however, is rare. Most industrial quality limestone is of biological origin. Massive beds of limestone accumulated over the millions of years of geologic time. Much of the North American continent in Paleozoic time was under water, allowing the formation of limestone deposits. Typically, limestone resources in the Midwest and the eastern United States are of Ordovician, Devonian, and Mississippian ages. Westward they are often of the younger Cretaceous age.

Most deposits are relatively unaltered with little faulting and folding except those in the mountainous West and the Appalachians where alteration is typical. Steeply sloping or near-vertical beds with not iceable of faults along faults are the rule in these regions. Along the Andes Mountains in South America, extensive alteration of limestone beds is the rule. The prevalence of volcanic action, often evident in the sulfur content of the limestone and the interbedding of volcanic deposits, limits the economic use of these limestones.

Deposits of the argillaceous minerals are also of sedimentary origin. Shales, mudstones, and sandstones are often interbedded with the limestone. Shales, typically beds of clay altered by pressure, and sandstone, beds of sand often cemented by precipitated

silica or calcium carbonate, were deposited as the vast inland waters and oceans covered the land masses. Clays are typically surface deposits of more recent times; in some cases from receding glaciers that covered much of the northern hemisphere.

PRODUCTION PROCESSES

The production of cement begins at the quarry with chemical assessment of the limestone and sources of argillaceous materials. The mining plan to extract these raw materials in today's plants is carefully designed to meet the chemical quality objectives of the various types of clinker to be produced. The height of benches and the extraction plan of the various beds of limestone are dictated by their chemistry and how best to blend these beds to achieve the chemical targets and maximize recovery of reserves. Subsequent process steps continually focus on chemical uniformity of the raw materials and of the feed to the kiln. Greater emphasis is now placed on quick analysis and frequent sampling of material streams including the practice of automated (robotic) sample preparation.

Fundamental Processing Steps

Modern plants, which are diagrammed in Figures 1 and 2, use the process steps described in the subsections that follow.

Crushing and Screening

Rigid rotor impactor-type crushers are favored in plants that use a vertical roller mill to grind the raw materials. Scalping ahead of the crusher reduces the fines and potential for clogging the crusher. Plants that use ball mills to grind the raw materials favor a hammermill-type secondary crusher. Screening the rock from the secondary crusher is the preferred process, with the oversize conveyed back to the crusher in closed circuit. The practice of using gyratory or jaw crushers at the primary stage has given way to use of impactor crushers for cost reasons. Similarly, the use of cone or roll crushers as secondary crushers and a tertiary crushing stage has disappeared except in unusual conditions.

Preblending

Depending on limestone variability and process considerations, preblending is now a common practice. It takes two basic forms; either (1) the limestone is laid down in longitudinal or circular beds in a chevron pattern and reclaimed by mechanical rakes that cut across the layers to produce a more chemically uniform limestone or (2) the various raw material components are stockpiled and reclaimed with weigh feeders in set proportions and laid down in longitudinal or circular beds in a chevron pattern and reclaimed by mechanical rakes that cut across the layers to produce a reasonably chemically uniform feed to the subsequent milling stage. An increasing number of plants use PGNAAs to adjust these weigh feeders to achieve superior blending and uniformity of mill feed. The method selected is dictated by factors such as the chemical and physical variability of the limestone, the moisture content of the raw materials, the physical characteristics (stickiness, particle size, etc.), the space available, number of raw material components, and capital cost.

Raw Material Storage and Milling

Storing raw materials ahead of the raw mill is usually limited to the preblend piles with minimal bin or silo storage. The capital cost of storing materials in silos is significant, and the pressure to minimize capital cost usually dictates only a few hours of mill feed held in bins. Weigh feeders withdraw raw materials from their respective bins in the desired proportion to achieve the required chemical composition and deposit them on a belt conveyor that

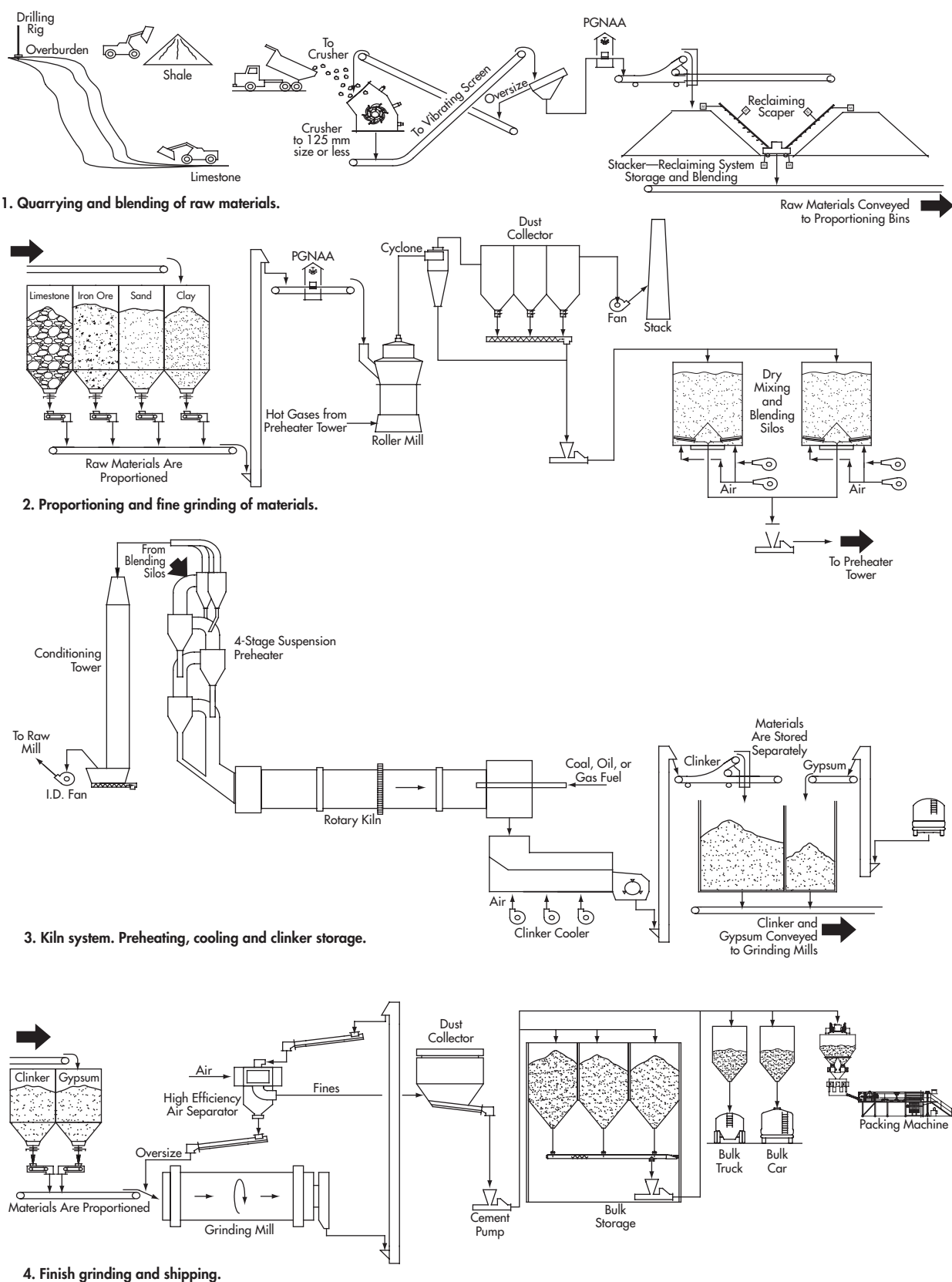


Figure 1. Steps in the manufacture of portland cement by the dry processes using a four-stage preheater

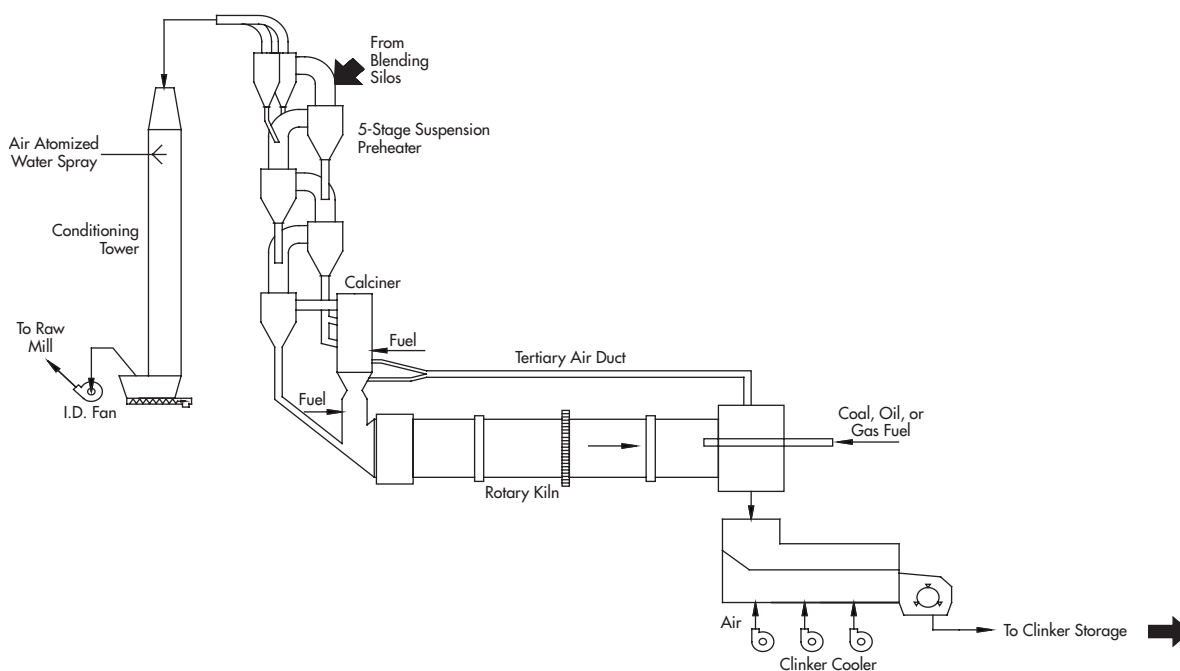


Figure 2. Kiln system with five-stage preheater and calciner

feeds the raw mill. A significant improvement in uniformity of mill feed and subsequent kiln feed is achieved by installing a PGNAA on either the mill feed conveyors or on the mill product stream. Although ball mills are occasionally selected to dry grind the raw materials, the preferred dry-grinding mill in the modern plant is the vertical roller mill. This type mill is superior in drying the raw materials using the hot waste off-gases from the kiln system and requires less power. For high raw material moistures (14% to 18%), the vertical roller mill uses a combination of waste kiln system gases and waste hot air from the clinker cooler to achieve a 0.5% to 1.0% product moisture, which a ball mill is unable to do. As plant capacities have increased, the vertical roller mill and its related structure and foundations have gained a capital cost edge. These mills operate at significant pressure drop, necessitating large drives on the exhaust fan and careful attention to the mill feed airlock. None of the types of airlock is problem free, each having their limitations, compromises, and cost consequences. Product fineness from the raw mill has increased in recent years from the 70% to 75% passing a 200-mesh Tyler screen (74 μm) acceptable 25 years ago to 82% to 86% in new plants. Wet- or semi-wet-process plants continue to use ball mills as the method of grinding the raw materials into a slurry. Either of two methods of classifying the slurry is in use: DSM screens or multiple cyclones. Each of these methods has its limitations, compromises, and consequences. Product fineness for the semi-wet-process applications has increased to the same level as that for dry-grinding systems. Slurry moisture content objectives for the older wet process and the new semi-dry processes have been reduced in continuing efforts to reduce fuel consumption. Filtration to lower water content of slurry either with plate filter presses or belt-type filters is encountered in very few older plants (none in the United States).

Blending and Kiln Feed

Blending systems for dry-process plants continue to evolve. The realization that large (50,000-t capacity) silos with a random multi-

ple withdrawal system are costly and do not provide commensurate improvement in blending has focused attention on smaller silos (5,000- to 10,000-t capacity) with inverted cone and random or sequenced multiple withdrawal systems. The older small-capacity silos agitated by compressed air (2,000 to 2,500 t) are rarely applied in modern plants, although they are still used in older plants. Separate kiln feed silos or bins are typically not applied in new plants or found in older plants. Kiln feed systems have undergone significant changes in recent years. Belt-type weigh feeders, always having problems because of the characteristics of kiln feed, have been replaced with flow meters coupled to weigh bins on load cells or the Pfister feeder. These new methods are totally enclosed and spill free, and provide lower operating cost and improved accuracy and reliability without capital cost penalties. Wet-process blending and kiln feed systems are unchanged with two or more slurry tanks, traveling rakes, and compressed air agitation. The number of slurry basins has been reduced and significant improvement in kiln feed uniformity has been achieved by using PGNAAs on the mill product stream to control weigh feeders. Flow and density meters continue to be used on the kiln feed system; using adjustable-speed drives on the kiln feed pumps, however, is the preferred method of adjusting flow rates in place of orifice-type control valves.

Preheater and Precalciner Systems

New plants typically adopt the newest precalciner preheater system. The preheaters are the classic cyclones but now typically of low-pressure-drop (100-mm WC [water column]) design. If kiln feed moisture is a factor, the preheaters will have three or four stages; otherwise the norm is a five-stage preheater. Few new plants are fitted with six stages because the incremental efficiency does not justify the added capital and operating cost. A number of plants in the United States and Canada installed in the 1970s have only preheaters, and typically four stages. Sixty percent to 70% of the calcining is in the rotary kiln portion of the kiln system, and the balance is in the preheaters or in the duct between the rotary kiln

and the lower stage preheater cyclone (riser duct). In most such systems, 15% to 20% of the fuel is introduced in the riser duct. Kiln manufacturers have achieved considerable development in precalciner technology in recent years. Depending on the raw material characteristics and emissions limits (especially NO_x), two-stage calciners and very tall calciners are used. Gas and kiln feed retention times are greater (8 to 10 sec), and various forms of staged combustion are the norm. The evolution of precalciners in the last 15 years has been significant and calcining rates of 90% to 95% are an accepted norm. The typical fuel consumption rate in these calciners is 55% to 60% of the total kiln system fuel. Combustion air for this fuel (tertiary air) is drawn from the clinker coolers through separate ducts at 70 °C to 80 °C. The term *precalciner* continues to confuse because effectively the industry has introduced a distinct step in the process to calcine the kiln feed before introduction into the rotary kiln. The rotary kiln's sole purpose is to complete the calcining and cause the chemical reaction that forms the clinker compounds. The result is smaller diameter and shorter rotary kilns turning at higher rates (240 revolutions per hour) to achieve any given capacity. A recent development has been the use of two support rotary kilns with these more efficient precalciners. This results in lower kiln shell stresses and, when offset by thicker kiln shells, less ovality and greater refractory life. It is not uncommon for these properly designed two-support rotary kilns to operate for more than 12 months without refractory failure or replacement, a significant productivity improvement. Fuel efficiency improvements have also been achieved, although the gap between normal operating fuel consumption and that demonstrated during initial performance acceptance tests remains. The kiln manufacturers continue to use net fuel calorific values in their performance guarantees, but producers must continue to deal in the real world in which fuel calorific values and pricing are quoted in gross values and the unwary encounter the 4% to 9% cost discrepancy in addition to the difference between performance guarantees and real-world operating fuel consumption.

Semidry Kiln Systems

A development of the last 10 years has been the commercialization of the flash dryer to use preheater gases to dry kiln feed slurry. These systems are applied in special circumstances such as converting wet-process kilns to achieve much higher production rates from an existing kiln and clinker cooler or transporting limestone to the plant as a slurry via overland pipeline. Typically a semidry system will double output and lower fuel consumption by about 15% to 20% of any given wet-process kiln. The preheaters are typically one stage and in some cases two stages. The flash dryer is a tall duct, often 100 m tall, in which preheater gases are fed into the bottom around a single-shaft, rigid-rotor crusher and the kiln feed slurry is injected into the hot gas stream. The mass of gas and kiln feed is drawn up the flash-dryer duct and separated in a cyclone. The kiln feed, now at very low moisture levels, is fed into the preheater cyclone for final drying. The kiln feed drops out from the preheater cyclone into either a calciner or a second-stage preheater cyclone and then the calciner. In these systems, the fuel consumption is greater in the calciner than in a typical dry-process precalciner system. Calcining rates typically are greater than 90% and overall fuel consumption is 35% to 50% greater than a five-stage dry-process precalciner system, but still less than a typical wet-process system. It is interesting to note that the most efficient wet-process systems, such as the Holcim plant in Clarksville, Missouri, have almost the same fuel consumption rate as a semidry system but not the rotary kiln refractory life and productivity.

Wet and Long Dry Kiln Processes

The wet and long dry kiln processes are treated together because they are essentially obsolete. They are diagrammed in Figure 3. A significant number of plants in the United States and Canada continue to operate with these types of kilns, their retirement being delayed by favorable economics of their use of waste fuels, relative newness, competitive location, difficult environmental situation preventing new plants from locating in their market area, or other factors. Fuel efficiencies have not changed in the last 20 years because there has been no significant improvement in chain systems or other means. These kiln systems have benefited from the improvement in kiln feed uniformity achieved by using PGNAAs and from introducing car and truck tires as fuel into the kiln downstream of the chain section (mid-kiln firing).

Clinker Cooling

A significant development of the grate cooler in the last 10 years has been the compact cooler with a deep clinker bed depth (800 mm to 1,000 mm) and reduced undergrate airflow rates (<3 kg of air per kg clinker) at significantly higher pressure (1,000 mm WC). These coolers are normally fitted with seven to nine static rows of grates and cooling air introduced to the fixed and movable grates through chambers, not undergrate compartments. The smaller grate areas and lower airflow rates result in a compromise in clinker temperature. The accepted norm of 80°C 25 years ago has given way to 120° to 125°C performance, a figure common 50 years ago but considered unacceptable in ensuing years. Newer plants are now dealing with the consequent problems in cement temperature and storing hot clinker. A perceived benefit of these modern clinker coolers is reduced exhaust airflow rates and higher tertiary air temperatures to the precalciner.

Fuel Firing Systems

Rotary kilns and precalciners are almost exclusively fired by coal or a combination of coal and petroleum coke. Kiln startup and warming is typically either with natural gas or No. 2 fuel oil. The degree of substitution of coal with petroleum coke is dictated by the ability of the grinding mill to reduce the pet coke to a high fineness (90% to 96% – 200-mesh Tyler, 74 µm) and by sulfur dioxide permit emissions rates, because the sulfur content of petroleum coke is significantly greater (5% to 7%) than typical rates in coal (1% to 3%). Outside the United States and Canada, allowable sulfur dioxide emission rates enable producers to use 100% petroleum coke to fire the rotary kiln when stable operating conditions prevail with the high fineness. The combustion temperatures in the precalciner are relatively low (<1,100°C) compared to the rotary kiln, restricting the use of petroleum coke. Direct grinding and firing of coal and petroleum coke has given way to indirect grinding and firing as a result of the need to fire two separate systems, the rotary kiln and the precalciner. The requirement to reduce NO_x emissions from existing kiln systems has also resulted in direct firing being replaced with semidirect firing and indirect grinding and firing to reduce primary air and allow the use of specially designed burners. A greater variety of coal (and petroleum coke) grinding mills is now found in U.S. and Canadian plants. The vertical roller mill with its high-efficiency internal classifier is increasingly used. Replacing the static classifiers with dynamic classifiers in older ring-roller mills has gained acceptance, particularly with the need to grind petroleum coke and coal to higher fineness. Many preheater kilns are now burning tires, often aided by a small tipping fee. The normal practice is to introduce whole tires into the kiln through airlock ports in the riser duct of preheater kilns or into the

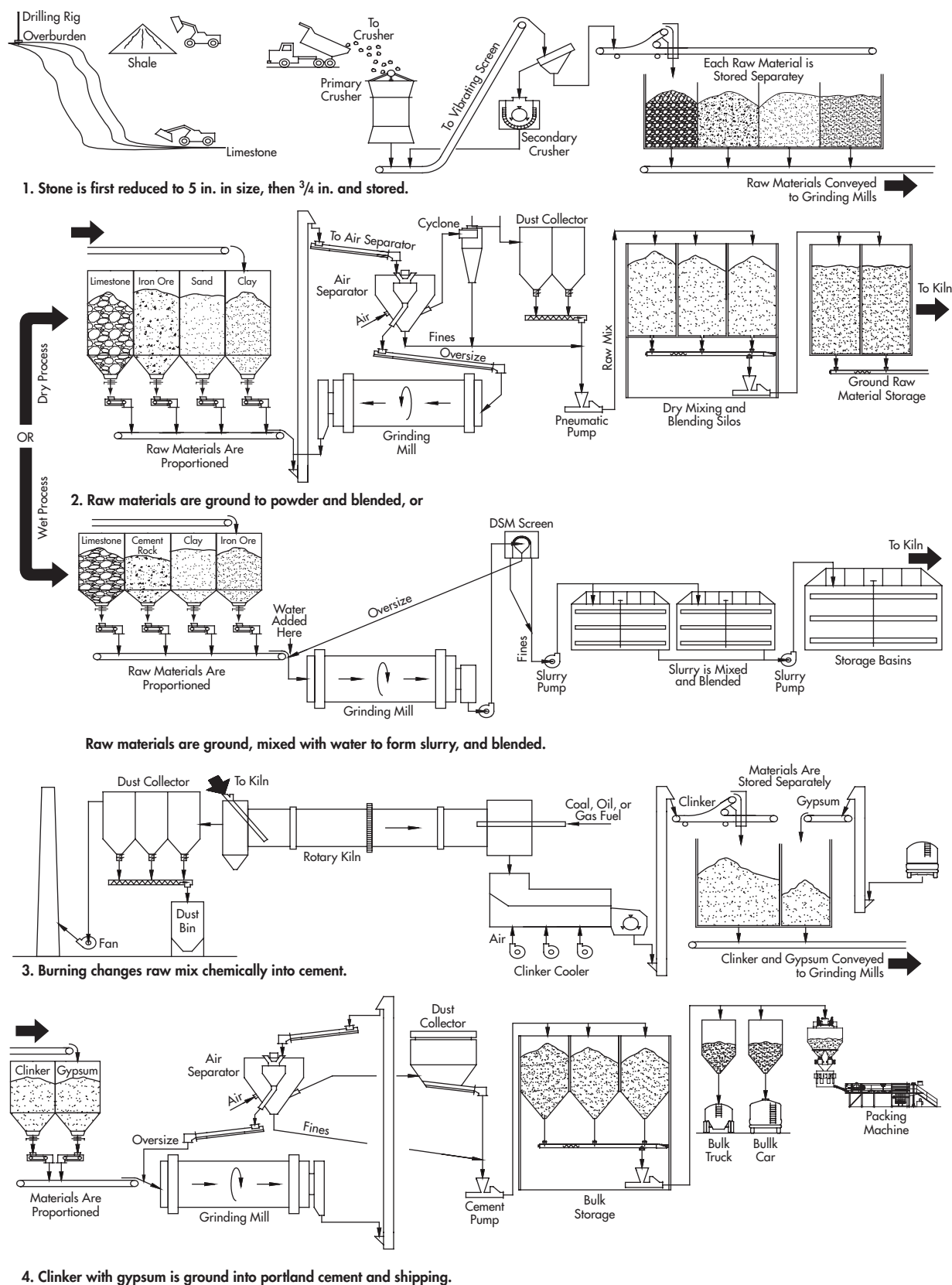


Figure 3. Steps in the manufacture of portland cement by the old processes

back end of precalciner kilns. Tires are introduced into long wet and dry kilns through openings in the shell downstream of the chain systems, a process covered by a mid-kiln firing patent issued to Benoit, Hansen, and Reese (1989). A few plants in produce tire chips; the economics, however, are not as attractive. Tires contain significant levels of sulfur and iron. Sulfur content limits substitution rates to typically $< 20\%$ of total kiln fuel. The iron content results in the need to adjust kiln feed chemistry and adds the complexity of a change in clinker chemistry when tire feed rates change abruptly before kiln feed chemistry can be changed. Using waste fuels is increasing, although using hazardous wastes as a fuel is static because of the high cost of permitting and ongoing permit compliance. Plants are seeking various combustible materials that ordinarily are wastes as substitutes for the normal coal or petroleum coke.

Clinker Storage

Environmental emission restrictions have made storing clinker in enclosed structures the norm. The choice of silos or domed or longitudinal storage buildings is typically dictated by economics. Silos (some as large as 50,000 t) offer 100% reclaim without mechanical reclaimers but typically cost more than US\$15 0/t, including the conveying systems. Domed or longitudinal structures require mechanical reclaimers or clinker must be reclaimed by a combination of gravity to conveyors in tunnels and front-end loaders or bulldozers. The capital cost of these systems ranges from US\$100 to US\$120/t of capacity but results in greater maintenance and higher operating costs. A significant trend in the industry is using pan- or bucket-type conveyors for conveying hot clinker. These units are favored when clinker must be elevated to the top of storage silos or circular or longitudinal storage buildings. Although relatively expensive, the low maintenance cost, reliability, low dust emission rates, and ability to convey red-hot clinker favor their use.

Cement Grinding

The industry continues to use the two-compartment ball mill in closed circuit with the air separator type classifier as the principal means to grind clinker and gypsum into cement. Almost all grinding circuits also use heat exchangers to cool the cement before conveying it to storage. There has been extensive application of the high-efficiency air-swept separator in place of the older-technology air separators. In addition to some cooling of the cement, these systems provide a better particle-size distribution, slight improvement in grinding efficiency, and typically improved cement strengths at a given fineness. The competitive conditions in the cement industry have resulted in marketing cements with much greater 28-day strengths in the last 10 years. To achieve these strengths, tricalcium silicate levels have increased and fineness of grind has increased by about 500 Blaine points.

There is considerable interest in using vertical roller mills rather than ball mills for grinding clinker and gypsum. Although the trend is still not established, one plant came on line in 2002 in the United States with this type of mill, and one new plant is still in the permitting stage plans to install four of these types of mills. There are several applications of this type of mill outside North America. Several plants using ball mills have installed high-pressure roll presses to prefracture the clinker before grinding in the ball mill. This technology, which Germany introduced into North America in the mid-1980s, results in a significant total power reduction and improved productivity of the ball mill circuit. The major drawback to its application is the need to maintain an inventory of "pressed" clinker ahead of the ball mill to not compromise ball mill production, because a change in the ball charge of the first

compartment of the ball mill is required. The preferred method of conveying cement to storage is still the screw-type pump pneumatic conveyor.

Cement Storage and Shipping

Cement shipments vary with the season, declining significantly during cold winter months and for short periods during severe hot spells or hurricane-type storms. Consequently, plants must maintain significant cement storage capacity either at the plant or in combination with distribution terminals and distant grinding plants. Those plants on the Great Lakes must also contend with closure of shipping because of ice, typically from mid-December to March. The typical practice of storing cement in silos has undergone an interesting change. The practice for many years was to carefully balance clinker storage with cement grinding capacity and cement storage. Until the mandated storage of clinker in enclosed structures for environmental reasons, clinker storage was less costly. Providing excess cement grinding capacity was economically sound in conjunction with limited cement silos. The recent trend is installing large dome structures to store greater quantities of cement because the cost is about the same as clinker storage. In new plants, cement grinding capacity is more closely matched to plant capacity. Storage silos are still needed to allow efficient loading of bulk trucks and railcars and to maintain an inventory of low-demand cements such as blended cements (Type IP), high early strength (Type III), and sulfate resistant (Type V). Very few plants operate bagging systems. In some cases, bagging cement has been contracted out; in other cases, bagging has been consolidated at one plant in a region. Southern Florida and southern California produce the highest levels of bagged cement.

Special Plant Processes

The production of cement is predominantly of gray cement using conventional fuels to fire the kilns. Three plants in the United States and one in Canada, however, produce white cement—although imports of white cement have a significant market share. One small plant in Juarez, Mexico, and one in Virginia produce special proprietary cements for the U.S. market. Colored cement is produced for decorative architectural purposes at several plants by carefully mixing dyes with gray or white portland or masonry cement.

Automation and Process Control

Considerable advances have been made in the last few years in automation of process control and in motor control. Distributed control systems (DCSs) typically control modern plants using fiber-optic cables as the data highway. Many older plants have been converted to DCSs but more commonly they are connected to programmable logic control (PLC) systems. Cost considerations and the unavailability of replacement parts have necessitated these conversions. The algorithms for process control have not changed significantly in the last 10 years, but the ability to provide quick response and finite control has improved kiln and mill operations. Additionally, the powerful data gathering and diagnostic capacity built into both the DCSs and the PLC systems has greatly improved the understanding of the processes, and has driven improvements in process control and improved compliance with emission limits. Virtually all plants now have a central control room from which the plant is operated, although a few plants still have two control rooms, one for the mills and one for the kilns and remainder of the plant. Commonly a single operator controls all processes from this room with an array of monitors using a trackball or touch screen for motor start and stop and a keyboard for process set-point adjustments. The large modern plants also have a process engineer at a nearby workstation to provide guidance to the

operator and assistance when operating parameters are exceeded or systems malfunction. Mimic boards have been replaced with graphics on the monitors that offer more information and the flexibility to make changes. The emission data gathered at some plants are now sent electronically to environmental agencies at periodic intervals, a feature unavailable just a few years ago.

CAPITAL COST OF MODERN PROCESS PLANTS

The trend to construct large plants has continued as older plants are shut down. A typical modern plant has a capacity of 1.5 to 2.0 Mtpy, although a few plants have come on stream in the last 10 years with capacities in the 0.65- to 1.0-Mtpy range. These smaller-capacity production lines have replaced older, lower-capacity, less-efficient processes. The capital cost for construction of a modern 1.5- to 2.0-Mtpy plant at the site of an older smaller-capacity plant is US\$125 to US\$175 per annual ton of capacity; and for the 0.65- to 1.0-Mtpy plant, the cost is US\$150 to US\$200 per annual ton.

Construction cost of a "greenfield" plant is very difficult to gauge because of the number of variables and the length of time it takes to permit and construct a new plant. Costs range from US\$200 per annual ton for a supersized plant of more than 3.0 Mtpy to US\$225 per annual ton for one of half that capacity.

PRODUCTION COSTS

Production costs in the industry vary depending on age of the plant, type of process, capacity, and unique features. Cash costs range from US\$27.50/t for a modern large-capacity plant to US\$50/t for older wet-process plants. The elements of cash cost are supervision and labor, purchased raw materials, fuel, power, maintenance and parts, operating consumables, local taxes, and miscellaneous costs. Capital recovery costs for a modern low-cost plant add US\$15/t to cash costs. When corporate overhead and sales costs are added, the industry is left with very narrow margins over recent selling prices.

Production costs can be classified as fixed or variable. Modern plants require significantly fewer people to operate and maintain, so labor and management are essentially fixed costs. Purchased raw materials, fuel, power, maintenance and operating supplies, and miscellaneous costs are essentially variable costs although some have a small fixed-cost element. Local property taxes, insurance, and capital recovery are fixed costs. Most kilns are fired with coal, but petroleum coke is substituted when pricing is favorable. A modern plant of 1.5-Mtpy capacity will typically operate at <0.2 worker-hours per ton of cement, 3.2 MJ of fuel per ton of clinker, and 140 kW-hr of electrical power per ton of cement.

EMISSION STANDARDS

U.S. cement plants must meet restrictive emission standards. Although federal regulations stipulate only a limit for particulates from the kiln and clinker cooler stacks, 0.3 lb/st of kiln feed (0.15 kg/t) and 0.1 lb/st (0.05 kg/t) of kiln feed, the reality is that plants have to meet much more stringent regulations, and these are multilayered and not necessarily codified as a uniform standard. The principal emission limits are set by the requirement to meet National Ambient Air Quality Standards (NAAQS) for particulates, sulfur dioxide, volatile organic compounds (VOCs), and carbon monoxide. Building a new plant or replacing an existing process system requires demonstrating that the plant will not "consume" more than the allowable increment of these pollutants in the area of impact. Additionally, these standards may be trumped by the need to comply with a state implementation plan (SIP) that mandates a lower emission level. Many plants are required to meet NO_x emission limits in order for the state to meet SIP requirements. Additionally, plants are now required to meet best available control

technology standards for certain pollutants such as particulates. The Clean Air Act Amendments of 1990 also imposed on cement plants the need to achieve the emission standards set to be the "Best 12%" of the plants. More recent emission standards require that cement plants meet dioxin and furan limits of 0.2 ng per dry standard cubic meter of stack gas. These multiple layers of regulations and emission limits have made permitting new greenfield plants a costly and time-consuming process. Even obtaining permits for new production systems at existing plants, where there are "offsets" created by the new process emitting fewer pollutants than the existing process, takes considerable time despite typically avoiding the more time-consuming permitting process of demonstrating compliance with Prevention of Significant Deterioration of Ambient Air Quality Standards (PSD Review) and the New Source Performance Standards (NSPS Review).

Table 6 presents the NAAQS that new cement plants must demonstrate they meet. This is a complex process that requires mathematical modeling of the emissions from the various parts of the process. Table 7 presents the emission limits of certain hazardous pollutants that new cement plants must demonstrate they meet.

The cement industry has also had to contend with more restrictive emission limits, especially of NO_x and SO₂ but also VOCs and trace amounts of metals. By definition, cement kilns are also major emitters of carbon dioxide, which is an unregulated gas but is a political issue.

Those plants that burn hazardous wastes as kiln fuel must comply with federal regulations under the Resource Conservation and Recovery Act of 1976 (RCRA). These regulations are in addition to those just discussed. Compliance with RCRA regulations imposes a significant cost, partly offsetting the economic benefits of this cost-saving measure.

The U.S. cement industry has developed interesting emission control techniques to comply with permit requirements. To control SO₂ emissions, lime slurry is added to the spray water in gas cooling towers. Although this technique works better with fabric filter air pollution control systems, it is applied on kilns with electrostatic precipitators. To meet NO_x emission limits, the cement machinery manufacturers developed staged combustion systems in the calciners that reverse the NO_x formed in the rotary kiln. Modern calciner kilns emit <25% of the NO_x of older long dry or wet kilns. Kiln burner manufacturers also developed burners that reduce NO_x by up to 66%. To meet the dioxin-furan emission limits, kiln gases are now cooled to <200°C in gas cooling towers or in specially configured duct systems. Modern compressed air atomizing spray nozzle technology combined with gas cooling towers and duct systems designed using computational fluid dynamics allows gas cooling to 120°C with no consequences such as wetting the dust, a remarkable achievement not possible 10 years ago.

The need for reliability in meeting emission limits from clinker coolers has forced plants to install gas cooling systems ahead of the fabric filters which are the preferred particulate removal devices. Very few plants use electrostatic precipitators or gravel bed filters for this function. The preferred gas cooling system is an air-to-air heat exchanger, although these devices are not without their problems due to abrasion, thermal expansion, and contraction resulting in fugitive emissions.

OUTLOOK, FUTURE TRENDS, AND DEVELOPMENTS IN THE INDUSTRY

The U.S. cement industry continues to install single large-capacity kiln and mill systems, a trend that began 50 years ago. In 1960, a very large kiln was 2,000 tpd of clinker. In 1967, the then-largest kiln in the world—4,000 tpd—was installed in Clarksville, Missouri. By

Table 6. National Ambient Air Quality Standards

Pollutant	Primary Standards	Averaging Times	Secondary Standards
Carbon monoxide	9 ppm (10 mg/m ³)	8 hr*	None
	35 ppm (40 mg/m ³)	1 hr*	None
Lead	1.5 µg/m ³	Quarterly average	Same as primary
Nitrogen dioxide	0.053 ppm (100 µg/m ³)	Annual (arithmetic mean)	Same as primary
Particulate matter (PM ₁₀)	50 µg/m ³	Annual† (arithmetic mean)	Same as primary
	150 µg/m ³	24 hr*	
Particulate matter (PM _{2.5})	15 µg/m ³	Annual‡ (arithmetic mean)	Same as primary
	65 µg/m ³	24 hr§	
Ozone	0.08 ppm	8 hr**	Same as primary
	0.12 ppm	1 hr††	Same as primary
Sulfur oxides	0.03 ppm (78.5 µg/m ³)	Annual (arithmetic mean)	No standard applies
	0.14 ppm (366 µg/m ³)	24 hr*	No standard applies
	No standard applies	3 hr*	0.5 ppm (1,300 µg/m ³)

Source: CFR 2004a.

* Not to be exceeded more than once per year.

† To attain this standard, the expected annual arithmetic mean PM₁₀ concentration at each monitor within an area must not exceed 50 µg/m³.

‡ To attain this standard, the 3-year average of the annual arithmetic mean PM_{2.5} concentrations from single or multiple community-oriented monitors must not exceed 15 µg/m³.

§ To attain this standard, the 3-year average of the 98th percentile of 24-hr concentrations at each population-oriented monitor within an area must not exceed 65 µg/m³.

** To attain this standard, the 3-year average of the fourth-highest daily maximum 8-hr average ozone concentrations measured at each monitor within an area over each year must not exceed 0.08 ppm.

†† The standard is attained when the expected number of days per calendar year with maximum hourly average concentrations above 0.12 ppm is ≤1. The 1-hr NAAQS will no longer apply to an area 1 year after the effective date of the designation of that area for the 8-hr ozone NAAQS. The effective designation date for most areas is June 15, 2004.

Table 7. Emission limits of hazardous pollutants and operating limits

Affected Source	Pollutant or Opacity	Emission and Operating Limit
All kilns and in-line kiln/raw mills at major sources (including alkali bypass)	PM	0.15 kg/Mg of feed (dry basis)
	Opacity	20%
All kilns and in-line kiln/raw mills at major and area sources (including alkali bypass)	Dioxins/furans	0.20 ng TEQ/dscm or 0.40 ng TEQ/dscm when the average of the performance test-run average particulate matter control device (PMCD) inlet temperature is 204°C or less. [Corrected to 7% oxygen]. Operate such that the 3-hr rolling average PMCD inlet temperature established at performance test.
		If activated carbon injection is used: Operate such that the 3-hr rolling average activated carbon injection rate is no less than rate established at performance test. Operate such that either the carrier gas flow rate or carrier gas pressure drop exceeds the value established at performance test. Inject carbon of equivalent specifications to that used at performance test.
New greenfield kilns and in-line kiln/raw mills at major and area sources	THC	50 ppmvd, as propane, corrected to 7% oxygen
All clinker coolers at major sources	PM	0.050 kg/Mg of feed (dry basis)
	Opacity	10%
All raw mills and finish mills at major sources	Opacity	10%
New greenfield raw material dryers at major and area sources	THC	50 ppmvd, as propane, corrected to 7% oxygen
All raw material dryers and material handling points at major sources	Opacity	10%

Source: CFR 2004b.

1990, a large kiln in the United States and Canada was considered to be 5,000 tpd, although larger ones were being installed in southeast Asia. Holcim is in the permitting stage of a 12,000-tpd kiln to be installed at a greenfield plant near Bloomsdale, Missouri, on the Mississippi River. Mills have followed a similar trend. Raw materials for a 6,000-tpd kiln system are ground in a single vertical roller mill.

Cement is ground in 6,000-kW ball mills, although typically two mills of this size are required to complement a 6,000-tpd kiln.

This trend to increasingly larger production units is driven by economics. The labor force requirements for a 12,000-tpd plant are 20% greater than those of one half that capacity. The most efficient modern large plants (5,000 to 6,000 tpd of clinker) operate with

100 hourly employees and 30 salaried personnel. The number of items of equipment dictates maintenance personnel requirements. The number of operating personnel is essentially static because of the modern central control systems, the computer controlled process, and the stability of preheater precalciner kilns. Quarrying operations require no more personnel because of the very large sizes of haulage and loading equipment, use of in-pit crushers, and belt conveyor transport systems.

Perhaps the future trend in the industry is described not in terms of major developments but in terms of continued development of large kiln and mill systems and more efficient grinding systems. The 10,000–12,000 kW ball mills are on the way. Vertical roller mills of 12,000 kW are also just a matter of time.

Considerable improvements in automation of process control have evolved over the past 15 years using the modern powerful PCs in tandem with PLCs for motor control and rapid data gathering. A modern plant uses a fiber-optic data highway for rapid data transmission which, with DCS and “smart PLCs,” maintains far more accurate control of the process. This trend is bound to continue as improvements in PCs and PLCs and the process control software continue.

Continued development of emission control systems, principally for SO₂ and NO_x reduction, can also be predicted. Some producers have declared the intention to reduce carbon dioxide emissions from kiln systems. To meet this objective, greater use of pozzolanic materials, both natural and synthetic, is likely. Alternative sources of calcium oxide are also objectives, reducing the amount of limestone required.

There has been considerable consolidation in ownership and number of plants in the last few years. This trend is likely to continue as company managements see the need to lower operating and administrative costs and build fewer, larger-capacity plants. Older wet- and dry-process plants will continue to be replaced with larger plants. The North American cement industry is dominated by major multinationals. About 62% of the production capacity is concentrated in six major international cement companies—Holcim, Lafarge, CEMEX, Italcementi, Buzzi Unicem, and Heidelberg Cement. All foreign companies combined control 80% of the clinker capacity and a greater percentage of cement sales.

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ADDITIONAL RESOURCES

A significant body of literature and information on portland cement and its producers exists, not only in the United States but also around the world. Numerous government and Portland Cement Association (PCA) publications cover all aspects of the industry and its vital contribution to raising standards of living. This section lists just a few of the publications readers may wish to consult for more details.

Select Organizations, Web Sites, Trade Journals, and Other Publications

- American Association of State Highway and Transportation Officials (AASHTO), <http://www.aashto.org>.
- American Ceramic Society, *Journal of the American Ceramic Society*, <http://www.ceramics.org>.
- American Concrete Institute (ACI), *Journal of the American Concrete Institute*, published monthly; *ACI Manual of Concrete Practice* (3 parts), current edition, ACI Special Publications, <http://www.aci-int.org>.
- Cement and Concrete Research*, published bimonthly, <http://www.elsevier.com>.
- Cement International*, published bimonthly, <http://www.verlagbt.de>.
- Concrete Construction*, published monthly, <http://www.concrete-construction.net>.
- Concrete Products*, published monthly, <http://www.concreteproducts.com>.
- Engineering News Record*, published weekly, <http://www.enr.com>.
- International Cement Review*, published monthly, <http://www.cement.co.uk>.
- PCA, various publications, <http://www.cement.org>.
- Pit & Quarry*, published monthly, <http://www.pitandquarry.com>.
- Rock Products and Cement Americas*, published monthly, <http://www.rockproducts.com>.
- SME, *Mining Engineering*, published monthly, <http://www.smenet.org>.
- U.S. Bureau of Reclamation, various publications; e.g., *Concrete Manual* (current edition), usually 600 to 700 pp., <http://www.usbr.gov>.
- U.S. Department of Defense, Army Corps of Engineers, various publications (e.g., *Handbook for Concrete and Cement*, 1949, with loose-leaf revisions, 928 pp.), <http://www.usace.army.mil>.
- U.S. Geological Survey, *Minerals Industry Survey* (Cement Monthly); *Minerals Yearbook* (Annual Cement Chapter), <http://www.usgs.gov>.
- World Cement*, published monthly, <http://www.worldcement.com>.
- Zement Kalk Gips International*, published monthly, <http://www.baudialog.de>.

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Flooring Materials

Robert C. Freas and Chris Lombardo

INTRODUCTION

One of the first things a person sees when entering a building or room is the floor. It makes no difference whether it is a personal residence, an office, a store, or even an airplane hanger—the floor surface makes a statement. Flooring can be both functional and aesthetic, it makes an impression, and it defines the purpose of the space. In the home, the flooring says something about the residents, their interests, and their priorities. In a commercial space, the floor treatment goes a long way in defining the purpose of the business and the space it occupies.

The selection of a floor treatment is based on the number of alternative choices available to the consumer and the interior designer and/or architect, as well as the functional purpose of the floor. Aesthetics will generally have a far greater impact on floor treatment selection in the home or office than will functional performance. Conversely, cost, functionality, and durability will likely have a greater impact on material selection than appearance in hospitals, schools, and other institutional space; government offices; and retail commercial space.

This chapter presents a review of a variety of flooring materials, the dynamics of the U.S. flooring market, and the role of industrial minerals in various flooring options. It also looks at market trends and the impact on industrial minerals specifications and usage. Although the market information focuses on the United States, the technology and mineral usage is similar to comparable flooring production in most global manufacturing enterprises.

MARKET OVERVIEW

Product Choices and Market Segmentation

Within the flooring industry, products are usually defined as (1) carpet and rugs; (2) resilient flooring, which includes both vinyl tile and sheet goods; (3) ceramic tile; (4) wood; (5) laminates; and (6) specialty flooring. Table 1 shows the 5-year history, in sales dollars, for these groups during the period 1999–2003. Table 2 presents a comparison for the same period based on the square footage of product sold.

Soft surface flooring, which is the industry term for carpet and rugs, is the largest segment of the flooring materials market in terms of both sales dollars and square footage covered. When looking at the sales figures, however, it is apparent that market share for this segment has been declining despite real increases in actual annual sales. In fact, over the past 10 years, this segment's share of

Table 1. U.S. floor covering market sales, 5-year history, million \$

Product Sector	1999	2000	2001	2002	2003
Carpet and rugs	12,248	12,911	12,868	13,200	13,230
Hardwood flooring	1,533	1,634	1,731	1,871	1,983
Ceramic tile	2,040	2,190	2,101	2,340	2,540
Vinyl sheet and tile	1,747	1,803	1,776	1,840	1,786
Laminate flooring	632	737	768	910	1,206
Other	284	290	286	294	302
Total	18,484	19,565	19,530	20,455	21,047

Source: Statistical Report '03 (2004).

Table 2. U.S. floor covering market sales, 5-year history, billion sq ft

Product Sector	1999	2000	2001	2002	2003
Carpet and rugs	17.17	17.92	17.00	17.50	17.38
Hardwood flooring	0.84	0.83	0.83	0.82	0.84
Ceramic tile	2.08	2.28	2.27	2.63	2.88
Vinyl sheet and tile	3.35	3.27	3.76	3.58	3.55
Laminate flooring	0.36	0.46	0.48	0.68	0.94
Other	1.45	1.47	1.48	1.47	1.50
Total	25.25	26.23	25.42	26.68	27.09

Source: Statistical Report '03 (2004).

the total floor covering market dropped from 66.8% in dollars and 71.9% in square footage in 1992 to 63.4% and 67.7%, respectively, in 2003.

Hard surface flooring has gained market share from soft surface, particularly in domestic markets where hardwood, laminates, and ceramic tile continue to make significant gains. Much of this is attributed to baby boomers and empty nesters who control a significant portion of the disposable income in the United States. This group not only prefers alternate materials, but they are also purchasing better quality goods.

Another factor driving the shift in market share is new home construction. Homes are not only increasing in square footage, but areas in which carpet and vinyl once were dominant—living rooms, dining rooms, kitchens, and baths—have seen an increased demand

for hard surface products. Kitchens, bathrooms, and entryways have been a significant factor in the gains made by ceramic tile, and hardwood and laminates are being specified in place of carpet for living rooms, dining rooms, and occasionally bedrooms.

Growth in market share for hardwood and laminates has been spurred by new product offerings designed for a diverse range of applications. These products include specialized milling to facilitate ease of installation, and include both standard board widths and wide planks. Hardwood products are essentially engineered materials that allow for a variety of design and installation options. Long-strip glueless and solid floors, prefinished flooring, and specialty design inlays are common options available to the residential customer. Wood choices range from the standard and ever popular maple, oak, and cherry to a number of exotic woods, and include such diverse materials as cork and bamboo. Engineered wood floors for high traffic and commercial space include products impregnated with acrylic.

Laminate flooring is an engineered and manufactured floor product that is lower in price than standard hardwood flooring. Laminate products have found wider acceptance over the last 3 to 5 years because the product has benefited by an increased array of products, improved product quality and durability, and an expanded distribution network. The product line has also benefited from the increased availability of trained installers familiar with laminate products and innovations such as glueless mechanical locking floor systems.

Ceramic tile also continues to grow in popularity in the United States. The Tile Council of America reports that per capita usage has increased from 5 sq ft per person in the 1980s to approximately 9.0 sq ft per person in 2002. Unfortunately for U.S. manufacturers, in 1985 imports made up 55% of that usage, and today imports account for approximately 77%. Of the 2.88 billion square feet of ceramic tile sold in the United States in 2003, only 662 million square feet were produced domestically.

The number of domestic ceramic tile producers has dropped dramatically as the trend toward a few large companies buying out smaller family-owned factories continues. Many smaller family-owned factories have simply gone out of business because they have been unable to compete with the lower sales prices available from the larger mass producers. Glazed floor tile that sold for \$0.80 per sq ft in 1990 sells for \$0.65 today, despite an increased array of product choices and designs. European trends toward large-format porcelain floor tile have also made their way into the United States. In the late 1980s and early 1990s, 8 × 8-in. glazed floor tile was most popular, followed by 12 × 12-in. glazed tile. Today, most U.S.-manufactured tile has trended toward large-format tile, up to 18 × 18-in. wall tile, while the majority of the 8 × 8-in. tile, along with new creative surface textures, is being imported. Principal tile-exporting countries to the United States are Italy, Spain, and Mexico.

Vinyl flooring, including both tile and sheet, has lost market share to hardwood and laminate, and to a lesser extent to ceramic tile. Manufacturers have been working hard to maintain market share while maintaining a nearly constant price per square foot. New design motifs with tile look-alike patterns and surfaces have been critical to retaining market share. Nevertheless, the sales of vinyl high-end goods have been steadily declining in favor of lower priced vinyl products. Although vinyl once was second only to carpet as a product of choice in remodeling, less than 22% of vinyl sales were to repair and replacement orders in 2003. At the same time, sales of less expensive vinyl products have increased 50% to 70%, depending on geographic location, as durability and price influence commercial and institutional purchase decisions. Schools, hospitals, and retail space have accounted for a large portion of these sales.

Specialty flooring covers a wide array of products, including terrazzo, natural stone, commercial nonskid surfaces, and so forth. This product group has been nearly constant at a 4.4% market share over the past 5 years. Each of the products included in the specialty flooring category are normally chosen for either a specific architectural effect or a specific functional purpose. These products are normally selected for specific projects, and as such are less subject to market swings associated with commodity-oriented alternate materials.

Sales and Distribution

The sales and distribution of flooring materials have undergone significant changes in the past 10 years. These changes have been brought about by consolidation of the manufacturing community within individual market segments, consolidation between segments, and the market influence of large national retail outlets. These retail chains can influence pricing through their volume requirements and the pressure they can exert on the manufacturer. These macro changes have also resulted in substantive changes throughout the rest of the distribution chain, particularly at the locally owned flooring sales centers.

Consolidation has certainly been evident within the carpet industry—Shaw Industries, Mohawk, and the Beau lieu Group, three of the largest U.S. carpet manufacturers—have all grown through acquisition and now dominate carpet manufacturing in North America. This consolidation has afforded these firms cost efficiencies through reduced overhead and the ability to dedicate individual carpet mills to specific brands and/or quality levels of product with fewer changeovers and larger operating runs. In addition, both Shaw and Mohawk have become more independent in their distribution and broader based in their product offerings. Shaw has gone so far as to open its own showrooms and independent sales centers, and both Shaw and Mohawk have broken away from the large industry shows (such as the annual “Surfaces”), and are doing their own trade shows that focus solely on their product lines.

Consolidation has also occurred in ceramic tile manufacturing. Two of the largest U.S. tile producers—Dal-Tile and Florida Tile—have been sold in the last 5 years. This included Mohawk’s acquisition of Dal-Tile to create the largest flooring manufacturing company in the United States. In addition, Marazzi (Italy) and Rocca (Spain) have either acquired U.S. manufacturing capacity or built plants of their own in the United States. As a result, the U.S. ceramic tile industry is, in large part, dominated and controlled by foreign interests.

On the distribution side, Home Depot and its Expo Centers has become the largest outlet for flooring in the United States. The company’s purchasing power has put tremendous pressure on manufacturers to control cost and has had a negative impact on some independent dealers. The outcome has been increased focus by independent carpet and floor retail stores on higher quality goods, custom products, and design assistance. This is particularly true with hardwood and ceramic tile, and the trend has been complemented by the company’s support and training of well-qualified installers. Many of these stores also carry adhesive, grouts, and the requisite installation tools.

Market Segments and Minerals Function

Carpet and Rug

Most wall-to-wall carpet is produced with a three-layer composite backing that includes a primary and secondary backing with an intermediate adhesive latex binder. The primary backing is usually a polypropylene woven fabric into which the carpet yarns are tufted.

The secondary backing, which is in actual contact with the floor surface, is a woven synthetic fabric that is laminated to the back of the carpet with an adhesive binder. The binder will normally consist of styrene butadiene rubber (SBR) latex in residential carpets or polyurethane foam for commercial and heavy-wear carpets.

The binder is the only element in carpet construction that uses mineral materials. Ground calcium carbonate (GCC) with 60% to 70% passing a 200 mesh screen is generally the filler of choice in residential carpet. GCC is used to lower the cost of the binder, and to increase weight and stiffness. Commercial grades of carpet will frequently use alumina trihydrate (ATH) in place of the GCC. ATH is a mineral fire retardant and is used to increase the UL rating of the carpet where more stringent fire regulations may apply.

Resilient Flooring

Resilient floor covering utilizes GCC, and occasionally titanium dioxide (TiO_2) or talc. Some specific product formulations may require minor amounts of kaolin. With few exceptions, the GCC utilized by this industry will have a whiteness and brightness specification with a minimum Hunter L value of 90, and usually higher. Mineral filler has a distinct impact on the color of the vinyl flooring and must have lot-to-lot color consistency and be totally free of dark specks or contaminants. Graphite specks are particularly detrimental as they may contribute to secondary color rings analogous to petroleum products in water. Depending on the desired color of the product, TiO_2 may be used to adjust and/or stabilize the whiteness of the product.

Talc and kaolin are minor fillers in resilient flooring; both are more commonly used in sheet goods than tile. When used, talc is normally used for color adjustment and as a replacement for both GCC and TiO_2 . Kaolin may be used in specific commercial products, particularly where durability and acid resistance are important functional features.

Ceramic Tile

Ceramic tile production can be distinguished by four uniquely different tile categories, as discussed in the sections that follow. Each type has its own specific raw material requirements and significantly different firing characteristics.

Wall tile is a low-temperature, glazed tile with weak fired strength and 15% to 18% water absorption. Formulas usually include talc and/or pyrophyllite and ball clay. This tile is used on walls and occasionally low-traffic and residential floors. Wall tile will not hold up in high-traffic areas.

Ceramic mosaic tile is a porcelain tile no larger than 2×2 in. It is fired to water absorptions of 0.1% or lower, and formulas use feldspar or nepheline syenite for a flux, and ball clay or kaolin for the clay fraction in the body.

Glazed floor tile (Monocottura) is usually 8×8 in. or larger. It is fired to 2% to 3% water absorption. Formula requirements include feldspar or a local flux, and ball clay that is used for the plastic fraction of the tile composition. Body color does not matter because this tile has a 100% glazed surface.

Porcelain (Porcellanato) is a high-temperature floor tile fired to 0.1% water absorption or lower. Its high strength allows it to be used in the most demanding commercial applications. Body color is important because only a portion of the surface is decorated. This tile requires feldspar or nepheline syenite as a flux. Ball clay and kaolin normally are used in the plastic fraction in the body.

Calcium carbonate is used in some, but certainly not all, tile formulations. When used, the carbonate may be present in either the body or the glaze, or in both. In the body, calcium carbonate helps control firing viscosity and reduces the temperature at which

the tile will cure. In the glaze, carbonate tends to reduce the gloss or luster and is used to enhance the color of several pigments such as chromium. Calcium carbonate, however, will increase brittleness and is normally restricted to wall tile.

Specialty Flooring

Terrazzo, nonskid epoxy industrial floor paints, and rubber are three flooring materials that use mineral products. Natural stone is cut or slabbed and is not really manufactured flooring.

Terrazzo is a composite material poured in place or precast. It consists of marble, quartz, glass, or another suitable chip, and is poured with a binder. The terrazzo is cured, ground, and polished to a smooth surface or otherwise textured finished surface. Terrazzo chips may include calcareous serpentine, marble, onyx, and so forth, which take on a polish when ground. Chips of other materials such as granite, quartz, and silica pebbles may be used when the surface does not require a polish.

Nonskid epoxy paints are used in a variety of commercial applications ranging from airplane hangers to warehouse floors. These paints utilize fine sand particles that provide skid resistance without creating such a rough texture that they impede oil and grease spill cleanup.

Rubber flooring may be filled or unfilled. Rubber floor mats, runners, and stair treads may contain GCC to lower cost and impart stiffness. Barytes may also be used to increase weight, and ATH is used to provide fire retardance.

Manufacturing Locations

Of all segments in the category of floor covering materials, carpet and rug manufacturing are by far the most geographically concentrated. More than 75% of manufacturing capacity in this industry is concentrated in northern Georgia, with the majority at Dalton, Georgia. Fifteen years ago, there were carpet mills scattered through Alabama, the Carolinas, Georgia, and Tennessee, but today there are only two major carpet mills in the Carolinas, one in Alabama, and one in Tennessee. Conversely, there are 51 carpet mills and finishing houses in north Georgia that together consume more than 590,000 t of mineral filler annually. There are several small mills scattered about the eastern half of the United States, principally in Pennsylvania and Virginia. The only area of major carpet production outside Georgia is in Southern California, where there are 12 mills using about 90,000 t of mineral filler annually.

Resilient flooring manufacturing plants, unlike carpet plants, are scattered about the United States, located strategically to serve major population centers. There are a dozen plants producing tile or sheet goods in eastern Pennsylvania, New Jersey, and New York. Plants are also located in California (5), northern Ohio (3), and scattered throughout the southwest and south-central states of Oklahoma and Texas. Nevertheless, several plants have closed in the last 3 to 5 years, and this trend is expected to continue as the industry consolidates production to reduce costs.

Ceramic tile is produced in several states but is notably concentrated in the states of Tennessee and Texas, where the plants are relatively close to the sources of one or more raw materials. New plant construction includes the expansion of Crossville Porcelain and the new GrantiFiandre plant, both located in Crossville, Tennessee, and Dal-Tile's new facility in Muskogee, Oklahoma. There are also several large ceramic tile plants in Mexico, although many of the raw materials are sourced in the United States. As noted previously, nearly 78% of the ceramic tile sold in the United States, especially floor tile, is imported, with 35% of these imports coming from Italy, 18% from Spain, 13.5% each from Mexico and Brazil, and the remainder from other countries.

Table 3. Raw material use by flooring industry segment, kt

Product Sector	ATH	Ball Clay	Calcium Carbonate	Kaolin	Silica	Feldspar	Talc	Wollastonite
Carpet	43	NA*	670	NA	NA	NA	NA	NA
Ceramic tile	NA	452	40	160	217	398	14	9
Vinyl sheet and tile	NA	NA	714	20	NA	NA	5	NA
Hardwood	NA	NA	NA	NA	NA	NA	NA	NA
Laminates	NA	NA	NA	NA	NA	NA	NA	NA
Specialty flooring	24	NA	5	2	25	NA	4	NA
Total	67	452	1,429	182	242	398	23	9

* NA = not applicable.

Raw Material Requirements

The specifications for individual minerals used in the flooring industry vary greatly, both by end use and by manufacturer. In many instances, the minerals provided are engineered blends that satisfy specific performance parameters required by the manufacturer.

Table 3 provides a general summary of the raw materials consumed by the various industry segments, including tile production in Mexico. It should be noted that the raw materials figures for ceramic tile are very generalized because there are at least four different primary tile types, including variations of each tile group. The same could be said of specialty flooring materials because so many different products and processes are included in the category.

Ball clay producers benefit from the trend toward porcelain tile. The consistent chemistry and processing characteristics of commercially produced ball clay are necessary for porcelain tile, but engineered clay blends designed to meet specific customer formulations must be used. Thus, the technical capabilities and support available from the clay producer has become increasingly critical to sustaining customer relationships.

Feldspar production from North Carolina has increased in volume because of the trend toward porcelain. The combined sodium and potassium content of 10%–15% makes this a good material to flux the body to below the required 0.50% water absorption.

Nepheline syenite from Arkansas currently is being used for glazed floor tile and is being evaluated for porcelain. The higher iron content of the Arkansas nepheline syenite, 3% to 5%, will not produce a white porcelain; however, Canadian nepheline syenite, with lower than 0.3% iron content, is being investigated for white porcelain needs.

Tables 4 and 5 show variations in the raw materials requirements of the different tile species.

SUMMARY AND CONCLUSIONS

A large volume of mineral materials is consumed by the floor covering industry. The changing dynamics of this industry, including major switches between market segments, consolidation among both consumers and producers of mineral products, pricing pressures driven by changes in the distribution chain, and engineering and architectural design trends continue to impose changes on the mix of minerals supplied to flooring manufacturers. Although GCC is expected to continue to dominate mineral use in flooring, specification revisions and increasing functional performance requirements are having an impact on even this mineral staple.

Particle packing, flowability, and controlled particle size distribution are just some of the issues being raised by manufacturers. It is becoming even more critical, then, for the mineral supplier to be able to provide competent technical support to the end user.

Table 4. Raw materials requirements for wall tile formulas

Raw Material	Composition Range, %
Non-talc	
Sodium feldspar	17–14
Silica	23–30
Whiting (calcium carbonate)	9–10
Ball clay	47–50
Fast fire	
Clay	41
Pyrophyllite	8
Talc	24
Scrap	12
Wollastonite	15
Other	
Pyrophyllite	0–35
Talc	0–66
Whiting	5–6.5
Wollastonite	0–10
Ball clay	28–43
Silica	0–18
Shrinkage	0.2–0.7

Table 5. Raw materials requirements for floor tile

Raw Material	Porcelain (Fast Fire), %	Monocottura (Glazed), %
Ball clay	23	45
Shale flux		55
Feldspar	52	
Kaolin	19	
Silica	5	
Talc	1	
Shrinkage	10	7.5

As demands for mineral performance increase and more rigid specifications are imposed, pressures to eliminate or reduce unit prices for mineral products also increase. The emergence of the “big box” building materials stores and their dominance in the sale of flooring products has placed enormous pressures on flooring manufacturers and consequently on the mineral producer. Unfortunately,

this pressure also has led to a decline in product quality, particularly in imported porcelain floor tile.

Two significant trends dominate the U.S. floor tile industry: the trend toward porcelain tile and the trend toward only large companies being economically competitive. The sale price for ceramic tile continues to drop, which is forcing companies to lower their production costs. In the case of porcelain tile, this has forced producers to push the limits of production specifications as they turn out thinner, lighter weight tile with higher water absorption and reduced strength. This favors large producers who can buy state-of-the-art production facilities and spread their overhead costs over millions of square feet.

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Gypsum Plasters and Wallboards

Paul J. Henkels

INTRODUCTION

Gypsum is one of the most widely used and versatile minerals. In the United States, gypsum resources are considered inexhaustible. Most gypsum is used to make wallboard for homes, offices, and commercial buildings; a typical new American home contains more than 7 t of gypsum (Olsen 2001). Moreover, gypsum is used worldwide in cement and concrete manufacture for highways, bridges, buildings, and many other structures that are part of everyday life. Gypsum also is used extensively as a soil conditioner on large tracts of land in suburban areas, as well as in agricultural regions. This chapter focuses mainly on the United States because it has the largest amount of gypsum in the world and because usage statistics are readily available through the U.S. Geological Survey (USGS) and organizations such as the Gypsum Association.

Gypsum has a long history of usefulness to humans. The earliest known use of gypsum plaster dates back some 8,000 years with the discovery of its use in Anatolia. Around 3700 BC, at the time of the pharaohs, Egyptians observed that gypsum rock broke down into a powder when exposed to fire, and that when it was mixed with water, it would form a putty that could be plastered on rough mud brick or stone walls to make a smooth finish. Iranians, Babylonians, Greeks, and Romans were familiar with the art of gypsum plastering as well. Examples of its use include the walls of Jericho, the pyramid of Cheops, the palace of Knossos, and the decorated interior walls of Pompeii.

Although gypsum was used in a limited way for ornamental purposes down through the centuries, gypsum plaster did not achieve wide acceptance because its quick (25 to 30 min) setting, or hardening, time made it difficult to use. The first real understanding of gypsum chemistry was developed in France about 1760 and the gradual growth of its present utilization dates from that time. Craftspeople firmly steeped in tradition, however, were slow to accept scientific explanations of gypsum properties. As a result, gypsum manufacture has developed into a modern industry only in the last few decades.

Gypsum refers to the dihydrate form of calcium sulfate. Anhydrite, the other principal calcium sulfate mineral, has a very limited use, to the point that separate statistics for it are not always kept but are usually included with those for gypsum.

Although often found in close association, gypsum and anhydrite have important chemical differences. Anhydrite is the anhydrous form of calcium sulfate (CaSO_4), whereas gypsum is the dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) form. Two molecules of combined water

result in significant differences in hardness, density, and solubility between the two minerals; however, the most important difference is their thermal properties. Gypsum, following the application of a modest amount of heat, can be converted to the hemihydrate of calcium sulfate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$; also known as *plaster of paris*), an intermediate product on which is based more than 90% of the value of all calcium sulfate end products. Anhydrite, on the other hand, is inert at these temperatures, and its uses are limited to those few cases where calcium sulfate in the anhydrous form has an advantage.

The first known utilization of gypsum in the United States was as a fine ground material for a soil conditioner at about the time of the American Revolution, in the late 1700s. Since that time, the term *land plaster* for ground gypsum has remained in use. Another cementitious material—lime or calcium oxide—was the preferred material for plastering, but by about 1870 a method for retarding gypsum plaster from setting quickly was discovered. Today gypsum has replaced lime almost completely as a plastering material.

In recent years, gypsum products sold in the United States reached a total valuation of approximately \$2.7 billion per year, as illustrated in Table 1.

STRUCTURE OF THE INDUSTRY

The gypsum industry is well developed in technologically advanced countries such as the United States, Canada, Western Europe, and Japan, where it is organized into large, well-financed, vertically integrated companies. In countries where gypsum usage is not as extensive, its production usually is accomplished by small operators with limited objectives and capabilities. Several North American and Western European companies operate on an international basis through subsidiaries or other arrangements. Western European companies in particular have significantly increased their international presence in recent years with the new global economy.

In 2002, 25 companies operated 50 mines that mined and/or processed gypsum in the United States. These range in size from large, multiplant, multiproduct companies to small, one-plant, one-product companies serving local markets for portland cement (as a retarder) or for agricultural gypsum. More than 75% of the gypsum was mined by 6 companies at 30 mines. Eight companies have calcining and wallboard manufacturing facilities, and the remaining 17 ship only uncalcined products. In 2002, the United States had 61 active calcining and manufacturing plants (Olsen 2002).

The larger companies are completely integrated—from mining and processing to marketing and distributing the finished products.

Table 1. Gypsum products (made from domestic, imported, and synthetic gypsum) sold or used in the United States, 2000–2002, by use

Use	2000		2001		2002	
	Quantity, kt	Value, \$1,000	Quantity, kt	Value, \$1,000	Quantity, kt	Value, \$1,000
Uncalcined						
Portland cement	3,800	44,100	2,690	34,400	2,620	32,400
Agriculture & other	1,920	28,100	844	22,000	985	23,300
Total*	5,720	72,200	3,530	56,400	3,600	55,700
Calcined						
Plasters	896	110,000	1,390	167,000	967	146,000
Prefabricated products†	22,900	2,680,000	24,300	2,250,000	28,500	2,480,000
Total calcined†	23,800	2,790,000	25,700	2,410,000	29,500	2,630,000
Grand total†	29,500	2,860,000	29,200	2,470,000	33,100	2,690,000

Source: Olson 2001, 2003.

* Data may not add to totals shown because of independent rounding.

† Includes weight of paper, metal, or other materials.

As the importance of wallboard has grown, some companies also have built paper mills to supply part or all their needs for face and back paper used on the board. This trend toward vertical integration has resulted in strong competition and the continuing need to control all phases of the business. As a consequence, there is practically no market for supplying crude gypsum rock to calcining–manufacturing companies.

World Trade

World trade in gypsum consists primarily in the movement of crude gypsum rock, although, to a limited extent, certain manufactured products do move across international boundaries. The United States is both the world's largest producer and importer of gypsum rock. Canada is the largest exporter of gypsum, almost all of it in the form of crude gypsum rock to the United States. In 2002, Canada was the third largest producer of gypsum rock.

In Western Europe, Spain is both the largest producer and exporter of gypsum; the country's exports are in the form of crude gypsum rock. Germany, France, and the United Kingdom also produce significant quantities.

Iran was the second largest producer of natural gypsum in 2002 and accounted for around 90% of Middle Eastern output (Olsen 2002).

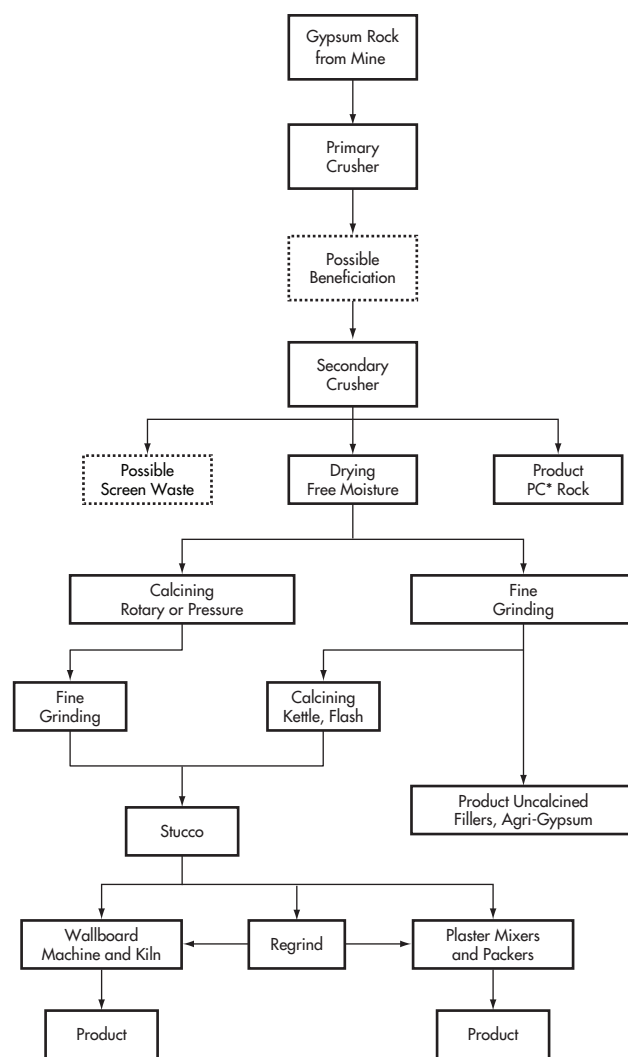
The primary reason for the limited amount of world trade in gypsum or its products is the widespread occurrence of deposits and in the relatively low ratio of manufacturing costs to product weight. Freight, therefore, is a major segment of delivery cost, a fact that discourages shipping gypsum long distances across international boundaries. For further discussion on the occurrence and place value, and for statistics on U.S. imports, the reader is referred to the Gypsum and Anhydrite chapter of this book.

BASIC PROCESSING METHODS

The processing of gypsum can be divided into three basic steps: (1) rock preparation, (2) calcining, and (3) formulating and manufacturing. This is illustrated graphically with the flow chart in Figure 1. The specifics of each step will vary with the quality of the gypsum and with the type of final product.

Rock Processing

Primary crushing is accomplished by gyratory, jaw, roll, or impact crushers, depending on the size of the mine-run rock, the desired throughput, and the type of subsequent processing. Secondary



*PC = portland cement

Figure 1. Gypsum process flow block diagram

crushing is done with a variety of standard units, but hammer mills, roll-type, and cone-type crushers are most commonly utilized. Fine grinding of uncalcined gypsum is generally accomplished by air-swept roller mills fitted with integral air separators for better particle size control, although high-energy impact mills with air classifiers also have been used.

Both primary and secondary crushing steps usually are conducted with vibrating screens in the circuit, in part to maximize crushing efficiency and to reduce the production of ultrafines, but also to recover portland cement rock, which is the first marketable product of gypsum processing. The particle size of portland cement rock will vary with the requirements of each individual cement plant, but in the United States, it most often falls within a range of 38 to 51 mm top size by 6 to 13 mm bottom size.

Drying (the removal of free moisture) may occur either before or after the secondary crushing stages, depending on the amount of free moisture in the mine-run rock. Because 5-mm crushed gypsum is difficult to handle, particularly if wet, drying often is required to ensure the free flow of material in subsequent steps. This is accomplished most often in rotary dryers and must be carefully controlled so that the temperature of the rock does not exceed 49°C, the point at which dissociation of combined water begins to take place.

In many cases, the purity or quality of mined gypsum is sufficiently high that it can be used without upgrading; however, beneficiation techniques are sometimes employed to meet the required specifications. The most common form of beneficiation is simple classification by particle size with dry screening, air separation, or other means wherein a size fraction containing a significant portion of impurity is discarded. In general, this method is used to reduce clay and/or sand (soil) impurities. In some cases, impurities, which are harder than gypsum and which tend to concentrate in coarser size fractions after crushing, also can be reduced by screening.

Washing and/or wet screening is used in a few cases, particularly where the need for whiteness exists. The use of gravity separation with high-density media for the removal of impurities currently is employed at two operations in Canada. In many cases, gypsum is amenable to other gravity methods of beneficiation, froth flotation, or to color sorting. Some laboratory work has been reported on these approaches (MacPherson 1950; French 1967). Their relatively high cost and the availability of high-quality deposits of natural gypsum and sources of synthetic gypsum, however, usually eliminate the need for these types of beneficiation.

Synthetic Gypsum

Over the last 25 years, the use of synthetic gypsum has gained in popularity. It often replaces natural gypsum and is used as feedstock in greenfield plants, particularly in industrialized nations. Today, about 25% of the gypsum consumed for wallboard manufacture in the United States is from synthetic sources. Its use is expected to continue to grow over the next 10 to 15 years. The availability of synthetic gypsum is lowering barriers for competing manufacturers entering new geographical markets.

Synthetic gypsum originates from several industrial processes. Mainly, it is a product resulting from industrial acid neutralization, or flue gas desulfurization (FGD), of fossil fuel combustion in power plants and can be as pure as 98% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$.

By far the largest amount of synthetic gypsum is obtained from the production of wet phosphoric acid from phosphate rock. But high levels of impurities and often low levels of radon render phosphogypsum useless or reduce it to insignificant levels. Other sources of synthetic gypsum include small quantities from the production of organic (e.g., citric, lactic, tartaric, and oxalic) and inorganic (e.g., boric) acids.

Today, it is common to use synthetic gypsum from FGD for wallboard manufacture. Its ever-increasing availability is a result of environmental regulations such as the Clean Air Act Amendments of 1990.

Synthetic gypsum usually is available in its granular form (30 to 60 μm), with moisture content varying from 6% to 15%. The product normally is dried by the consumer to less than 1% moisture content prior to calcining and then handled in the same manner as natural gypsum throughout the manufacturing process. The major advantage of using synthetic gypsum is its low cost, so it is a matter of economics. The cost of transportation is usually the determining factor. As requirements for reducing sulfur dioxide emissions are implemented throughout the power-generating industry, the availability and use of synthetic gypsum are likely to increase in the foreseeable future. The Flue Gas Desulfurization chapter in this volume contains additional information.

Calcining

In the gypsum industry, calcining reduces the dihydrate of calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to the hemihydrate ($\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$) or anhydrous (CaSO_4) forms. In the very early history of making gypsum plaster, pieces of gypsum rock simply were heated in an open wood fire to bring about dehydration. Then crude ovens were built, into which fist- or head-size particles of gypsum were calcined, and, later, vertical kilns were used. The latter still may be found in less technically developed countries, operating with crude burners, and with little or no prior preparation of the rock. Where the utilization of calcined gypsum has developed on a broad scale, more sophisticated methods of calcination have evolved that require preparation of the gypsum as previously described.

Hemihydrate

Considerable research has been performed on the thermodynamic properties of the $\text{CaSO}_4 \cdot \text{H}_2\text{O}$ system (Kelley, Southard, and Anderson 1941; Riddell 1950), and therefore extensive literature exists in this regard. Four calcined products are manufactured on a commercial scale: the two forms of hemihydrate (alpha and beta); a soluble anhydrite; and an insoluble or dead-burned anhydrite. Within the industry, all the hemihydrates usually are called *stucco* regardless of how they are processed, but this term should not be confused with the portland cement and sand mixture used for exterior application on buildings. The term *plaster of paris* often is used for hemihydrate; its origin comes from the large deposits of gypsum that were mined from under and near the city of Paris.

Hemihydrate is the only lower hydrate of calcium sulfate for which an identity has been established with any degree of certainty (Riddell 1950). Although two forms of hemihydrate—alpha and beta—have been identified, the beta form has a higher energy content and a higher solubility rate. The two forms can only be distinguished by sophisticated analytical methods. The alpha form of hemihydrate is less reactive than the beta form and has a slower rate of strength development. These are disadvantages when used for stucco; nevertheless, rehydrated alpha hemihydrate makes a denser, stronger plaster, which is advantageous in other uses. Table 2 gives the principal characteristics of these two forms of hemihydrate.

Alpha hemihydrate can be prepared by dissociation of gypsum in a water-saturated environment above a temperature of 97°C. This usually is accomplished at an elevated pressure in an autoclave in the presence of steam. Beta hemihydrate can be prepared by dissociation of gypsum in a vacuum at 100°C, but in practice it is done in an undersaturated environment at atmospheric pressure.

The greatest use of calcined gypsum is in the manufacture of wallboard and the formulation of plasters for building markets.

Table 2. Characteristics of alpha and beta hemihydrates

Type	Normal Consistency*	Setting Range, min†	Typical Set Expansion, %	Average Compressive Strength, kPa, Dry†	Reaction
Alpha	30–45	15–25	0.30	38,000	Neutral
Beta	64–76	10–20	0.20	14,000	Neutral

* Parts water to 100 parts stucco by weight to make a pourable slurry.

† Per ASTM C472-99(2004).

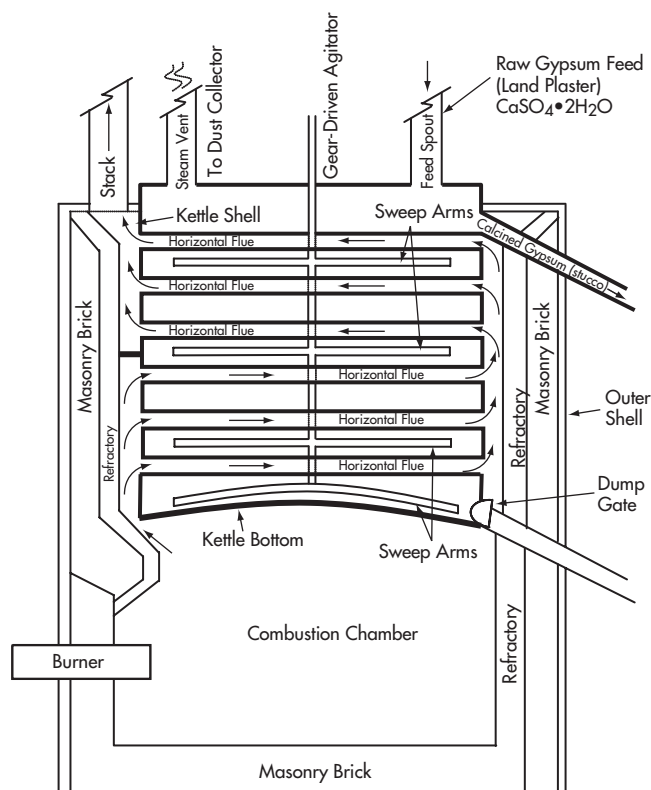


Figure 2. General sections of a calcining kiln

Beta hemihydrate gypsum is suitable for construction applications where early high-strength development is necessary. Because alpha hemihydrate makes a denser, higher-strength cast, it is preferred for industrial uses where these characteristics are important. Other factors considered in the utilization of these two forms are cost (beta is considerably less expensive to make) and water demand (alpha requires less water, above that which is necessary for rehydration, to make a slurry of equivalent consistency or viscosity).

Although other methods of calcining gypsum are gaining in popularity, the kettle is still the most commonly used vessel. Its basic design originated around 1870, and its general features are illustrated in Figure 2. In its simplest form, the kettle is a cylindrical steel vessel with a height greater than its diameter, and is enclosed in a refractory shell (Figure 3). Heat is introduced in a firebox below the vessel and flows upward around it. To improve heat transfer to its pulverized gypsum contents, four or more horizontal cross-flues are installed. The gypsum is agitated by means of a vertical, rotating shaft with sweeps or rabble arms that stir the con-



Figure 3. Exterior view of gypsum kettle

tents. Normally operated in continuous mode, the kettle is filled from the top, and the overflow is directed through a side opening in the kettle. The kettle also is used in batch mode for plaster products, especially in the United States.

For the production of stucco in wallboard manufacture, pulverized gypsum (land plaster), with a fineness of about 90% of –100 mesh is metered into the kettle at a constant rate by a screw or rotary feeder supplied through a large bin. Continuous kettles discharge finished stucco through an overflow apparatus connected to the hot pit or product bin. As fresh, cool land plaster enters the kettle top, it sinks through the hot, less dense, calcining mass, forcing calcined stucco out through the overflow pipe as a result of this density displacement. Stucco typically is discharged from the continuous kettle at 138 °C to 154 °C. One variant on the continuous kettle is the use of submerged combustion where the process takes place inside the kettle shell, resulting in better energy efficiency but producing a more violent calcination.

A kettle is run in a batch mode to produce stucco with high plasticity, high strength, and high density—characteristics that are desirable for construction and industrial plaster. The full cycle from filling to dumping the batch requires 1.5 to 3 hr. Although kettles have been built for 1.8- to 27-t capacity, the normal size is 10 to 18 t. A normal cycle requires 25 to 40 min to fill the kettle and an additional 90 to 120 min to bring the entire mass up to the desired temperature after the kettle is filled. Dumping is usually accomplished in 5 min or less, with the finished stucco being fed by gravity through the dump gate into the vented hot pit where it is held for up to 1 hr to allow as much of the entrapped steam as possible to escape before it is transferred to a storage bin at the point of use.

During calcining, gypsum begins to lose its water of crystallization when it reaches a temperature of 43°C to 49°C. During the

filling part of the cycle when gypsum is filling the kettle, the firing rate is controlled to keep the kettle contents at a temperature of about 100°C. When the kettle is filled, the firing rate is adjusted accordingly; different firing rates will produce different properties in the finished stucco. As the temperature of the mass rises, water of crystallization is released as steam, and at 116°C to 121°C the mass boils vigorously as the vapor pressure of the released steam reaches atmospheric pressure. When boiling ceases and little or no steam is released, the contents of the kettle settle to about 85% of its original volume. This quiet period indicates that most of the gypsum particles are dehydrated to the hemihydrate form. Heating continues to dry the mass until its temperature reaches 149°C to 166°C, at which point it is dumped into the hot pit and the cycle is complete.

The product of the foregoing operation is known as *first-settle stucco*, and it contains from 5% to 6% combined water, compared with 20.9% contained in pure gypsum; approximately 75% of the water of crystallization is driven off. Because this reaction takes place at atmospheric pressure in an undersaturated environment, most of the resulting hemihydrate is in the beta form.

Aridized stucco refers to first-settle stucco to which a small amount of a soluble salt is added during the filling part of the cycle. In general practice, approximately 0.68 kg of calcium chloride (CaCl_2) is used per ton of stucco; the exact amount depends on the purity of the gypsum rock and what impurities are present. This treatment increases the vapor pressure in the kettle, allowing the calcination to occur at a lower temperature. The resulting stucco is used in the formulation of many industrial plasters.

Low-water-demand stucco also can be produced by adding water to the kettle after the batch calcination cycle is complete. The stucco is quenched to about 93°C and then reheated to drive off excess water before dumping it into the hot pit. Alternatively, low-water-demand stucco can be made by adding a measured amount of water to the stucco after it has left the kettle.

Other methods have been utilized in the production of beta hemihydrate. Jacketed hollow-flight screw conveyors have been limited use. The hollow-flight screw and jackets are filled with circulating heated liquids or gases. In recent years, flash calcination techniques have gained in popularity, especially with the rising use of synthetic gypsum. Air-swept heated impact mills are becoming more commonly used for calcining, because they can readily accept fine and coarse rock or synthetic gypsum feedstock. Flash calciners that concurrently grind and calcine gypsum rock are becoming popular as well.

Flash calcining in a hot air stream with subsequent separation in a cyclone or baghouse dust collector can be done either after or in conjunction with final grinding. High-temperature hammer mills or roller mills have seen increased use as hot air-swept grinder-calciners for efficient stucco production. These mills typically are fed 50-mm gypsum rock. In some parts of the world, the rotary kiln still is used for calcination, especially for construction plasters, but in the United States these have been replaced almost totally by kettle or flash calciners.

Pressure calcining in steam autoclaves, with or without the addition of a crystal modifier, is used to make high-strength plasters for certain industrial uses. The gypsum may be introduced into the vessel either as a crushed, sized rock or as a slurry; the stucco is dried as soon as calcination is completed. This method produces all alpha hemihydrate and is relatively expensive. Its use is limited to those products requiring high-strength specialized plaster. Alpha hemihydrate also may be produced by dehydration of gypsum in hot, salty water.

Soluble Anhydrite

If desired, a second-settle stucco can be made after reaching the first boil and first-settle stages. This is done by increasing the temperature to about 177°C, the point that gypsum again starts to boil and give off steam. This second boil is of shorter duration and less vigorous than the first, because there is a smaller percentage of water of crystallization to remove. The batch material is dumped at about 210°C, the point at which almost all the water of crystallization has been removed. The dumped material usually is referred to as *soluble anhydrite*. It differs from first-settle stucco in that it has less plasticity, but after rehydration it has a greater density and strength. Also, it has a high affinity for moisture and is utilized as a desiccant.

Insoluble Anhydrite

Dead-burned gypsum, or insoluble anhydrite, is made in beehive kilns, rotary calciners, or flash calciners using high temperatures (up to 540°C). The result is anhydrous calcium sulfate that does not rehydrate at any appreciable rate; it is the least soluble form of calcium sulfate (Riddell 1950). The primary uses for dead-burned gypsum are to make Keenes cement (chemical accelerators are added to restore its setting properties) and to produce a mineral filler by fine grinding.

Hydraulic gypsum refers to lump (25 mm) gypsum that is heated to about 899°C, the temperature at which calcium sulfate begins to dissociate, releasing sulfur as sulfur dioxide (SO_2) gas. This increases the calcium oxide (CaO) content, resulting in a material which, when mixed with water, is slow-setting compared to other plasters. It provides a very hard, dense product that is quite durable, sometimes referred to as *Estrich gypsum* (a German term). Although it has been used in Europe as flooring material, it has not found an application in the United States.

Formulation and Manufacturing

Calcined gypsum products commonly undergo additional processing such as cooling, grinding, mixing with additives, or rehydrating and casting into block or wallboard. Kettle stucco, the most common calcined material, is a mixture of calcium sulfate particles in varying states of dehydration ranging from dihydrate to anhydrous forms; the forms vary according to the method of calcination. The amount of variation is minimized by carefully controlling the calcining process, which may be a factor in the type of treatment subsequently applied to the stucco.

The earliest attempt at formulating calcined gypsum to improve its utility probably was the addition of fibers and/or aggregates; however, the single most important discovery was that the setting time could be either retarded or accelerated to very exact rates by adding certain materials to stucco (plaster of paris). When mixed with water, properly calcined gypsum will have a natural setting (hardening) time of 15 to 25 min, which is usually too fast for satisfactory application on walls or ceilings. In the mid 1870s, a method was discovered that retarded the setting to 2 or 3 hr (or longer). This led to the manufacture of "slow-set plaster," which was the key to the rapid growth of the use of gypsum in the U.S. building industry. Retarders are made from organic compounds from several different materials. For the most part, these are formulated and manufactured by the major gypsum companies for their own consumption. Accelerators can be natural or synthetic salts, such as potassium sulfate, or gypsum itself. Finely ground raw gypsum is commonly used to accelerate the set of stucco for the manufacture of wallboard.

With the correct proportions of these materials, gypsum plaster can be accelerated to set within 2 to 3 min, or be retarded so that

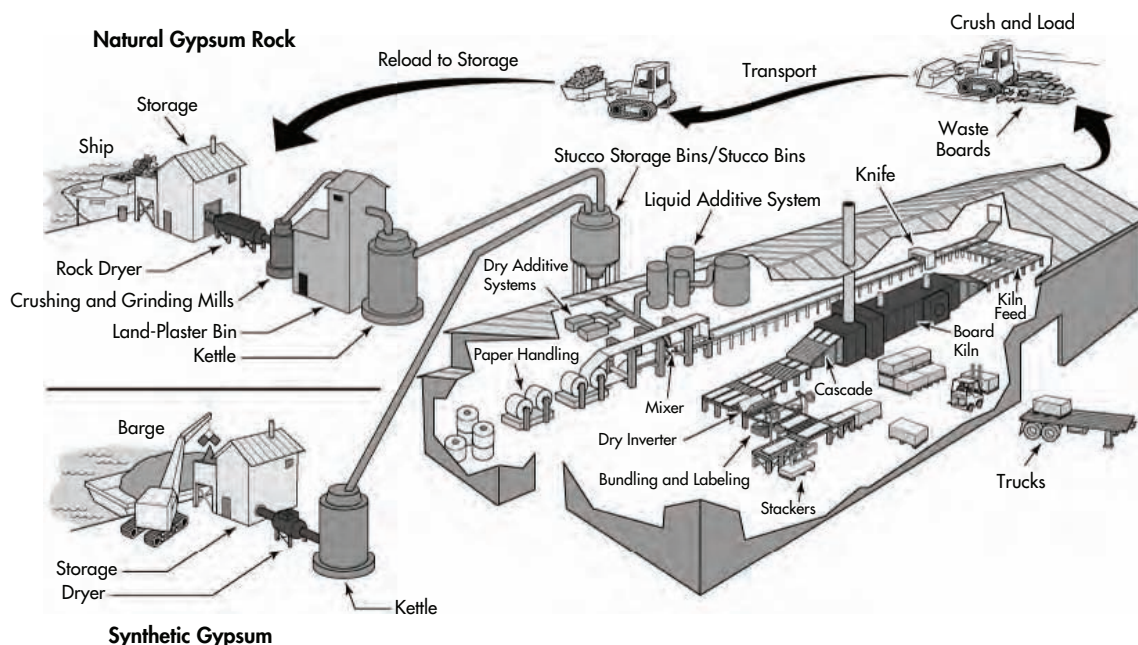


Figure 4. General process flow of a wallboard plant

it does not set for several hours. Adjustment of the set can cause variations in other properties, especially strength, so care must be exercised when adding these materials.

The type of stucco and the characteristics of the plaster being formulated are controlled by other additives mixed in precise proportions prior to bagging; these formulas are the result of extensive research. Plasters premixed with sand, expanded perlite or shredded polystyrene, and exfoliated vermiculite aggregates are available to the building trades; a wide range of plasters also are formulated for industrial use.

Gypsum is often re-ground after calcining to impart special qualities to the stucco. The classic buhrstone mill once used for this purpose has been replaced by high-energy impact mills. When stucco is used with aggregate (as for "sanded" or "perlited" wall plaster), a tube mill is used for regrinding. Roller mills operating in closed circuit with air separators often are used in conjunction with rotary kilns.

One of the early uses of gypsum as a construction material was to cast it into blocks or tile. Continuous casting machines were developed for this purpose along with drying kilns to hasten the removal of excess moisture. Blocks are cast either as solid masses or as hollow tiles, and can be made in any desired dimension. Metal reinforcement is used in some products, and others are cast into a metal form to produce floor access panels. The addition of fiber for reinforcement is a common practice; the use of an accelerator hastens the initial set of the stucco in the mold.

The largest use for gypsum today is in the manufacture of wallboard; nearly 90% of the gypsum consumed in the United States is used for this purpose. In its simplest form, wallboard is a thin, flat slab of formulated gypsum made by casting a slurry of stucco and water in a paper envelope; that is, a gypsum core with specially prepared paper bonded to both sides and edges. This is a sophisticated product, made on high-speed, highly automated machines to a wide range of precise specifications.

The bond between the paper and the gypsum core in wallboard is produced by the growth of gypsum crystals into the fibrous pores of the paper as the stucco is rehydrated, and not by the use of adhesives. Although significant research has determined the formulas for the gypsum slurry used in wallboard, it essentially consists of beta hemihydrate, an accelerator, fibers, starch, and a foaming agent, with stucco making up at least 95% of the material used prior to mixing with water. Figure 4 shows a general process flow diagram of a wallboard plant.

In the wallboard-manufacturing process, the dry components are mixed with water in a high-energy mixer designed for a continuous flow-through of material. The resulting slurry is fed onto a moving strip of paper, the edges of which are turned up to form a wide, shallow trough. This batch of slurry and paper then moves under a second strip of paper, and the roughly formed board moves between edge guides (Figure 5) and under a 610-mm-diameter roller called a *master roll*, or a stationary steel forming plate, that precisely imparts the specified width and thickness of the board. The edges of the bottom paper are turned over to form square or rounded corners, and an adhesive is added to bond the top paper to the lower paper along the edges. The thickness of the board can be adjusted by raising or lowering the master roll or forming plate. The now fully formed board moves along on a flat conveyor belt several hundred meters in length.

The speed of the board line varies with the design of the machine and the type of wallboard manufactured, but it usually ranges between 0.5 and 3.0 m/sec. The length of the board line is designed to provide sufficient time (2 to 5 min) for the stucco to set. At that point the moving strip is cut at specific intervals by a rotating knife to produce individual boards for drying in order to remove excess free moisture. This is accomplished by moving them through a continuous, multideck board kiln that is heated directly by hot air, or indirectly by steam coils. Drying is closely controlled to prevent recalcining the gypsum core.

After emerging from the board kiln, the board moves automatically through devices that smooth its ends and cut it into specified lengths. Usually, one surface ("the face") is made with light colored, smooth textured paper that will form the finished (painted) wall surface. Two boards are placed with these surfaces together ("face to face") to protect them as they are bundled for shipping. If specified, the board can move onto a finishing machine where a special surface film is added, such as vinyl or imitation wood veneer paper, to make a predecorated panel. The most popular size of wallboard is 1.2 m \times 2.4 m \times 12.7 mm thick, but a wide variety of sizes is made for specific markets.

Gypsum sheathing is made in the same general manner except that asphalt-impregnated paper is used. To improve its water resistance, an asphalt or wax emulsion also may be added to the core. Plasterboard is a 406-mm-wide board used as a base for plastered walls, instead of wood or metal lath, and is made on the same machine as wallboard. Shipment of the finished products is by truck or rail. Most wallboard plants have large warehouse space at the plant in order to store adequate stocks of various product types and sizes.

Energy Considerations

The gypsum industry is energy intensive, particularly regarding fuel used in rock drying and calcining operations, in manufacturing paper, and in drying excess moisture from wallboard. An average 2.8 GJ is required per 100 m² of 12.7-mm-thick wallboard. The drying of both rock and wallboard usually is accomplished in direct fired kilns (although steam coils can be used for wallboard) in which a clean-burning fuel (preferably natural gas) is required to prevent contamination of the product. The calcination step, particularly when carried out in a kettle, requires the ability to change the intensity of the heat quickly, and either natural gas or fuel oil is preferred, although coal also can be used.

The rise in energy costs over time encouraged the development and implementation of conservation methods, including the investigation of process technology to reduce energy requirements. As a result of increasing energy prices, fuel substitution may be necessary.

Major Categories of End Uses

Gypsum products are divided into several categories based on end uses and/or processing methods. Three major groups are generally recognized: (1) construction products used directly in construction or building material, (2) industrial products used in the manufacture or processing of other materials, and (3) agricultural products. The construction group utilizes about 75% of the gypsum rock used in the United States and produces approximately 95% of total product value. The industrial group uses about 17% of gypsum production but yields only 3% of the product value. Agricultural gypsum accounts for the balance.

The amount produced for each major application varies considerably from country to country, and in many instances the only use of gypsum is in the industrial category as portland cement retarder. In the following section, a few of the more important end uses will be reviewed.

Construction Uses

Gypsum products are used in the building and construction industry as covering and finishing materials. They are not the structural components that provide the frame or support for a building, which are wood, steel, concrete, concrete block, and brick (fired or adobe). It is in the covering of a structural frame (Figure 6), or in the finishing of masonry walls, that gypsum products find their greatest utilization, and they compete in these applications with



Figure 5. Forming section of wallboard machine showing stucco slurry feeding onto bottom paper at forming plate



Figure 6. Installing gypsum wallboard partition using steel studs

other covering or finishing materials, such as wood, plastics, or other cementitious (cement, lime, or, in less-developed regions, even mud) products.

The favorable characteristics of gypsum that give it value in the manufacture of construction materials are its fireproofing qualities, its versatility, which comes from being able to use it in many forms, and its low cost of application. It is used entirely in its calcined form, as formulated and/or manufactured stucco in plasters, block or tile, and wallboards. In recent years, approximately 96% of the gypsum used in the United States for construction materials was in



Figure 7. Boom truck stocking a house with wallboard



Figure 8. Veneer plaster application

the manufacture of various sizes and types of wallboard, with a total surface area of some 2.8 million m² per year (Olsen 2002).

Gypsum is noncombustible, making it one of the most effective fireproofing materials known, a property owed to its combined water content. When the hemihydrate form of gypsum (stucco) is rehydrated to make a covering material, it reverts back to dihydrate, so that when heat from fire comes in contact with a plaster wall (or gypsum wallboard), it begins to lose combined water as steam, inhibiting the transmission of heat. Extensive research into gypsum's fireproofing property has resulted in products with a high fire rating—an important reason for the wide acceptance of gypsum products by the construction industry, particularly when wood framing is used.

The versatility of gypsum is also a major advantage. By the use of different calcining methods and additives, the physical properties of plaster, wallboard, and cast blocks and tiles can be adjusted to meet a wide range of requirements. This versatility gives the architect and builder many choices in design and affords them maximum flexibility to produce a structure that meets the customer's specifications.

The economics in the application of building materials usually is measured by the cost per square meter of finished wall or floor space, or of cubic meters of material. It also is a function of the cost of delivering building material to the jobsite plus the cost of installation.

The wide use of gypsum construction products is based on the industry's ability to keep manufacturing and distribution costs low, and to minimize the amount of labor in product installation. For example, the boom truck (Figure 7) was developed to decrease the amount of manual handling and also to provide delivery of gypsum wallboard directly to the jobsite.

Part of the low cost of processing gypsum during manufacture is because of its softness (2 on the Mohs scale of hardness), resulting in less abrasion. Energy costs also are kept low due to inherently low calcining temperatures. The wide geographical distribution (high place value) of gypsum deposits and sources of synthetic gypsum results in low transportation costs.

Although plastering walls and ceilings was widely practiced in the United States in the early 1900s, this has given way to drywall construction employing gypsum wallboard. Today, one-coat and two-coat veneer-type plasters (Figure 8) have been developed and applied over 1.2-m-wide plaster bases; many plasters are now formulated for machine mixing right at the jobsite and pumped to the point of application. Plastering continues to be used where special effects are desired, and its flexibility provides wide latitude in finishing design. Outside the United States, plaster is still commonly used over block wall construction.

Gypsum wallboard originally was developed in the United States. Made in about 1890, the first wallboard product consisted of four sheets of felt or paper with thin layers of gypsum stucco between them. By 1914, the development of wallboard with only a top and bottom sheet of paper, and a single gypsum layer between, had been perfected. The use of this product received a big boost in the construction of buildings during World War I. After World War II, increases in hourly wages raised the cost of plastering walls, causing the rapid expansion of gypsum wallboard, which provided lower labor requirements than the traditional two-coat plaster wall.

The present dominant position of wallboard stems not only from its economy of installation but also from the variety of applications that the industry has developed. Examples include movable partitions, enclosures for elevator shafts in high-rise buildings, and sound-rated wallboard systems for multiple-unit housing.

Other construction uses of gypsum include self-leveling floor underlayments, water-resistant sheathing, plaster baseboard, ceiling tiles, and fireproofing building steel.

Industrial Uses

Industrial gypsum can be divided into three broad categories: calcined, anhydrous, and uncalcined, each utilizing distinct properties of the mineral.

Although the industrial segment of the gypsum industry is well developed in the United States, markets are widely scattered geographically. Many product lines tend to be specialized, and, with the exception of portland cement retarder rock, individual customers are likely to want tens or hundreds of tons of product, rather than thousands of tons.

Calcined Industrial Gypsum

Perhaps the largest industrial use of calcined gypsum is for making molds for sanitary ware, pottery, metal casting, and decorative objects.

Molding plaster is made from high-purity gypsum (95% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or greater) at select locations and is marketed on the basis of its water demand, strength, white color, setting time, and closely controlled expansion/shrinkage qualities. It may be made from either beta or alpha hemihydrate, or a combination of the two.

High-density, high-strength plasters are used in the maintenance of floors and for quick patching of high-use surfaces (such as highways) that cannot be closed down for more conventional repairs. In this application, gypsum plaster may be mixed with other cementitious materials to obtain optimum results.

Anhydrous Gypsum

In addition to the hemihydrate industrial plasters already described, several products are made from calcium sulfate with no water of crystallization, which is from second-settle stucco made when the calcining temperature has been raised to about 200°C. This material is often referred to as soluble anhydrite.

When calcination proceeds to a temperature of 480°C, a dead-burned or insoluble anhydrite product is formed, which is used for the manufacture of Keenes cement. Dead-burning usually produces a whiter product and is preferred where color (that is, lack of color) is important. Keenes cement is a generic name for dead-burned gypsum that, with the use of additives, can be made to set and harden after mixing with water. The usual set specifications fall in the range of 4 to 12 hr. Its major use is in wall plaster where extra density, strength, and hardness are desired. Keenes cement is made in only a few locations and only in small quantities.

Uncalcined Industrial Gypsum

This category, sometimes referred to as raw gypsum, is used as a retarder in portland cement. By volume, this is the second largest use of gypsum outside of wallboard manufacturing. In 2002 (Table 1), 2.6 million t, or 8% of all the gypsum used in the United States, was consumed by this market (Olsen 2002).

It is well known that calcium sulfate compounds control the setting time of portland cement—both the rate at which the cement paste develops strength and the shrinkage of portland cement products during drying. The use of calcium sulfate compounds in portland cement has been the subject of extensive research and is standardized by the American Society for Testing and Materials (ASTM). The amount of gypsum (or gypsum-anhydrite [GA] blend) depends on: (1) the SO_3 content of the gypsum, (2) the type of portland cement, and (3) the mix of raw materials used to make cement clinker. In practice, the amount of gypsum will vary from 4% to 6%, averaging approximately 5% by weight of finished portland cement. As it is fed into the grinding mill, the gypsum is ground with clinker, and the two materials are mixed together.

The setting and strength development of portland cement is based on several complex chemical reactions. As these are better understood, raw material specifications are tightened, with particular emphasis placed on the homogeneity of the constituents. A trend toward increasing the amount of sulfur trioxide (SO_3) per unit volume of portland cement will increase the demand for a uniform grade of gypsum and anhydrite products for portland cement manufacture.

The use of anhydrite in portland cement represents the largest market in the United States for this mineral; however, it is a highly fragmented market because not all portland cement plants want anhydrite in their retarder component.

Table 3. Average gypsum prices (2002)*

Gypsum Product	Price, \$/t
Portland cement retarder	12.37
Agricultural gypsum	23.65
Plasters	150.98
Wallboard, 12.7 mm	87.02

Source: Olsen 2003.

* Based on total quantities and value of these products as shown in Olsen 2003.

Where anhydrite is used, it generally is blended with gypsum; the usual blend contains 40% anhydrite. Because many plants prefer straight gypsum to a GA blend, any one cement plant might use only 4,500 to 9,000 tpy of anhydrite. It is estimated that probably no more than 5% of the 3.9 million t of gypsum reportedly used for portland cement retarder in 1990 was the mineral anhydrite (Kebel 1994).

MINOR USES FOR CALCIUM SULFATE

The use of anhydrite to construct load-bearing packwalls and to provide support for longwall gate road steel arches in underground coal mines is practiced extensively in Germany and to a lesser degree in Great Britain and France. Anhydrite is crushed, sized, and then transported pneumatically underground to the application site. An accelerator consisting of potassium sulfate and ferrous sulfate is mixed into the crushed anhydrite, and the material is wetted during emplacement. This process produces a quick-setting, high compressive strength, monolithic material.

Prices

In Table 3, the average prices of four representative gypsum products are shown for 2002 and are typical of the wide range in value among different products. These figures correspond to the amount of processing and beneficiation of the products: the greater the amount of processing, the greater the cost to consumers. These figures represent mill net prices and are averages across the United States. Prices at any given location will vary widely from these averages, and freight and other distribution costs must be added. Delivered costs, based on list prices, are quoted for several cities in *Engineering News-Record*, which is considered an industry standard source for this information.

Table 4 shows the recent trend of gypsum prices. Gypsum prices peaked in 1999 as U.S. housing construction grew strongly and outstripped U.S. industry capacity. Additional wallboard capacity from traditional U.S. producers and new wallboard capacity from foreign-based companies entering the U.S. market began to come on-line in the late 1990s. Gypsum prices dropped correspondingly to moderately lower levels, reflecting the growth in industry capacity, while demand for gypsum products remained high into the early 2000s (Figure 9).

FUTURE TRENDS

Gypsum will continue to be widely used for years to come. As the housing boom in the United States continues, demand for wallboard is expected to grow. U.S. wallboard suppliers are meeting this need by expanding existing manufacturing plants while building high-capacity greenfield manufacturing plants as well. For some new plants, synthetic gypsum will be the normal feedstock.

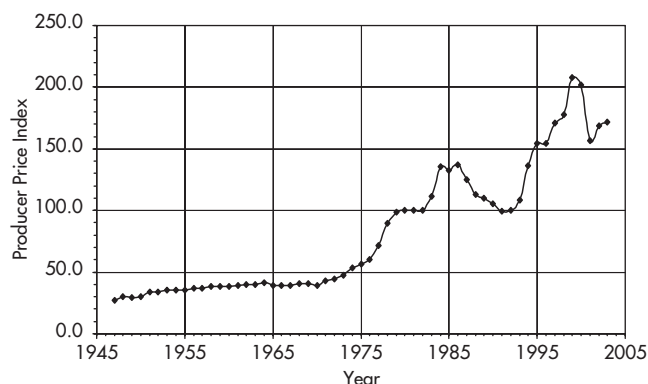
In wallboard manufacture, synthetic gypsum has become an important substitute for mined natural gypsum. In 2002, synthetic

Table 4. Gypsum products price index (1982 = 100)*

Year	Index	Year	Index
1980	100.1	1992	99.9
1981	100.1	1993	108.3
1982	100.0	1994	136.1
1983	111.7	1995	154.5
1984	135.4	1996	154.0
1985	132.3	1997	170.8
1986	137.0	1998	177.6
1987	125.2	1999	208.0
1988	112.9	2000	201.4
1989	110.0	2001	156.4
1990	105.2	2002	168.9
1991	99.3	2003	171.5

Source: U.S. Department of Labor 2004.

* U.S. Bureau of Labor Statistics: Producer Price Indexes, Series ID: WPU137.

**Figure 9. Producer price index of gypsum products**

gypsum accounted for 24% of the total U.S. domestic supply (Olsen 2003). The use of synthetic gypsum should continue to increase and may very well account for up to 50% of the U.S. supply within the next 10 years.

Although the most popular size and type of wallboard will continue to be the 1.2 m × 2.4 m × 12.7 mm-thick paper-clad sheet, new types of gypsum wallboard are expected to grow in popularity. For example, fiber gypsum board, a nonpaper face and back board, incorporates a homogeneous blend of gypsum and paper fiber for abuse-resistant floor underlayment applications. Another example

is a gypsum wallboard with water-resistant sheathing application that utilizes fiberglass scrim to replace the face and back paper.

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Insulation

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INTRODUCTION

The numerous products on the market used for thermal and acoustical insulation consume substantial quantities of a variety of industrial minerals.

Acoustics is the science of sound, and architectural acoustics deals with sound in buildings; most acoustical insulation, however, is manufactured for transportation vehicles. *Sound* is defined as the auditory sensation in the ear, or the disturbance in a medium which causes this sensation. Acoustical insulation is used to reduce or eliminate *noise*, which is defined as unwanted sound. Noise can be controlled by reducing sound radiation at the source, by using sound-reducing construction methods such as staggered studs and so forth to control sound transmission, or by using sound-absorbing material on walls, ceilings, and floors (Rossing 1985).

Acoustical insulation absorbs the energy in sound waves in a porous material. As the sound waves penetrate the pores, contact with the pore walls dissipates the sound waves by reducing the amplitude of vibration of the air molecules, and the sound energy converts to heat energy. Acoustical insulation is generally highly porous, 1.3 cm or greater in thickness, and has interconnected pores. Acoustical insulating materials include fibrous vegetable or mineral matter and cellular organic and inorganic material such as natural or manufactured foams (Sabine and Moulder 1979). Acoustical materials are most commonly porous boards and tiles, which are often composite materials with perforated facing. Roof insulation board and lightweight concrete also can contribute to noise absorption.

Thermal insulation is defined as material used to control the flow of heat. It can be used for heat control from low cryogenic temperatures (below -100°C) to more than $2,200^{\circ}\text{C}$ for applications such as ablative shields for spacecraft. Heat transfer occurs by *conduction*, *convection*, or *radiation*. Conduction is the transfer of heat without the movement of the conducting medium, as through a metal. Heat convection through a liquid or gas takes place by movement of the medium. Forced convection is the basis for heating and cooling equipment, using pumps or blowers to transfer the thermally conditioned fluid. Free or natural convection occurs because of density differences in the fluid. Radiation is the transfer of energy in space (Eckert 1985).

Insulating the body with foams, fibrous material, or small-celled granular material reduces heat conduction through a solid. Heat transfer through a gas (convection) is controlled by creating many small pores that inhibit movement of the fluid, substituting a

gas of low thermal conductivity, or evacuating the space. Heat radiation can be reduced using materials that reflect or absorb the energy (Glaser 1967). Thermal insulating materials can be vegetable or mineral fibers, organic or inorganic particles, or foams with small pores, generally used to form a low-density thermal barrier. They can be blocks, poured lightweight cementitious materials, and bricks, among others.

RAW MATERIALS AND PRODUCTION

Industrial minerals and rocks commonly used in acoustical and thermal insulations are perlite, pumice, vermiculite, clays, silica, and diatomite (Coombs 1989). These and other raw materials are used to produce common insulation varieties such as calcium silicate, glass fiber, rock wool, and refractory insulation. Other, less common varieties are ceramic fiber, foamed metal, and cementitious foam insulation.

Calcium Silicate Insulation

Calcium silicate insulations comprise industrial minerals, hydrated lime, and a silica source such as ground silica, diatomaceous earth, or perlite ore. These raw materials are discussed in more detail in this section. Small quantities of organic or inorganic fibers are added as reinforcement. In 2003, there were 90 plants that produced lime in the United States (Miller 2004). The silica source for calcium silicate thermal insulations can be finely divided silica from sandstone, quartzite (i.e., quartzose rock used to make silica flour), perlite, or diatomite.

Producing calcium silicate insulations is relatively straightforward. Hydrated lime, the silica source material, reinforcing fibers, and water are mixed and reacted at an elevated temperature. The slurry is then pumped to molds and pressed to remove water and form the finished part. The product is then autoclaved for completion of the chemical reaction and oven dried.

Thermal insulating products made by this process are pipe covering, blocks for the insulation of pressure vessels, etc., and low-density structural sheets used for paneling on ships, chutes for the conveyance of molten aluminum, and other specialty items. Calcium silicate insulations are classified as Type I for service temperature to 649°C and Type II for service to 871°C (ASTM 2004a). Service temperature is the maximum temperature at which a material can be used for the given application. Above this temperature, the material degrades rapidly.

Diatomite

As previously noted, diatomite is used as a silica source in producing calcium silicates. Diatomite can be more reactive in the hydrothermal chemical reaction with lime than silica flour because of its high surface area and its amorphous nature. Other uses of diatomite as insulation include insulation in safes and fireproof filing cabinets. It has been used as loose-fill insulation, but these applications now are limited because of loose diatomite's dustiness and subsequent health concerns. Details on diatomite are provided in the Diatomite chapter in this book; a brief review of its origin and production is given here.

Diatomite is a rock composed of siliceous skeletal remains of diatoms, which are algae that lived in salt or fresh water. It is usually 85% or more amorphous silica, with bound water, alumina, iron, and other minor constituents. It generally is mined by open-pit methods, and the production of natural (uncalcined) grades consists of crushing, drying, and classification by cyclones and separators. The United States is the largest producer and consumer of diatomite with domestic production estimated at 624,000 t (689,000 st). In 2003, seven companies were producing diatomite in four states with a total of 13 processing facilities. California and Nevada accounted for 70% of U.S. production in 2003 (Dolley 2004a). Between 2002 and 2003, production decreased by less than 1%, and its value increased by less than 1%. The next largest producing countries in 2003 were (in decreasing order of production) China, Denmark, Japan, the former Soviet Union, France, and Mexico. Insulation applications accounted for just less than 4% of domestic production in 2003, and insulation uses accounted for 17% of total global production. Average price per ton for insulation in 2003 was \$35.71 (Dolley 2004b). The diatomite market should remain stable over the next several years, and the export market is expected to strengthen as more uses, particularly as a filtration medium, are implemented.

Industrial Sand

The mineral quartz (SiO_2) is the predominant component of industrial sand. The term *PV* contains two primary subsets of products: silica flour and ground silica. Ground silica is used as a functional filler and pigment extender in many industrial products and is also the major batch component in the production of continuous strand fiberglass. Silica flour generally is sold into lower-value markets, whereas ground silica is generally sold into higher-value markets. Details on industrial sand are provided in the Industrial Sand and Sandstone chapter in this book; a brief review of its origin and production is included here.

The five leading producers of industrial sand in the United States are, in descending order, Unimin Corp.; U.S. Silica Co.; Fairmont Minerals Ltd.; Oglebay Norton Industrial Sands, Inc.; and Badger Mining Corp. Domestic production is dominated by Wisconsin, Michigan, Indiana, and Ohio, with a combined production of 9.62 Mt in 2003. These four states comprise more than one third of domestic production (Dolley 2004c). This area is also where the highest quality industrial-sand deposits are located. These deposits usually contain less than 20% deleterious materials (Pettijohn, Potter, and Siever 1987) and are contained within the Midcontinent marine quartz arenites. Significant production also occurs in California, Texas, Oklahoma, New Jersey, and North Carolina, though these sands are generally of lower quality than sands produced in the Midwest. In 2003, the average selling price in the United States for PV used in fiberglass was \$37.37/t. The provinces of Quebec, Ontario, and Alberta are the primary producers of industrial sand in Canada (Dumont 2001). The leading recipients for U.S. exports in 2003 were, in descending order, China, Canada, Mexico, and Japan.

Leading global producers, after the United States, were Slovenia, Germany, Belgium, France, and Spain. Because of recycling and substitution, the overall demand for industrial sand may decrease; the value of the production may increase, however, because of higher selling prices for value-added products such as PV.

Economic industrial sand deposits are market driven, so physical exploration techniques vary, depending on site conditions and end use. The most important element of exploration is collecting clean, unoxidized samples. Industrial sand mining methods depend on the type of deposit. Some unconsolidated deposits are mined using front-end loaders, scrapers, or bulldozers; others are mined using dredges or draglines. At well-consolidated deposits, conventional drill-and-blast methods are used. Although uncommon, underground mining also can be used to extract competent, well-lithified sandstone or quartzite. Processing distinguishes industrial sand from common construction sand, and differentiates the various uses of industrial sand. Regardless of markets, sands are, at a minimum, washed, dried, and screened. Material for high-purity products is acid leached; PV is chemically treated for some applications.

PV products also are used as the primary aggregate in both shape and monolithic-type refractories to provide high-temperature resistance to acid attack in industrial furnaces. Surface-modified PV (chemically treated) and uncoated PV are used as functional filler to modify the physical properties of a product (e.g., altering the thermal characteristics of a product).

As with many other raw materials used in insulation manufacture, health considerations are expected to have a significant effect on the industrial sand business. Regulatory agencies such as the U.S. Occupational Safety and Health Administration (OSHA) are working to lower the personal exposure limit (PEL) for respirable silica. This will have a significant effect on the building materials and recreation market segments, where limestone could replace industrial sand. To reduce or eliminate the amount of unreacted crystalline silica in the end product, finely divided (baghouse) perlite ore is sometimes used as the silica source in producing calcium silicate insulations.

Perlite Insulation

Perlite is discussed in a separate chapter in this book, so only a brief overview is given here. Perlite is a naturally occurring volcanic rhyolite glass, most commonly found in domes and flows of Tertiary or Quaternary age. Perlite volcanic glasses occur within high-silica (71 to 75 wt % SiO_2) volcanic domes, lava flows, and welded ash-flows. It is composed primarily of aluminum silicate, forms from the hydration of obsidian, and typically contains 2% to 5% water (Breese and Barker 1994). Perlite deposits are widespread in the western United States. New Mexico is the leading producing state, with commercial production also in Arizona, California, Colorado, Idaho, Nevada, Oregon, and Utah. Major foreign producing countries (in decreasing order) are Greece, Japan, Turkey, Hungary, and Mexico. The amount of domestic (U.S.) processed crude and expanded perlite produced and consumed decreased by about 5% from 2002 to 2003 (Bolen 2004). The decrease could be attributed to increasing imports coupled with weak demand from some construction markets. Perlite expanding plants mostly in the eastern United States continued to purchase less expensive, imported perlite. Consumption of perlite for low-temperature and masonry/cavity-fill insulation was 1.1% of total perlite usage in 2003. In 2003, the average value for low-temperature insulation was \$429/t and \$359/t for cavity-fill insulation, increases of 18% and 48%, respectively, over 2002 values. Domestic consumption of processed and expanded perlite is expected to exhibit slight growth. New mine

openings coupled with increasing imports should restrain price increases (Bolen 2004).

Nearly all perlite is used in its expanded form, and finds use in a variety of thermal and acoustical insulation applications. The efficiency and degree to which perlite ore expands and the characteristics of the expanded material determine whether the perlite is of commercial quality and its appropriate markets. All mines except one in east-central Nevada are open pits. In some open-pit operations, the perlite is hard and must be drilled and blasted. In others, the perlite breaks easily and can be extracted with scrapers. The milling procedure consists of crushing, drying, and screening to produce closely sized ore grades, which are thermally expanded for various end-product uses. Some producers crush perlite at the mine whereas others crush at the plant.

Perlite is custom-blended and shipped, usually by rail, but sometimes by truck, in bulk or bags to expanders near end-use sites. Some operations have expanders at or near the plant, but most move crude perlite to expanders in various parts of the country (Austin and Barker 1995). The cost of shipping the low-density expanded perlite mandates that it be used close to the expansion facility.

The commercial value of perlite derives from the fact that when flash-heated, the contained water converts to steam, expanding the viscous glass particle. Expansion is accomplished in vertical or horizontal furnaces at approximately 870°C. Density for roof insulation board is typically 4 lb/ft³, 2 to 4 lb/ft³ for low-temperature insulation, and 6 lb/ft³ for cavity-fill insulation (Bolen 2004).

Beyond the use of perlite for producing calcium silicate insulations, another major market for perlite is in acoustical tile for residential and commercial buildings. Perlite can comprise approximately 15% of the formulation. Formed cellulosic boards, which may contain as much as 70% perlite, are used for a thermal insulating substrate for built-up roofs in commercial and industrial buildings. Another major market for expanded perlite is block fill. After a cement block or other cavity-type masonry wall is constructed, loose perlite is simply poured in to the block cavities for thermal insulation. Perlite fills the irregular void spaces without bridging. The perlite usually is treated with silicone to reduce water absorption (ASTM 2004 b). Perlite used in this manner can increase the fire rating of a block wall from 2 to 4 hr. Competitive materials for this application are vermiculite and expanded polystyrene beads and inserts. Thermal-insulating block and pipe covering is made from expanded perlite and sodium silicate or another suitable binder (ASTM 2004c).

Perlite is used as a lightweight aggregate in portland cement and gypsum plasters for exterior and interior applications, for encasement of structural steel members and placement on floor and roof assemblies, as a base for ceramic and masonry veneers and tiles, and in stucco formulations (Bodycomb and Stokowski 1994). These plasters serve as fire protection and contribute to thermal and acoustical insulation, depending on usage. As an aggregate for lightweight concrete, perlite contributes sound- and heat-insulating properties when the concrete is used as a substrate for built-up roofing, floor fill, structural decks, and similar applications. Perlite concrete is also used as a thermal insulating base for swimming pools, and as a permanent insulation and structural support for underground piping. Another use for this material is to relined existing chimney flues to prevent damage to mortar.

Small particle size perlite expanded to a very low density is used as cryogenic insulation in storage tanks and vessels containing industrial gases such as liquid natural gas, hydrogen, oxygen, helium, and nitrogen, which are stored and transported at very low temperature. The annular space in a double-walled vessel is pneumatically filled with perlite and then air is evacuated from the cavity

for thermal insulation. Portable expanders frequently are used at the jobsite to expand the perlite for cryogenic use. One of the few uses of perlite ore is as ladle topping in foundries. Added to pouring ladles, perlite acts as a slag coagulant and forms a crust on the surface of molten metal to maintain the melt temperature (Bodycomb and Stokowski 1994).

Glass Fiber Insulation

Fibrous glasses, or glass wools, are used in a wide variety of thermal and acoustical insulating applications. The major industrial minerals used in the manufacture of fibrous glasses are silica sand, soda ash, and limestone (Bodycomb and Stokowski 1994). Other raw materials are dolomite, feldspar, nepheline syenite, fluorspar, and various borates (borax, colemanite, ulexite, and szaibelyite).

Glass wools are produced by one of two methods. In the less common pot- and-marble system, the constituents are mixed, melted, and formed into marbles. These preforms are then remelted over platinum nozzles. The melt, passing through the nozzle, is drawn into continuous filaments or formed into discontinuous fibers by steam or, more commonly, by flame attenuation. Generally, however, insulating glass wools are produced by melt-spinning or centrifugal spinning. The glass melt is introduced into a bowl, or inner centrifuge. The melt exits through apertures in the bowl and enters a second-stage centrifuge. Fiberization takes place when the material exits through holes in the second-stage centrifuge (Jarvela, Pohjonen, and Tormala 1990). The glass fibers bond with organic resin binders. Glass wool products are rated for use at temperatures as high as 538°C when phenolic binders are used, but most products are designed for use at lower temperatures.

Glass fiber products are tested exhaustively not only for thermal and acoustical insulating performance but also for fire resistance, flame spread, smoke generation, corrosivity, water absorption, resistance to fungus, physical strengths, and so forth. Table 1 gives some applicable test methods, designed by the American Society for Testing and Materials (ASTM). Numerous government, Underwriters Laboratory, and other testing laboratory specifications may apply.

Fiberized glass is ubiquitous as a material in building applications. Fiberglass batt, blankets, rolls, and loose-fill insulation (insulation produced as shreds, granules, or nodules that typically are blown into building cavities using special equipment) find common application in insulating buildings of all types, for both thermal protection and sound control. Batting and rolls come with or without vapor-retarding facings, which resist the movement of moisture to cold surfaces where it could condense and cause water damage to the building. Ease of installation by semiskilled labor contributes to the use of glass fiber in new and retrofit residential construction. A recent development is to encapsulate light-density batts in plastic sheathing for a product that is easier to handle and has less associated dust (K. Schaal, personal communication). Fiberized glass is also important in air handling and in HVAC systems, where duct board, duct wrap, and duct liners are used for temperature and acoustic control. Fiberglass blankets used in HVAC systems are subject to requirements for corrosiveness, moisture vapor sorption, fungi resistance, temperature and erosion resistance, odor emissions, surface burn characteristics, thermal conductivity, and sound absorption coefficients.

Other common applications are acoustical control for office cubicles, acoustical and temperature control in household appliances, temperature control and flame resistance in aircraft, and various thermal and acoustical applications in the automotive and marine industries. Newer applications are fiberglass blanket bonded with melamine resin used to insulate cryogenic tanks; a number of

Table 1. ASTM specifications and test methods applicable to glass fiber insulation

Test No.	Test Name
C-335	Standard Test Method for Steady-State Heat Transfer Properties of Horizontal Pipe Insulation
C-356	Standard Test Method for Linear Shrinkage of Preformed High-Temperature Thermal Insulation Subjected to Soaking Heat
C-411	Standard Test Method for Hot-Surface Performance of High-Temperature Thermal Insulation
C-518	Standard Test Method for Steady-State Thermal Transmission Properties by Means of the Heat Flow Meter Apparatus
C-547	Standard Specification for Mineral Fiber Pipe Insulation
C-553	Standard Specification for Mineral Fiber Blanket Thermal Insulation for Commercial and Industrial Applications
C-585	Standard Practice for Inner and Outer Diameters of Rigid Thermal Insulation for Nominal Sizes of Pipe and Tubing (NPS System)
C-612	Standard Specification for Mineral Fiber Block and Board Thermal Insulation
C-795	Standard Specification for Thermal Insulation for Use in Contact with Austenitic Stainless Steel
D-257	Standard Test Methods for DC Resistance or Conductance of Insulating Materials
D-638	Standard Test Method for Tensile Properties of Plastics
D-790	Standard Test Methods for Flexural Properties of Reinforced and Unreinforced Plastics and Electrical Insulating Materials
D-792	Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement
D-828	Standard Test Method for Tensile Properties of Paper and Paperboard Using Constant-Rate-of-Elongation Apparatus
D-3679	Standard Specification for Rigid Poly Vinyl Chloride (PVC) Siding
E-84	Standard Test Method for Surface Burning Characteristics of Building Materials
E-96	Standard Test Method for Water Vapor Transmission of Materials
E-136	Standard Test Methods for Behavior of Materials in a Vertical Tube Furnace at 750°C

filtration uses (liquid–gas separators, liquid–liquid coalescers, and oil and gas coalescing, among others); and microfibers (glass fibers having diameters ranging from less than 0.05 μm to 2.5 μm) in clean-room applications and for filtering blood particles (K. Schaal, personal communication).

Mineral or Rock Wool Insulation

Mineral, rock, and slag wools are synthetic inorganic insulating materials composed of vitreous glass fibers. The term *mineral wool* designates a silicate–glass–wool insulating material. They range in color from white or green to brown or black and have slag (generally an iron blast furnace slag) as the primary raw material. Rock wools use naturally occurring rock as the raw material. Slag wool designates a product made from slag and is synonymous with the present usage of mineral wool.

Historically, Illinois and Ohio dominated woolrock production (Lamar et al. 1934) with additional production in California, Indiana, Kentucky, Minnesota, Pennsylvania, Washington, and Wisconsin (Thoenen 1938). The mined units generally were argillaceous limestones and dolomites, sometimes along with quartzites, shales, granites, and other rock types used as additives. Woolrocks also occur in Alabama, the Carolinas, Kansas, Mississippi, West Virginia, and Virginia (Gonge 1931; Logan 1932; Plummer 1937; Morse and McCutcheon 1945).

Subwoolrocks, more common than woolrocks, are carbonate rocks that are less argillaceous than woolrocks, but more shaley or

sandy. They must be mixed with a flux rock such as shale, sandstone, limestone, or dolomite to produce a mixture with the proper chemical composition for wool production. Granites, wollastonite, basalt, and peridotites also have been used as subwoolrocks or flux rocks. Slags also are used as the raw material. Iron blast-furnace slags are often used and are typically available in areas near their market. Copper, phosphate, and other slags are also suitable.

The raw materials used in wool production must be capable of melting at the lowest possible temperature that will yield a liquid with the proper viscosity for forming fibers. The fiber diameter is directly related to the acid/base ratio (on a molecular basis) in the molten glass, with values less than 1.8 yielding satisfactory diameters. An empirical rule-of-thumb regarding woolrocks is that natural rocks have the proper composition if they have 20% to 30% CO_2 (Lamar et al. 1934). The raw material must be 4 to 25 cm to forestall material from being blown out of the melting furnace and to maintain the proper draft. This is very significant to the raw materials producer, largely because of the possibility that a percentage of the smallest material will be wasted in the process.

The production of both mineral and rock insulating wool starts with melting it, generally in an unlined, water-jacketed, steel kiln. For wool rocks, melting generally occurs at about 1,400°C to 2,100°C; slags melt at 1,100°C. The energy savings that result from the lower temperature used in the latter is the primary reason that many slags are currently used. Slags also have transportation and yield advantages because they are essentially free of volatiles such as CO_2 , making transportation safer and hence more economical.

Two processes can be used to produce the wool fibers. In one process, steam at 550,000 to 690,000 pascals is blown through a molten stream of glassy raw material. The steam creates globules with fibrous tails; it is from these fibrous tails that wool fibers are produced. In the other process, the molten stream of glass is poured onto a spinning, cast-iron disc, which centrifugally forms the material into thin fibers. The wool product consists of fibers and shot. The fibers are generally 2 to 10 μm in diameter and up to several centimeters long. The shot, small spherules or teardrops of glass, is about 50 μm in diameter. Manufacturers limit the amount of shot in the product during the processing operation. The collected mineral wool fibers are either used loose or shaped into batts, blankets, sheets, or blocks with a resin (generally phenolic) binder.

Recent developments include a softer, batt-type mineral product that is denser, fits more tightly into standard wall cavities, and is more resistant to air convection thermal losses than standard fiber-glass batt products. Its thermal resistance is comparable to sprayed cellulose insulation or high-density fiberglass batts (NAIMA 2004a).

Refractory Insulation

Refractories are heat-resistant materials that line high-temperature furnaces and reactors and other processing units. In addition to being resistant to the thermal stresses and other physical phenomena induced by heat, refractories must also withstand physical wear and corrosion by chemical agents. Refractories are more heat resistant than metals and are necessary for heating applications above 538°C. Refractory products fall into two categories: brick or fired shapes, and specialties or monolithic refractories. Refractory linings are made from these brick and shapes; from specialties such as plastics, castables, gunning mixes or ramming mixes; or from a combination of either category. Many refractory products, in final shape, resemble a typical construction brick; there are, however, many different shapes and forms. Some refractory parts are small and possess a complex and delicate geometry; others are massive

and weigh several tons in the form of precast or fusion cast blocks (The Refractories Institute 2004). Refractories contain and control heat in myriad end-use applications ranging from residential fireplaces to linings for high-temperature furnaces, kilns, ovens, and boilers in a wide variety of industries. A recent trend is reduced installation costs, in part because of the increasing use of air-placed castable materials, which are composed of manufactured aggregates and cementitious binders that are chemically inert. Portland cement cannot be used because of the highly corrosive nature of cooling flue gases (The Refractories Institute 2004).

Approximately 70% of refractories are aluminosilicates, 15% are silica, and 15% are basic refractories (e.g., magnesite, dolomite, and chromite) (McMahon 2002). Although certain refractories are designated as insulating products (e.g., low-density insulating brick), all refractory products are thermal insulators because they contain and control heat.

Various raw materials are used in refractory products (Norton 1967; The Refractories Institute 2004). Fireclay refractories, including firebrick, are made from plastic and flint kaolin clays (hydrous aluminum silicates) formed and fired. High-alumina refractories, originally made from diaspore, are now primarily manufactured from bauxite and have higher service temperatures than fireclay products. Silica brick is manufactured from quartzite. Basic refractory materials are magnesite brick (magnesite) and chrome brick (chromite). Insulating (fireclay) brick has low density, achieved by adding an organic burnout material, perlite, vermiculite, or expanded clay to achieve high porosity and reduce thermal conductivity. Zircon, andalusite, sillimanite, and kyanite also are used in refractories (Crookston and Fitzpatrick 1983).

Of the 383,000 t of fireclay consumed in 2001, 146,000 t (38%) was used for firebrick; the average price reported by domestic producers was \$23.54/t. In 2002, 7 firms operated 44 pits in 7 states (Virta 2003a). Of the 4.38 Mt of Georgia kaolin produced in 2003, 258,000 t (just under 6%) were for refractory uses with an average price of \$28.57/t (Virta 2003a). Of the 9.97 Mt of bauxite consumed in 2002, 115,000 t (just over 1%) were for refractory uses (Plunkert 2003). The refractory industry continues to consolidate to become more competitive and to address asbestos liability issues. As with most other insulation materials, health and safety issues dominate current innovations.

Vermiculite Insulation

Vermiculite is the mineralogical name generally applied to that group of minerals with micaceous morphology commonly formed by the alteration of biotite and iron-bearing phlogopite. A comprehensive discussion of vermiculite is presented in a separate chapter in this book. When vermiculite particles are heated rapidly at high temperature, water molecules within the internal structure turn into steam and dramatically increase the volume: flat plates of vermiculite turn into elongated, concertina-like (vermiform) particles. The increase in volume caused by this thermal exfoliation is normally in the range of 10 to 20 times, with typical exfoliated densities up to 90 to 110 kg/m³ and as low as 50 kg/m³. In its exfoliated form, vermiculite has the low density and biological inertness comparable with expanded perlite, while maintaining a chemically active surface. Most of the vermiculite mined worldwide ultimately is consumed in the thermally exfoliated form.

Vermiculite currently is mined in at least nine countries. Over the last 15 years, producers outside the United States have dominated the U.S. market. South Africa, in particular, produced 207,345 t in 2003. Other countries currently producing vermiculite are Australia, Brazil, China, Egypt, India, Japan, Kenya, Russia, and Zimbabwe (Potter 2004). The decline in domestic production

can primarily be attributed to the closure of the Zonolite operation in Libby, Montana, in 1990, which was the major source of vermiculite in the United States. Production in the United States currently is limited to South Carolina and Virginia. Two potential new vermiculite sources are being developed in Ontario, Canada.

Exploration for vermiculite deposits is straightforward because they are the products of surface and near-surface weathering. Unlike most other ores, the value of a vermiculite ore depends on the distribution and efficient recovery of relatively large particles. Vermiculite typically is mined by open-pit methods, and milling/concentration consists of flotation using a variety of surfactants. The vermiculite concentrate is shipped to exfoliation plants near the end markets.

Most vermiculite is consumed in thermally exfoliated form. In the United States, most exfoliation is accomplished using vertical furnaces. When the concentrate is flash-heated at approximately 750°C to 800°C, bound water between the micaceous sheets explosively turns into steam, expanding the vermiculite particles. Additional water may be liberated above approximately 870°C, resulting in a weak, powdery product.

Vermiculite is used in a wide variety of thermal and acoustical insulations because of its low bulk density. Vermiculite and perlite share many similar applications. Treated with either asphalt emulsion or silicone for water resistance, vermiculite is used as cavity fill for thermal insulation in cement block and other masonry structures (ASTM 2004d). Coarser grades of vermiculite are used as loose fill in residential attics and walls, an inappropriate use for perlite because of its dustiness. These applications also contribute to acoustical insulation of buildings.

Vermiculite is used in building boards of various types. Fine-sized, untreated vermiculite concentrates are used in fire-resistant plasterboard (Tomandl 2002). As heat from a dwelling fire increases, the vermiculite particles expand, compensating for the shrinkage of the gypsum matrix and maintaining the structural integrity of the board. Pressed vermiculite board could be used as a replacement for gypsum plasterboard in many applications. An important market for vermiculite is in sprayable fireproofing for structural steel members. Another use is in intumescent coatings: when heated, the material expands, forming a low-density thermal barrier. Vermiculite is used in refractory brick, castables, ramming mixes, and other articles for service temperatures up to 1,250°C. Vermiculite is used in portland cement and gypsum plasters, enhancing both thermal and acoustical insulating properties. It also is used in acoustical panels and ceiling tiles, but its dark color is a limiting factor in this market.

Since most end uses of vermiculite are associated with construction and industrial uses, the consumption of vermiculite in the United States generally tracked the national economy until the Libby, Montana, mine closure in the early 1990s eliminated the only major U.S. source of coarse-sized concentrates. Typical current market prices for U.S. vermiculite concentrates range from \$60 to \$170/t, depending on size and grade. Imported vermiculite concentrates range from \$127 to \$240/t, f.o.b. (free on board) Gulf Coast ports (Moeller 2004). Current trends in the vermiculite industry are new products and their applications. By mid-2004, there were 23 pending U.S. patent applications dealing directly with vermiculite.

Lightweight Aggregate Insulations

Lightweight concretes are widely used for their contribution to the thermal and acoustical insulation of a structure. Their low density derives from lightweight aggregates used in the formulation. Several categories of lightweight aggregates are used in insulation products. Lightweight aggregates by their nature also enhance the insulating

and fire resistance of a structure when incorporated in concrete products. The air voids in a typical lightweight aggregate act as an insulator. Generally speaking, the lighter the weight, the better insulating and fire-resistant properties (refer to the Lightweight Aggregates chapter in this book). As with perlite and vermiculite, clays, shale, and slate are heated until they bloat. Of the four main categories of lightweight aggregates, three are used in insulation. ASTM compiled specifications for using various lightweight aggregate materials, and these standards should be consulted as required (ASTM 2004e).

- **Natural lightweight aggregates:** These aggregates are prepared by crushing and sizing pumice, scoria, tuff, breccia, volcanic cinders, and other natural materials.
- **Manufactured structural lightweight aggregates:** These are prepared by pyroprocessing shale, clay, or slate in rotary kilns or on traveling-grate sintering machines. A porous but relatively impermeable texture makes these materials not only lightweight but also both thermal and acoustic insulators; makes them desirable for bulk use in floor and roof fill; and gives them an added advantage in saving weight in concrete. Insulating concrete (nonload bearing), weighing as little as 15 lb/ft³, can be made with these aggregates. Fire resistance is enhanced by the low probability of physical breakdown at temperatures below the melting point of the aggregates, by their low shrinkage characteristics, and by their minimum thermal expansion.
- **Manufactured insulating ultralightweight aggregates:** These are prepared by pyroprocessing ground vermiculite and perlite to achieve expansion. Very little use is made of the raw material in its unexpanded form. The most used ultralightweight materials are vermiculite and perlite, but less than 25% is used as construction aggregate. In recent years, significant price increases for expanded perlite and exfoliated vermiculite gave them a large market share in terms of value (approximately 32% in 2002), despite contributing only about 5% of the tonnage.

Foamed Insulation

Foam insulation products tend to be more expensive than other more common types of insulation but are desirable when there are space limitations. Foam insulation can provide up to three times more resistance to heat flow per unit thickness than other types of insulation, and can more effectively control air infiltration if properly installed. Three common varieties are foamed glass, foamed metals, and cementitious foam.

Foamed glass insulation is used for pipes and vessels and also in walls and roofs. Service temperatures for some of these products are as high as 538°C. Foamed glass forms when powdered glass and a blowing agent are heated to form a plastic mass. Gas expansion from the blowing agent forms a closed-cell structure. Foamed metal insulation forms when aluminum and zinc are heated with blowing agents and is similar to foamed glass. Foamed aluminum is very stiff at a very low weight. In addition, it is fireproof, completely recyclable, and very effective in terms of acoustical absorption, electromagnetic shielding, and structural damping (Alulight International GmbH 2004). Cementitious foam, also called foamed portland cement, for mixes when aluminum powder and flake are added to concrete and react with the high pH matrix to form hydrogen gas, resulting in bubbles or cells in the material. It is pumped into closed cavities. The initial consistency of the foam is similar to shaving cream and after curing is similar to a thick pudding. It is easily damaged by water, but is nontoxic and flame resistant.

Other Insulation Materials

Many insulating products contain industrial minerals as a relatively minor constituent or ancillary use; these products have insulating properties as a secondary attribute of their overall performance, or that represent a relatively small market or market segment.

Refractory or Ceramic Fibers

A wide variety of these materials are being produced, including those made from kaolin–aluminum, silica, zirconia, lanthanum chromite, and others. One rather exotic use is in ablative materials that operate in extremely high temperature environments such as spacecraft heat shields. They act as heat sinks, and heat dissipation is accomplished by mass removal. Refractory fibers are used as reinforcement in some of these products. Other uses are in the reinforcement of various resin systems. These materials have found a number of new applications over the past decade. Ceramic fibers are used as high-temperature loose fill in expansion joint construction, furnace walls, and packing around hard refractory furnace components. Older blends were typically kaolin based, but alumina–silica–zirconia and alumina–silica–chromia blends are gaining in popularity.

Asbestos

For health and environmental reasons, asbestos usage for insulation in the United States essentially is nonexistent; in some countries, however, asbestos fiber is still used as reinforcement in calcium silicate insulation. In such products as insulating board, a sandwich construction of two sheets of asbestos cement with a core of insulating material is produced for both interior and exterior use (ASTM 2004f). Asbestos is no longer mined in the United States. Most imports are from Canada. U.S. consumption declined from 6,850 t in 2002 to 4,650 t in 2003 (Virta 2003b). For more detailed information, refer to the Asbestos and Asbestos Substitutes chapters in this volume.

Ceiling Tile

The production of acoustic ceiling tile is mentioned here as an example of an insulation product that consumes large quantities of industrial minerals and rocks in the United States. Currently, the most common composition is spun mineral wool bonded with starch. Another typical composition is 15% clay, 55% mineral wool, 15% perlite, and 15% starch.

Concrete Block Insulation

Concrete block insulation comes in several varieties. In one, the cores of concrete masonry units are filled with insulation, whether poured in, blown in, or foamed in, except for those cells requiring structural steel reinforcing and concrete infill. In some applications, expanded polystyrene is mixed with portland cement, sand, and chemical additives, and polystyrene inserts are placed in the block cores to increase the unit thermal resistance. Hollow-core units made with a mix of concrete and wood chips are also available. They are installed by stacking the units without using mortar (dry stacking). Structural stability comes from the concrete fill and appropriate reinforcing rods throughout for structural walls.

Solid, precast, autoclaved concrete masonry units, commonly used in European construction since the late 1940s but recently available in the United States, have 10 times the insulating value of conventional concrete and are easily sawn, nailed, and shaped with ordinary tools. This type of concrete uses fly ash instead of high-silica sand as its distinguishing component.

Industry Trends

In the past, innovations in the insulation industry tended to focus on improving energy efficiency; in the last decade, however, research focused on health issues. Today a significant portion of industry promotional materials pertains to such topics as airborne dust, free respirable silica, and other health considerations.

Glass fiber and other fibrous mineral insulation materials are of particular interest because of the link between asbestos and cancer. In October 2002, the International Agency for Research on Cancer removed glass, rock, and slag wool fibers from its list of substances possibly carcinogenic to humans (NAIMA 2004b).

Because the fundamental purpose of the mineral insulation is energy conservation and efficiency, these topics remain a key component in insulation industry research. Industry trade groups, most notably NAIMA, work closely with building code officials around the country through the National Association of State Energy Officials to ensure that local, state, and federal regulations are in step with economical and realistic expectations for manufacturers. At the international scale, the focus has shifted from energy conservation to climate change. NAIMA, along with insulation industry trade groups from Europe, Australia, North America, and Asia, issued the 1997 Lisbon Declaration to the United Nations International Framework Convention on Climate Change. The Lisbon Declaration concurs with findings that space heating and cooling of buildings in the developed world is the major contributor to CO₂ emissions and hence greenhouse gases, and that the best method to reduce energy use is to use adequate thermal insulation (NAIMA 2004c). The declaration projects decreases in CO₂ emissions that would result from increased use of building insulation. In the environmentally sensitive sociopolitical climate of the last two decades, the use of industrial minerals in insulation materials is a good example of how mining provides a clear benefit to the environment.

Insulation is one of the few items in new or retrofit residential construction that can be shown to have a finite pay back period, actually saving money for the homeowner. As energy costs inevitably increase over the long term, insulation usage should increase based solely on economics.

The producers of most mineral insulation materials must address the fact that their manufacturing processes are energy intensive. To remain competitive with other insulation materials, these producers should conduct ongoing research to reduce the energy required in these processes, lest the very factors that encourage the increased use of insulation prohibitively increase their production costs.

The use of mineral and mineral-containing insulation will depend on the development and marketing of cost-effective products of high quality while stressing permanence, ease of installation, safety, and performance over competitive products.

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Pozzolans and Supplementary Cementitious Materials

Gretchen K. Hoffman

INTRODUCTION

Pozzolans and supplementary cementitious materials (SCMs), either natural or artificial, are often used as a cement replacement or as an enhancement in concrete. Physical and chemical properties of a material determine their pozzolanic or cementitious properties. Table 1 lists the selected characteristics for the major pozzolans and SCMs. Pozzolans react with the calcium hydroxide liberated as concrete hardens, forming compounds with cementitious properties (American Geological Institute 1997). The pozzolanic and cementitious properties along with other characteristics make these materials attractive partial substitutes for portland cement in concrete applications or interground with portland cement clinker to create blended cements. Pozzolans can counteract adverse effects of undesirable aggregates used in concrete and help to create a concrete highly resistant to penetration and corrosion.

For centuries, many of the natural pozzolans have been used in concrete or cement. With increasing fuel costs and environmental concerns over the carbon dioxide (CO₂) emissions associated with the production of portland cement clinker, several pozzolanic by-products of industrial processes are gaining acceptance as admixtures to concrete products. Table 2 lists the major pozzolans and SCMs with production, consumption, and price, where available.

CLASSIFICATION

Pozzolans are siliceous or siliceous and aluminous materials that alone possess little or no cementitious value, but will, in a finely divided form and in the presence of water, chemically react with calcium hydroxide, such as found in cement at ordinary temperatures, to form compounds possessing hydraulic cementitious properties. SCMs are finely divided and noncrystalline or poorly crystalline materials similar to pozzolans that possess latent cementing properties that are activated in the presence of portland cement and water (Malhotra and Mehta 1996). Pozzolans and SCMs are mineral admixtures when added to concrete or blended cements. (For a complete discussion of cement, refer to the Cement and Cement Raw Materials chapter.)

Pozzolans

Pozzolans fall into two categories, either natural or artificial, depending on their provenance. Natural pozzolans are either raw or calcined natural materials—such as volcanic ash, opaline chert, tuff, some shale, and some diatomaceous earth—that have pozzolanic properties (American Concrete Institute 2000). The amount of

amorphous or unstructured material often determines the reactivity of the natural pozzolans. There are three categories of natural pozzolans: (1) volcanic ash, called tuff when indurated, in which the amorphous constituent is a glass produced by rapid cooling of magma; (2) those derived from rocks or earth in which the silica is mainly opal, and diatomaceous earth; and (3) some clays and shales. Volcanic glass has a disordered structure because of the relatively quick cooling time and tends to have a porous texture created by escaping gases. Hydrothermally altered volcanic glass can become zeolitic, and when finely ground, zeolitic tuffs become reactive with lime. Deposits of trachyte tuff from a volcanic eruption near the town of Pozzuoli (Italy) are the source of the term *pozzolan*. Romans used this material with lime to form cement for many of their large building projects. Today, volcanic tuffs and pumice are still used as pozzolans throughout the world and are often referred to as *pozzolana* in the literature.

Moler is a Tertiary-age deposit of diatomaceous earth with significant amounts of clay. These deposits are on the island west of Limfjord, Denmark. Diatomaceous earth is amorphous hydrated silica derived from skeletal remains of diatoms, which are tiny aquatic plants. High-purity diatomaceous earth deposits are pozzolanic, but often they contain large amounts of clays. Depending on the clay content of the deposit, calcination or grinding may be necessary for use as a pozzolan (Flechsigg 1990). Found in France, gaize is a soft, porous, highly siliceous sedimentary rock consisting mainly of opal. Before gaize can be used as a pozzolan, it is calcined at 900°C (American Concrete Institute 2000). Gaize and moler are two examples of natural pozzolans used for their pozzolanic properties. A typical use of moler and gaize is in cement subject to seawater attack.

Although clay and shale are naturally occurring, calcination enhances their pozzolanic characteristics. Calcining is necessary to destroy existing crystal structure and to form an amorphous or disordered aluminosilicate structure. As an example, metakaolin, derived from high-purity kaolin that undergoes low-temperature calcination and grinding to a fine particle size, is a highly reactive product having excellent pozzolanic properties. Not all clays and shales, however, are suitable as pozzolans, even when calcined.

Artificial Pozzolans

Artificial pozzolans used today are mostly from by-product materials. Silica fume is a by-product of the reduction of high-purity quartz with coal in electric arc furnaces in the production

Table 1. Physical and chemical properties of pozzolans and SCMs

Properties	Silica Fume	Ground, Granulated Blast Furnace Slag (GGBFS)	Fly Ash (Class C and Class F)	Calcined Clay, Shale	Diatomite	Rice Hull Ash
Physical	Very fine, tiny spheres (0.1 μm), high surface area—acts as filler	Angular, ground to <45 μm	Fine-grained, spherical, <45 μm	<45 μm rough texture because of grinding	Very fine-grained (1 μm). Porous skeletal remains of single-cell plants	Highly cellular, creating large surface area, >45 μm
Chemical	Amorphous silica	Silicate glass, high in calcium	Aluminosilicate	Aluminosilicate glass; may contain quartz, feldspar, mica	Amorphous silica	Pure silica, noncrystalline

Adapted from Malhotra and Mehta 1996; Lohtia and Joshi 1995.

Table 2. Statistics for major pozzolans and SCMs in the United States as raw materials

Pozzolan or SCMs	Consumed as Clinker (2003), <i>kt</i>	Consumed as Blended Cement (2003), <i>kt</i>	Price, US\$	Production, <i>kt</i>
Diatomite, and other microcrystalline silica (silica fume)	129	49	Diatomite,† 970/t	Diatomite, 0.003
Burned clays and shales, other natural pozzolans	na‡	25	na	na
Pumice and pumicite§			27/t	42
Fly ash	2,250	39	18–41/t	63,682
Granulated blast furnace slag**	17	333	60/t (ground) 30/t (unground)	3,800††

Adapted from van Oss 2003a, 2003b, 2004; Bolen 2003; ACAA 2004a, 2004b.

* Material used as raw feed; does not have pozzolanic or cementitious properties.

† Includes absorbents and silicate admixtures (Dolley 2003).

‡ na = not available.

§ Use listed as concrete admixture and aggregate combined (Bolen 2003).

** Includes both ground and unground material.

†† van Oss estimates GGBFS sales 20% of total slag market (van Oss 2004).

of ferrosilicon alloys and silicon metal. The silicon dioxide (SiO_2) that vaporizes during this process condenses to very fine (0.1- μm diameter) noncrystalline spheres (Malhotra and Mehta 1996). Use of these pozzolanic spheres in blended cement or as a mineral admixture produces a high-strength concrete. Rice hull (or husk) ash, when burned in the production of electricity or milling, produces a high-silica ash. This ash has potential as a pozzolanic admixture in concrete.

Fly ash is a by-product of burning finely ground coal either for industrial application or in the production of electricity. The largest producers of fly ash are electricity-generating stations. The amount of fly ash available is greater than for any of the other by-product materials used in cement or concrete. The composition of fly ash is dependent on the composition of the coal feed and the efficiency of the combustion process. Most fly ash particles are spherical and glassy, and possess pozzolanic properties.

Supplementary Cementitious Materials

SCMs include ground, granulated blast furnace slag (GGBFS) and high-calcium fly ash. Blast furnace slag, a by-product of pig-iron production, when rapidly cooled yields a granulated product that is high in calcium content (35%–40%; Malhotra and Mehta 1996). GGBFS mixed with portland cement has hydraulic properties, creating cement that will harden under water.

Other Considerations

With the exception of silica fume, natural pozzolans and industrial by-products generally cost less than portland cement. The cost savings and beneficial properties of pozzolans and SCMs have increased the use of these products. Most natural rock material used as pozzolans undergo some processing, either grinding or calcination, to improve their reactivity. The percentage of amorphous

Table 3. Natural and artificial pozzolans and SCMs classified by reactivity

Degree of Reactivity	Material
Cementitious and pozzolanic	GGBFS (cementitious) High-calcium fly ash (cementitious and pozzolanic)
Highly active pozzolans	Silica fume Rice hull (or husk) ash from electrical generation
Normal pozzolans	Low-calcium fly ash Natural pozzolans—clay, shale, diatomaceous earth, opaline cherts
Weak to very weak pozzolans	Slowly cooled blast furnace slag Bottom ash Boiler slag Field burnt rice hull ash

Adapted from Malhotra and Mehta 1996.

material in the pozzolan often determines the reactivity of a natural pozzolan. Many of the by-products of manufacturing or electrical generation have acquired pozzolanic or cementitious characteristics during these mechanized processes, and for a few, grinding enhances these properties. The degree of pozzolanic reactivity can vary depending on the method of processing. Rice hulls burned in a furnace reach higher temperatures than those burned in the rice fields and yield a more reactive product. The quality of the original feed, or the combustion and cooling method, can also determine the pozzolanic or cementitious properties (Table 3).

NATURAL POZZOLANS

Industry Structure

Cement companies or businesses specializing in mineral admixtures mine, process, and market natural pozzolans. Depending on the raw material, processing may include grinding, drying, purifying, and calcining. Many of the rocks or minerals used for their pozzolanic properties also have other uses such as lightweight aggregate, soil amendments, filters, or fillers. The product sold as a pozzolan can be a minor fraction of the total end use. In the United States, using natural pozzolans is economic when locally available for bulk concrete construction or in the manufacturing of concrete products. The use of natural pozzolans is more widespread in Europe and Asia than in the United States (American Concrete Institute 2000); the four largest producers of natural pozzolans are Italy, Chile, Greece, and Cameroon (Table 4). Home construction techniques in Europe use less gypsum sheetrock and more stone and concrete than in North America. Prefabricated lightweight concrete walls using pumice as a cement admixture are shipped to the construction site. Pumice as a lightweight pozzolan works well for the European style of construction (Bolen 2003).

Raw Materials and Processing

Natural pozzolans such as calcined siliceous clay and shale, diatomaceous earth or diatomite, and volcanic tuff can be used either as a mineral admixture in concrete or interground with clinker to create blended cements. Most of these raw materials have a variety of applications. The respective commodity chapters in this volume provide more detail on the mining and processing of these materials. Clay, shale, volcanic tuffs or pumicite, and diatomite are commonly quarried with rippers, dozers, and front-end loaders, and then transported to a processing plant. Most of the pumicite mined in the United States comes from western states, including Arizona, California, Idaho, Kansas, Nevada, New Mexico, and Oregon (Bolen 2004). California and Nevada have large diatomite deposits. One location in Nevada is a combination of diatomaceous earth and a diatomic pumicite. The diatomite or diatomaceous earth is processed near the mine site because of the expense of transporting a raw material with high water content. This raw material goes through a series of crushing, drying, and comminution steps. Calcining in a rotary kiln and classifying by particle size with heated air are common processes used to produce a pozzolanic material from diatomite (Dolley 2002).

Water processing of kaolin removes impurities to lighten color and control particle size. Calcining the purified material at 600° to 900°C results in dehydroxylation and a disordered and essentially amorphous state. The product is then pulverized to 1–2- μ m diameter creating a highly reactive pozzolanic product called metakaolin. The use of metakaolin as a mineral admixture has been growing since the mid-1980s (American Concrete Institute 2000). Heating other siliceous clays and shales at 700°–800°C makes them reactive by destroying the crystalline structure of the clays and other minerals in shales. Heating increases the pozzolanic reactivity of zeolites as well (Virta 2002).

Specifications

The American Society for Testing and Materials (ASTM) C311-02 (2003a) specifies the methods for testing raw or calcined natural pozzolans and fly ash for use in portland cement concrete. ASTM C618-03 (2003b) outlines the specifications for use in concrete of natural pozzolans and fly ash, dividing these into Class N for natural pozzolans and Class C and F for fly ash. Comparing the requirements for natural pozzolans to the fly ash classifications,

Table 4. World production of pozzolan in 2003

Country	Commodity	Production, kt
Algeria	Pozzolan	400.0
Austria	Trass	5.0
Cameroon	Pozzolan	600.0
Cape Verde*	Pozzolan	1.0
Chile	Pumice and pozzolan	830.0
Ecuador	Pozzolan	23.0
France*	Pozzolan and lapilli	450.0
Greece*	Pozzolan	750.0
Honduras	Pozzolan	190.0
Italy*	Pozzolan	4,000.0
Saudi Arabia*	Pozzolan	160.0
Tanzania	Pozzolan materials	43.3
Uganda	Pozzolan materials	12.4
Total pozzolan production†		6,180.0

Adapted from Bolen 2003.

* Estimated.

† Total is rounded; may not add to totals shown. Total is taken directly from Table 4 of Bolen 2003.

there are few differences between low-calcium fly ash (Class F) and natural pozzolans (Class N). The major differences are (1) the maximum loss on ignition (LOI), or amount of unburned carbon, is greater for natural pozzolans; and (2) the maximum water requirement is greater for natural pozzolans (see section on Fly Ash in this chapter for specifications table). ASTM specifications are not the only standards used in the United States or the world. Almost every country has a different set of specifications for pozzolans used in concrete. Within the United States, each state has its own specifications for use of pozzolans in portland cement concrete for road construction.

Finished Product Uses

A major use of natural pozzolans is in mass concrete, such as dams, where there are large pours and the risk of thermal cracking from the heat produced from the chemical reactions during hydration of portland cement minerals. For example, the Los Angeles Aqueduct (rhyolitic pumicite), the Glen Canyon Dam (pumice; Figure 1), and Flaming Gorge Dam were all constructed using natural pozzolans (American Concrete Institute 2000). Adding natural pozzolans slows down the cementation process, reducing the temperature. Many of the natural pozzolans also improve the workability of the concrete pour, which is beneficial in massive concrete structures. Grouts and mortars are another market for natural pozzolans.

Finished Product Marketing

Markets for natural pozzolans are in blended cements, intergrinding the pozzolan with the portland cement clinker, and as a mineral admixture for concrete. Mining a deposit for a particular project that is nearby and closing the pit when the project is completed is a typical strategy for using natural pozzolans. Natural pozzolans that do not require calcining are the most attractive for marketing beyond a local market. Calcined clay and shale tend to be marketed for blended cements and therefore are used directly by the cement companies. Cement companies have a local market area, because the transportation costs are a limiting factor. Companies mining and marketing diatomite and pumicites as pozzolans often sell these materials as mineral admixtures.

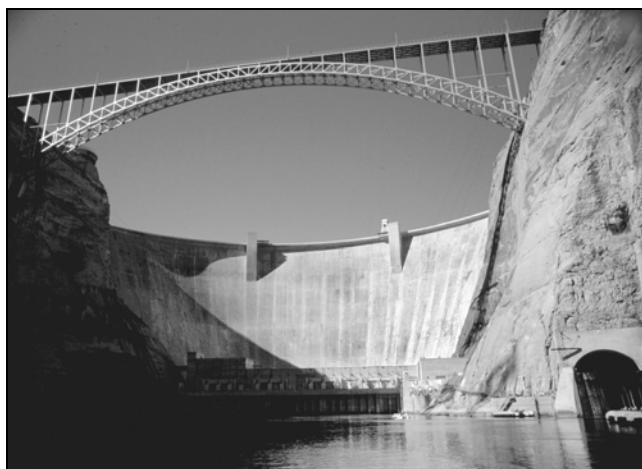


Photo by L. Greer Price.

Figure 1. Glen Canyon Dam (concrete in dam was made with pumice from Arizona, used as pozzolan admixture)

ARTIFICIAL POZZOLANS AND SCMS

Industry Structure

Prevalent use of by-products in the cement and concrete industries is a recent development, particularly in the United States. Using by-products reduces the need for portland cement and uses a product created from expending energy to create another product or electricity. When the by-products are not used, they must be disposed of, which has environmental implications as well. Market barriers for many of these by-products include the wide variety of state regulations regarding their use. If a marketer is transporting the material from one state to another, problems can arise because of the lack of standardization of regulations.

For pozzolanic or cementitious materials such as GGBFS, silica fume, and fly ash, the companies producing the iron or energy generally contract with a mineral admixture marketer or slag processor to handle their by-products. Trade associations such as the Slag Cement Association, the Silica Fume Association, and the American Coal Ash Association (ACAA) represent marketers of these products. These associations promote the product by providing information and technical reports to the buyers and marketers. A discussion for each of the major by-products being used today as a pozzolan or SCM follows. Included is a brief discussion of rice hull ash, although it is not marketed to any extent in the United States.

Silica Fume

Silica fume is a by-product of producing silicon metal or ferrosilicon alloys by reduction of high-purity quartz with coal or coke and wood chips in an electric arc furnace (Figure 2). The silica fume is condensed from gases escaping from the furnace. During the production of silicon metals and alloys, baghouse filters collect the silica fume from the furnace gases. The gas has a very high content of amorphous SiO_2 . Depending on the process, silica fume is 94%–98% SiO_2 from silicon production and 85%–90% SiO_2 from ferrosilicon production (Harben 2002). Silica fume is a very fine, gray powder consisting of glassy spherical particles in the size range of 0.1–0.2 μm with surface areas of 20–23 m^2/g . As a comparison, fly ash is typically less than 45 μm in diameter. The chemical composition, size, and surface area of these particles create a



Courtesy of Silica Fume Association.

Figure 2. A silicon metal furnace

Table 5. ASTM C1240-03 chemical and physical requirements for silica fume as a mineral admixture

Chemical Requirements	
SiO_2 , minimum	85.0%
Moisture content, maximum	3.0%
LOI, maximum	6.0%
Physical Requirements	
Oversize:	
Retained on 45- μm (325) sieve, maximum	10%
Retained on 45- μm (325) sieve, maximum percentage variation from average*	5%
Accelerated pozzolanic strength activity index:†	
With portland cement at 7 days, minimum percentage of control	105%
Specific surface, minimum	15 m^2/g

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* Average is determined by the average of 10 preceding tests or all preceding tests if less than 10.

† A measure of the reactivity (not compressive strength) of given silica fume with a given cement and may vary with the source of both silica fume and cement.

very reactive pozzolanic material. The limited availability of silica fume increases the cost of the finished concrete when added to portland cement, limiting its use to projects where cost is not a primary consideration and the improved performance of silica fume, such as high compressive strength and increased resistance to sulfate attack, are required in the concrete application.

Specifications. ASTM C1240-03 (2003c) outlines the standards for silica fume as a mineral admixture. Table 5 lists the chemical and physical requirements for silica fume. A minimum 85% SiO_2 is required with a maximum of 6% LOI. Physical requirements are concerned with the size and strength when added to mortar. The ASTM requirements also include optional physical requirements for air-entrained concrete, reactivity with alkalis, and sulfate resistance expansion.

Silica fume is the one mineral admixture not considered a lower-cost partial replacement for portland cement in concrete; the cost of silica fume is equal to or greater than portland cement. Using silica fume for its high reactivity creates a high-compressive-strength product that is very durable and can reduce the amount of reinforcing steel required in concrete applications.

Finished Product Uses and Marketing. Concrete admixture suppliers market silica fume. Silica fume in the United States comes from a few producers; the Silica Fume Association lists five member producers. Silica fume products include a fine powder (Figure 3), a densified form, a slurry for mix with water, or a pelletized form for intergrinding with portland cement. The as-produced fine powder is difficult to handle and is generally used in bagged products such as grouts or repair mortars (Silica Fume Association 2004). Densified silica fume is in an agglomerated form created by aerating the as-produced material and creating a net electrostatic charge between the particles. Bulk tankers can transport densified silica fume to concrete batch plants. Unless densified, silica fume is difficult to intermix to form blended cement or to use with portland cement to make concrete, because it tends to float on the surface of the mixture (H.G. van Oss, personal communication). Bulk tankers transport silica fume slurry to storage tanks at construction sites. Often another level of regional supplier repackages the material for the end user in their area. Silica fume is a value-added product in the United States for making high-compressive-strength concrete used in high-rise buildings, parking structures, bridge decks, and girders. In Canada and Europe, silica fume is more often interground with portland cement to create blended cements with high compressive strength, and the cost of the material is much less in this form (Kuennen 1996). Other uses of silica fume include shotcrete mixtures, grouts, concrete blocks, and bricks.

Ground, Granulated Blast Furnace Slag

The iron-making process creates slag during a high-temperature reaction with carbon-reducing agents and fluxes. The impurities of the iron oxide ores and fluxing agents combine to form a liquid silicate melt, called slag, that floats on top of the liquid crude iron. The slag is removed or tapped from the blast furnaces separately. There are several methods of cooling the slag, but quickly quenching the slag in water creates sand-sized particles of glass, granulated blast furnace slag (GBFS; Figure 4), and grinding of this granulated slag increases the surface area and the reactivity of the GGBFS product.

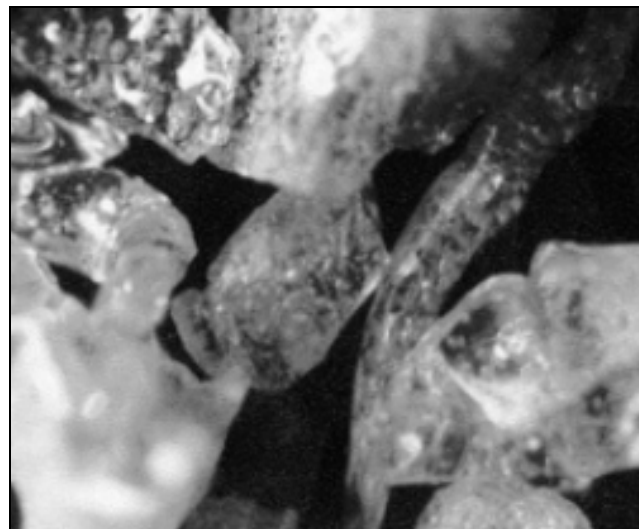
Raw Materials and Processing. The amount of slag produced from a blast furnace is dependent on the chemistry of the raw material, and the grade of the iron ore is the major factor. Ore feed of 60%–66% grade iron in a blast furnace will yield about 0.25 to 0.3 t of blast furnace slag per ton of crude iron produced (van Oss 2003b). Lower grades of ore will yield greater amounts of slag. Blast furnace slags are typically composed of SiO_2 (33%–36%), CaO (calcium oxide, 37%–40%), Al_2O_3 (aluminum oxide, 7%–9%), Fe_2O_3 (iron oxide, 1%–10%), and MgO (periclase 10%–11%). Of the by-products, the chemical composition of slag is closest to that of portland cement; however, slag has a higher silica and lower calcium content (Lohtia and Joshi 1995).

The quenching or cooling process for the slag determines whether the material will be reactive. To form GBFS, the slag is removed from the furnace and rapidly quenched with water in a granulator. The result is glassy granules (Figure 5) that are then dried and ground or interground with portland cement to create blended cement, or the GGBFS is marketed as a mineral admixture for concrete. GGBFS is a hydraulic cement admixture that works with portland cement to create high-strength concrete (Slag Cement Association 2003). Quickly cooled slag using water or steam to



Courtesy of Silica Fume Association.

Figure 3. Silica fume powder after collection and processing



Courtesy of Slag Cement Association.

Figure 4. Microscopic view of GBFS



Courtesy of Slag Cement Association.

Figure 5. Unground GBFS

Table 6. Physical and chemical requirements for GGBFS from ASTM C989-99

Physical Requirements		
Fineness: Amount retained when wet screened on a 45- μ m (325) sieve, maximum		20%
Air content of slag mortar, maximum		12%
Slag activity index,* minimum	Average of Five Consecutive Samples, %	Any Individual Sample, %
7-day index:		
Grade 80	NV†	NV
Grade 100	75	70
Grade 120	95	90
28-day index:		
Grade 80	75	70
Grade 100	95	90
Grade 120	115	110
Chemical Requirements		
Sulfide sulfur (S), maximum		2.5%
Sulfate ion reported as SO ₃ , maximum		4.0%

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* Slag activity is evaluated by determining the compressive strength of both portland cement mortars and corresponding mortars made with the same mass of 50–50 combinations of slag and portland cement. Slag activity index is the strength activity index (SAI) determination of slag.

† NV = no value given.

form pelletized slag can be interground with portland cement but is often used as a lightweight aggregate.

Specifications. ASTM C989-99 (2003d) classifies GGBFS into three grades based on the slag activity index. This index measures the compressive strength of the mortar prepared in accordance with test method ASTM C109 (2003e). Test mortars containing an equal weight of blast furnace slag to portland cement are compared to standard portland cement mortars. The slag activity index is measured after the mortar has set 7 days and again at 28 days. Measurements are taken on the average of five consecutive samples and individual samples (Table 6). Slag activity index grades are based on minimum percentages; most GGBFS marketed in the United States is 120 grade that has a 95% minimum slag activity index for 7 days and 115% for 28 days. ASTM C595-03 (2003f) states the specifications for using GGBFS in blended hydraulic cement.

Finished Product Uses. Iron-producing companies contract with a processing business to handle the slag. The processor crushes or grinds the slag to meet market specifications, using screens and magnetic separators to recover any metal. GGBFS is a value-added product selling for about \$60/t that can be shipped greater distances. GGBFS can replace from 25% to 50% of portland cement in concrete (Slag Cement Association 2002) and is used in manufactured products such as block, segmental retaining wall units, and pavers. Mixed with hydrated lime, GGBFS can be used in flowable backfills. Specialized concretes can use a combination of GGBFS, fly ash, and silica fume. GGBFS is valued as an admixture in cement for its light color, resulting in a very light colored concrete. Adding GGBFS to a cement mixture gives the concrete greater resistance to sulfate and alkali-silica attack, increased workability while pouring concrete, and durability of the finished product.

Finished Product Marketing. GGBFS production and sales are limited to the eastern United States, near iron and steel manu-

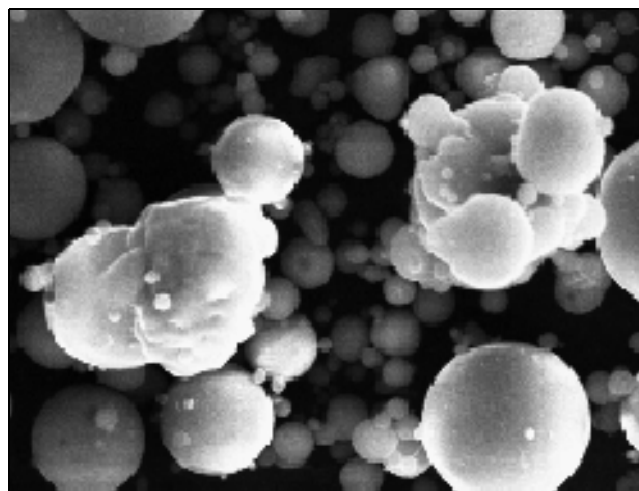


Figure 6. Secondary electron image of fly ash with glass spheres and masses. End product from Salt River Minerals Group, Cholla Generating Station, Arizona. Field of view = 42 μ m.

facturers or near ports where they can receive imported material to grind and market. More than a dozen grinding plants are operating, and the number of blast furnaces in the United States is on the decline. Using existing slag piles, however, is an economical way to remove these piles from the landscape if the material meets specifications (van Oss 2004). If weathered, the slag may not be acceptable for use as a mineral admixture to concrete but can be used as a fine-grained aggregate in cement.

Fly Ash

Fly ash is the major coal combustion by-product of electrical generation from coal-burning power plants. The amount of coal combustion by-product produced at each power plant varies, depending on the type of burners and precipitators, and the percentage of ash in the coal source. The ratio of fly ash to bottom ash produced by coal combustion depends on the type of burner and the type of boiler. Electrical or mechanical precipitators collect fly ash from the flue-gas stream coming from the combustion chamber. This material is glassy, predominantly spherical, and less than 45 μ m in size (Figure 6).

Raw Materials and Processing. Ash in coal consists of minerals and rock particles deposited in the peat swamp or introduced authigenically during the coalification process. Most (95%) of the mineral matter present is clay, pyrite, and calcite. Clay minerals constitute from 60% to 80% of the total mineral content of coal. The types of clay minerals depend on the chemical conditions of the depositional environment. Clays can be detrital in origin or be secondary precipitates from aqueous solutions. Kaolinite is the dominant clay mineral in coals developed in freshwater environments. Illite is dominant in coals overlying marine sediments, developing in moderately alkaline environments. Clays may be finely dispersed in the coal or concentrated in layers, such as tonsteins developed from volcanic ash layers. The mining process also introduces minerals by mining small partings within a seam or from roof or floor material. This dilution adds to the total content of noncombustible material in the coal that ultimately becomes part of the ash by-product.

Coal for electricity generation is finely crushed, typically in ball or roll mills, and air-fed into a 1,037°–1,482°C combustion chamber where the carbon immediately ignites. During coal combustion, the volatile matter vaporizes and carbon burns to heat the

boiler tubes. The inorganic material such as clays, quartz, and feldspar becomes molten and remains in the combustion chamber as slag on the boiler tubes, is carried away by the flue-gas stream as fly ash, or falls through to the bottom of the boiler as bottom ash. The molten material solidifies in the flue-gas stream leaving the combustion chamber, giving approximately 60% of the fly ash particles a spherical shape.

Air pollution control devices, commonly electrostatic precipitators (ESPs), collect the coarse fly ash (>44 μm) first. The finer material is collected later along the air-stream path. ESPs have an overall efficiency of 99%+ (Helmuth 1987). Mechanical precipitators are typically baghouses, cyclones, or venturi scrubbers. Baghouses use fabric filter-tubes or envelopes for capturing fly ash from the flue gas. Baghouses are very efficient for all size ranges (0–44 μm), with an overall efficiency of 99%+ (Helmuth 1987). Several hoppers collect the fly ash particles by size along the length of the ESPs. The captured fly ash can be sent through an air classifier system to ensure consistent grain size.

Depending on the sulfur content of the coal, flue-gas desulfurization (FGD) is necessary to remove sulfur dioxide (SO_2) to meet the 1990 Clean Air Act Amendment standards. Dry scrubbers inject a very fine mist of lime into the unfiltered exhaust gas. The small amount of water used for injection evaporates in the hot exhaust, leaving calcium sulfate (CaSO_4), which is removed with the fly ash. Dry scrubbing creates a fly ash high in sulfur trioxide (SO_3) that is not marketable for most fly ash applications and is disposed of in ponds. Wet scrubbers spray the filtered exhaust gas with a solution of lime, limestone, quicklime, or soda ash as a reactant with SO_2 . In the wet scrubber process, the fly ash is captured before the lime solution is added; therefore it has the potential for being marketed as a pozzolan. Saleable fly ash is loaded into pneumatic containers, either truck or rail, and the remaining fly ash goes to disposal ponds.

Specifications. ASTM C 618-03 (2003b) defines fly ash as finely divided residue that results from the combustion of ground or powdered coal and is transported by flue gases. This definition does not include residue from burning municipal garbage or other refuse with coal, injection of lime directly into the boiler for sulfur removal, or “incinerator ash,” the result of burning industrial or municipal garbage in incinerators.

ASTM C311-02 (2003a) includes chemical analyses and physical methods for testing fly ash used as a mineral admixture in portland cement concrete, and ASTM C618-03 (2003b) outlines the physical and chemical requirements (Table 7). ASTM C618-03 has optional requirements that apply to air entrainment, effectiveness of alkali silica reaction, and sulfate resistance. For use in concrete, state departments of transportation, the Bureau of Reclamation, and the Army Corps of Engineers may have further requirements; Canada and Europe have other standards for fly ash.

In the United States, ASTM C618-03 (2003b) classifies fly ash into two categories (Class C and F) as an artificial pozzolan for use as a mineral admixture in portland cement concrete and Class N for all natural pozzolans (Table 7). Class C normally results from burning sub-bituminous coal or lignite and Class F from burning bituminous coals; however, there are exceptions to this generalization. As an example, lignite and sub-bituminous coal can produce either a Class F or a Class C fly ash. The type of fly ash depends on the depositional environment of the peat swamps from which the coal developed. Classes C and F fly ash differ significantly based on total $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content; Class F has a minimum of 70% and Class C has a minimum of 50%. Fly ash not fitting within these two classes may be well suited for other applications such as soil and waste stabilization but cannot be used in concrete or port-

Table 7. Summary of chemical and physical requirements for fly ash and natural pozzolans defined in ASTM C618-03

	Class N	Class F	Class C
Chemical Requirements			
($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$), minimum %	70.0	70.0	50.0
SO_3 , maximum %	4.0	5.0	5.0
Moisture content, maximum %	3.0	3.0	3.0
LOI, maximum %	10.0	6.0	6.0
Optional chemical requirements:			
Available alkalis, as Na_2O , maximum %	1.5	1.5	1.5
Physical Requirements			
Fineness: Amount retained when wet-sieved on 45- μm (325) sieve, maximum %	34	34	34
SAI: [*]			
With portland cement at 7 days, minimum, % of control	75	75	75
With portland cement at 28 days, minimum % of control	77	75	75
Water requirement, maximum % of control	115	105	105
Soundness: Autoclave expansion or contraction, maximum %	0.8	0.8	0.8
Uniformity: [†]			
Density, maximum variation from average %	5	5	5
Percent retained on 325 sieve, maximum variation, percentage points from average	5	5	5

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^{*} The SAI comes from a control mixture of portland cement mortar and a test mixture of portland cement and test sample in accordance with ASTM C311-02 (2003a). SAI with portland cement is a measure of reactivity with a given cement and can vary as to the source of both the fly ash or natural pozzolan and the cement.

[†] The density and fineness of individual samples must not vary from the average established by the 10 preceding tests, or by all preceding tests if the number is less than 10.

land cement. The intent of these minimum requirements is to ensure that sufficient potentially reactive material is present.

Class F fly ash with less than 10% CaO is considered low calcium and is not self-hardening but exhibits pozzolanic properties. Often this type contains >3% LOI. Quartz, mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), and hematite are major crystalline phases identified in North American Class F fly ash (Lohtia and Joshi 1995).

Class C fly ash containing more than 10% CaO is classified as high calcium and is cementitious. Class C fly ash typically is derived from sub-bituminous coal and some North Dakota and Gulf Coast lignite. Commonly, the higher the CaO content, the greater the degree of self-hardening. Class C often has a very low LOI of less than 1%. Crystalline phases of the Class C fly ash often include anhydrite, tricalcium aluminate ($\text{C}_3\text{A} \cdot \text{Al}_2\text{O}_3$ or $3\text{CaO} \cdot \text{Al}_2\text{O}_3$), lime, quartz, MgO , mullite, merwinite ($\text{Ca}_3\text{Mg}(\text{Si}_2\text{O}_8)$), and ferrite (Lohtia and Joshi 1995).

Physical characteristics of fly ash and natural pozzolans include size, morphology, fineness, and specific gravity. Fineness is determined by the percentage of the ash retained on a 45- μm (325-mesh) sieve. ASTM C618-03 (2003b) requires that no more than 34% of the fly ash be retained on a 325-mesh screen. Particle-size distribution can be quite variable, depending on the collection method and size,

and can differ within coal from the same mine. The coarser material tends to be less reactive as a pozzolan.

Specific gravity of fly ash is related to chemical composition, color, and shape of the particles. The inconsistency of coal and its minerals makes this quite variable. Specific gravity is increased by opaque spherical magnetite or hematite particles if they are present in sufficient quantity. These materials, along with unburned carbon (% LOI), affect the color of the fly ash. Greater amounts of quartz and mulite decrease the specific gravity. Grinding fly ash may release some volatiles trapped inside the spheres, increasing the specific gravity. Fly ash with a large fraction of low-density particles is more reactive than fly ash with higher density particles, which have iron impurities. Pozzolanic reactivity depends on the amount of low-specific-gravity glass present.

Finished Product Uses. Concrete is a major use of fly ash.

Class F fly ash is used to prevent alkali-silica reaction (ASR) in concrete and is preferred in many southwestern states where the aggregate tends to have reactive material. Light-colored concrete is desirable in some markets, particularly California. A low percentage of LOI results in a light-colored fly ash. LOI percentage can also be a factor in using fly ash in air-entrainment admixtures to counteract freeze-thaw cracking. The type and amount of unburned carbon material can be detrimental to these admixtures. Adding fly ash to a concrete mixture at 15%–25% by weight is common practice. Fly ash works as a fine-grained aggregate in concrete. Processing coal fly ash into pellets through a sintering process allows some systems to use any of the unburned carbon remaining in the fly ash for heat generation.

Fly ash, particularly high-calcium fly ash, combined with lime improves soils for roadway construction. Fly ash can be mixed with recycled pavement to create a new base course, reducing the need for additional aggregate. Roller-compacted concrete (RCC), a very stiff concrete rolled out with asphalt paving equipment, requires large amounts of fine aggregate that can be satisfied with fly ash. Fly ash's pozzolanic properties increase the strength of RCC, lowering the cost. Because RCC is often used in large structures such as dams, lowering the heat of hydration by adding fly ash is very important to minimize cracking. The use of fly ash for these large pours has greatly diminished the demand for Type IV portland cement.

Backfill is low-strength concrete used for infilling trenches. For this use, fly ash is mixed with water and small amounts of sand and portland cement, if necessary. Using Class C fly ash may require less portland cement to form a competent backfill. Fly ash backfill is gaining popularity because it can be poured in place and is less time-consuming than conventional backfilling with compacted soil (Bryggman and Nallick 1993).

Finished Product Marketing. Marketing of fly ash is similar to that of most industrial minerals; quality, consistency, and class of fly ash are very important in determining usage and market area. FGD gypsum contamination by the type of scrubber system installed at a power plant restricts a significant amount of fly ash from use. LOI content can limit usage because unburned carbons are detrimental to concrete or color characteristics. Transportation infrastructure is important, and pneumatic or bottom-dump truck transport is preferred except when large quantities can be shipped by rail and sold to distant markets. Storage facilities at different locations in the market area increase sales but are economically feasible only if the quality of the product is in demand. Fly ash can behave like a specialty mineral in that if the fly ash is of superior quality, distance from market is less of a factor.

Most electrical utilities contract with ash marketers to handle and sell their fly ash as a pozzolanic admixture if it is suitable for concrete. There are more than 40 commercial ash-marketing firms

throughout the United States. Most utilities also employ an ash market specialist to monitor ash quality, use, or disposal and to interface with the ash marketers under contract with the utility (U.S. Department of Transportation 2004). A few utilities have dedicated in-house ash-marketing programs. Ash marketers supply the product to concrete or cement marketers in bulk. Many ash marketers are divisions of concrete companies. In Europe and Asia, fly ash is more often blended in to portland cements; in the United States, fly ash typically is sold as an admixture to the concrete (Table 2).

Ash marketers have load-out facilities and testing facilities at the generating station. They sample and test the fly ash coming from each unit to ensure consistency of the % LOI, fineness, and color (brightness) of the product. Some marketers also air-classify the fly ash they receive from the power plants to maintain consistency of particle size in their product. Marketers also maintain storage facilities in their market areas to absorb excess fly ash production and to maintain a steady flow of material to their customers on short notice. In the United States, fly ash production is greater during certain months of the year when the electricity usage is high, such as summer months in the south and winter months in the north. These times may not coincide with the peak usage times of fly ash, so if the fly ash is highly marketable, storage units are feasible.

Use-Specific Transportation. Concrete, concrete products, and grout are the principal products using fly ash (ACAA 2004a). Fly ash, like many of the other mineral admixtures to concrete, is shipped in pneumatic tanks, bottom-dump trucks, or pneumatic railcars. Many fly ash marketers use trucks as their main mode of transportation if the plant is close to their markets, or if they do not have rail load-out facilities. Where the marketer does not sell large enough quantities of fly ash, rail transport may not be economically feasible. If sales are significant, fly ash is stored dry in silos in population centers to provide an on-demand source of material.

Although today's fly ash marketers analyze the fly ash coming from the collectors on a regular basis to keep their product consistent and maintain quality, this was not always the case, and some concrete producers are still skeptical about using fly ash in their product. Ensuring the quality of fly ash is critical to the growth of the industry, especially in portland cement application (Schwartz 2003). Environmental concerns about concentrations of trace elements in the ash and the possible leaching of these elements also act as market barriers. These concerns are more of an issue in other uses of fly ash, such as structural fill, than in concrete where the fly ash is locked into the concrete matrix. Many of the trace elements have very low solubility in the ash (glass) matrix (D. Pflughoeft-Hassett, personal communication). Using fly ash in cementitious material can reduce the solubility of potentially toxic elements by both chemical and physical mechanisms and can prevent them from leaching into groundwater (Bryggman and Nallick 1993).

Rice Hull Ash

Rice is a primary staple crop in the world, and rice milling produces more than 100 Mt of hulls annually (King 2000). The common practice of burning rice hulls in the field creates a pollution problem. The combustion of hulls to produce energy or burning hulls to complete the milling process creates ash. Collecting and grinding this ash creates a product similar to silica fume. The cost of installing an electric power plant in the United States using rice hulls as fuel is about \$1 million/MW of electric power capacity and requires 1.5–2 t of hulls per MW-hr. In California, 20–25 MWe facilities use rice hulls as a fuel source in the milling process (TropRice 2003). California and Louisiana have rice hull power plants near rice-producing areas. Rice hull ash has the greatest

Table 8. Effects of pozzolans and SCMs on the performance of concrete

Property	Silica Fume	GGBFS	Fly Ash (Class C and Class F)	Calcined Clay, Shale	Diatomite	Rice Hull Ash
Water demand	Depends on mixture	Decreases	Generally decreases; with higher % LOI and coarse (>45 µm) particles, increases	Increases	Decreases because of microporosity	Increases
Workability	Decreases, becomes sticky	Improves	Improves	Improves	Unknown	Improves
Flow of pour	Decreases	Increases	Increases	Unknown	Unknown	Unknown
Compressive strength	High compressive strength attained in same time as portland cement	Lower during first 3–7 days. By 28 days, meets or exceeds strength of portland cement.	Increases slower than normal; with time (+60 days), exceeds strength of portland cement.	Increases with time, slower than portland cement	Increases with time, slower than portland cement	Moderately high, greater than portland cement
Durability	Increases	Increases	Increases	Increases	Increases	Increases
Heat of hydration	Accelerates temperature rise in first 72 hours	Lower	Lower, except in high-calcium fly ash	Lower	Lower	Same as portland cement
Air-entrainment agent	Increases demand	Increase demand	Higher % LOI, greater demand	Unknown	Unknown	Increases demand
ASR resistance	Increases	Increases	Increases	Increases	Increases	Increases
Sulfate resistance	Increases because of refined pore structure	Increases	Increases with Class F fly ash	Increases	Increases	Increases
Bleeding of hydrated lime, Ca(OH) ₂	Lower than normal; increases potential for cracking	Generally lower	Generally lower	Lower than portland cement	Lower than portland cement	Negligible difference

Adapted from Malhotra and Mehta 1996; Lohtia and Joshi 1995.

potential in major rice-producing countries such as China and India. The market for rice hull ash has not developed in the United States to the point of having specific marketers of the product.

ADVANTAGES OF POZZOLANS AND SCMS

Mineral admixtures have many advantages in portland cement applications where they can improve the properties of concrete. Their pozzolanic or cementitious nature adds a component by replacing part of the portland cement in concrete, in general reducing cost. Offsetting the use of portland cement by using mineral admixtures can save energy and lower CO₂ emissions from cement plants.

The chemical and physical properties of the different mineral admixtures (Table 1) when added to concrete determine what properties of the concrete are enhanced. Table 8 lists the effects of these admixtures on the performance and other attributes of concrete. Characteristics of concrete influenced by adding pozzolans or SCMs are discussed in the following paragraphs.

The very fine particle size of many of the mineral admixtures can be advantageous when the aggregate is deficient in sand-sized material (Lohtia and Joshi 1995). The admixtures act as filler and are part of the cement paste, reducing the total surface area to be coated with cementitious material. Adding fine (1–20 µm), spherical particles such as fly ash can also refine the pore structure in the concrete, which reduces the amount of water needed to produce a concrete of certain consistency. Conversely, the angular shape and microporosity of some natural pozzolans increase the water demand in the concrete mixture. The percentage of LOI can also affect the amount of water needed to create the needed consistency of the concrete.

Workability is the homogeneity and ease with which concrete can be mixed, transported, compacted, and finished (Ramachandran

and Feldman 1995). The spherical shape of the fly ash, in particular, acts like ball bearings and increases workability of the concrete, decreasing the need for aggregate fines. Calcined shale and clay also improve the workability of a concrete pour; silica fume, however, actually decreases workability because of its highly reactive nature.

Strength and durability of concrete are improved by the fine-grained nature of mineral admixtures, which decreases the porosity of the concrete (Lohtia and Joshi 1995). Formation of cementitious compounds by pozzolanic reaction causes pore refinement and reduces microcracking in the transition zone between the concrete and aggregate. This significantly improves the strength and durability of the concrete. Because of retarded heat of hydration, adding fly ash, GGBFS, or natural pozzolan to concrete lowers the early strength. Strength increases over time and eventually meets, and can exceed, the strength of concrete made with portland cement alone. Silica fume is highly reactive, and concrete made with silica fume attains high compressive strength in the same time as portland cement concrete and exceeds the norm in 3 days (Lohtia and Joshi 1995).

Heat of hydration is an exothermic reaction during hydration of portland cement. Pozzolanic reactions occur after cement hydration begins when Ca(OH)₂ becomes available. Replacing a portion of the portland cement with fly ash or most natural pozzolans retards rate of hydration and manifests pozzolanic reactions late in the aging process of the concrete. As a rule of thumb, the percent reduction in heat liberated at 7–28 days is about one half the percentage of mineral admixture substitution for portland cement. Conversely, silica fume is highly reactive and accelerates the temperature rise in the first 72 hours (Lohtia and Joshi 1995). Heat of hydration is slower for GGBFS than for portland cement, and the hydration products tend to be more gel-like than portland cement, filling voids and increasing the ultimate strength of the concrete. Reduced heat of hydration is particularly important in

massive structures where the temperature increase becomes significant and can lead to cracking because of thermal stresses induced in hardened portions of the concrete mass.

Using air-entrainment admixtures (AEAs) in cement or concrete enhances the freeze-thaw resistance by increasing the void content of the concrete. The addition of most mineral admixtures increases the demand for AEA. Class C fly ash (high calcium) generally requires less AEA than Class F. The key factor is the % LOI, which appears to increase the need for AEA. This increased demand can influence the amount of water used in the mixture, depending on the type and amount of admixture added.

The presence of reactive material in the aggregate, such as opal, chalcedony, siliceous shale, and schist, causes ASRs in concrete. ASR occurs when silicate minerals react with alkali metal ions (as Na_2O and K_2O) in portland cement paste, forming a gel. With moisture, the gel can swell and expand and crack the concrete around the individual aggregate particles, causing pop-outs. Most mineral admixtures are effective in controlling ASRs. The available alkali in the mix is reduced by the amount of admixture added, as long as this material itself does not contain soluble alkalis. The size of the particles (0–45 μm) improves the packing of cementitious materials and reduces the permeability of the concrete because of the pozzolanic action. This reduces the ion migration and available external moisture in the concrete, increasing the resistance to ASR. The smaller particles of the pozzolans are preferentially attacked by alkaline solutions (sacrificial silica), forming a calcium-silicate hydrate (C-S-H) that is more stable than the silica gel and protects the aggregate from ASR attack. Some high-calcium fly ash (Class C) containing large amounts of soluble alkali sulfates increases the alkali-silica reactivity. For this reason, Class F fly ash is preferred to counteract ASR. Natural pozzolans, silica fume, and GGBFS are also effective in dealing with alkali-silica reactivity.

Concrete in certain applications must resist chemical attack by seawater, sulfate-bearing groundwater, or leaching by acidic waters. Sulfates such as gypsum react with hydration products of the tricalcium aluminate (C_3A) phase of portland cement to form ettringite. This formation of ettringite can cause swelling and internal cracking, which ultimately weakens the concrete. Adding mineral admixtures improves the resistance of the concrete to these chemical attacks through lowering the amount of C_3A by reducing the percentage of portland cement. The pozzolanic reactions of the mineral admixtures help decrease the permeability of the concrete, making it harder for harmful chemicals to penetrate the concrete.

GOVERNMENT, ENVIRONMENT, AND HEALTH CONSIDERATIONS

The biggest challenges for natural pozzolans are environmental concerns of CO_2 reduction and conservation of natural resources. Mining the natural pozzolans also requires energy, and often the raw materials then undergo drying, grinding, and calcining, which uses significant energy and produces some CO_2 . Using industrial by-products recycles materials and reduces the depletion of natural resources. Although these by-products were created through industrial processes requiring energy that creates CO_2 emissions, little or no additional energy is needed to create a usable product, making by-products very attractive to the portland cement industries, competing directly with many of the natural pozzolans. As an example, CO_2 emission savings for fly ash are almost a 1:1 exchange by weight (B. Kepford, personal communication).

Challenges lie ahead in the utilization of fly ash. The 1990 Clean Air Act Amendments requires power plants to reduce nitrogen oxide (NO_x) emissions. Lowering NO_x emissions generally restricts oxygen during the combustion process, resulting in more

unburned carbon (% LOI) in the fly ash. Unless the fly ash goes through a washing process to remove the carbon, the fly ash is unsuitable for use in concrete, its largest market. Some NO_x removal systems leave residual ammonia on the fly ash. Depending on the type of coal, the amount of ammonia adsorbed can differ. Although the ammonia does not have a detrimental effect on the performance of fly ash in concrete, ammonia fumes liberated in the concrete mix can be objectionable under certain working conditions (EPA 2003b). There is some concern of health problems related to the direct inhalation of fly ash (EPRI 1998). Because fly ash particles are spherical, they may be less likely to lodge in lung tissue than angular particles from other sources. Very small particles (<10 μm), however, can go deep into the lungs. Coal ash does contain small amounts of other materials, and there is the potential for irritation and inflammation of lung tissue. Personnel working in the ash collection process, as ash haulers and silo operators, have the greatest potential for inhaling this material. An Electric Power Research Institute technical report (1993) concluded that routine operating activities did not produce hazardous exposure.

On the positive side, the use of fly ash reduces greenhouse gases; for every ton of coal ash used, there is a 0.89-t reduction (this can vary) of greenhouse gas (Schwartz 2003) created in the production of portland cement. Using fly ash in concrete or in blended cement reduces land disposal requirements and reduces the use of raw materials in creating portland cement clinker.

Silica fume is a very fine-grained material and should be treated as any other respirable dust. Although silica fume is amorphous silica, some small amounts of crystalline silica are present below measurable limits. The presence of any quartz requires warnings on the material data safety sheets for silica fume.

TRENDS AND OPPORTUNITIES

Portland cement and concrete are major growth industries, and in the past 10 years, more portland cement manufacturers have realized the benefits of using pozzolans and SCMs in their product. Pozzolans and SCMs add durability to the concrete, extending the life cycle of a project. Another industry trend is the increased use of by-products over calcined clay and shale. As part of implementing sustainable development, conservation of natural resources has added to the desirability of using SCMs derived from industrial by-products. Production of blended cement containing natural pozzolans decreased from 192,000 t in 2001 to 187,000 t in 2002 in the United States. Fly ash is the leading by-product used in part because of the large volume produced—more than any of the other by-products—and its lower cost. Silica fume is a high-value product and only has certain applications. GGBFS use is limited in the United States by the decline in production from blast furnaces; sales of GGBFS have grown, however, and the need for GGBFS is being met by importing material. Fly ash use in clinker and blended cement has increased over the past several years in the United States, and clinker's predominant use is as a partial substitute for portland cement. The U.S. cement industry's 2003 consumption of fly ash for clinker was 2,250 kt and 39 kt for blended cement (van Oss 2003a). The concrete industry consumes a significantly larger volume of fly ash (11.1 Mt) as a substitute for portland cement in concrete (ACAA 2004b). Primary consumption of GGBFS is for blended cement, which has decreased from 369 kt to 333 kt for 2002 and 2003, respectively (van Oss 2003a). van Oss hypothesizes that this decrease is because of "lower sales volumes of slag-rich blends of concrete" or decreased use of slag as a grinding aid to make Type 1 portland cement.

The demand for cement worldwide is projected to rise 4.1% through 2006, with China as the largest market. Other developing

countries in Asia/Pacific, Latin America, and Eastern Europe are expected to have greater demands for cement as well (*Mining Engineering* 2002). Along with this growth, the demand for blended cements and pozzolanic materials will increase. Blended cements are attractive because of the potential to lower carbon emissions by partial replacement of cement clinker with industrial by-products and the superior performance of blended cements in certain applications. Barriers to greater usage of blended cements depend on availability, transportation costs, building code standards, and other legislative requirements (Worrell et al. 2001). Potential for CO₂ reduction varies by country, depending on current use of blended cements and the availability of blended materials. As an example, China's use of coal for power generation and significant iron production make it a candidate for using blended cements. Currently, China uses primarily portland cement. By using blended cements, China could significantly reduce its carbon emissions from clinker production (Worrell et al. 2001).

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Roofing Materials

Daniel N. Leavell

INTRODUCTION

The roofing industry offers many opportunities for industrial minerals and rocks suppliers to develop high-value, year-round markets for their products. This market opportunity is not widely known in the aggregates industry, and few of the manufacturers of roofing materials have a good idea of the alternate materials available near their plants. Materials routinely produced for aggregate may be graded in relatively narrow size ranges, and offered as components for use in a wide variety of composite roofing types.

Many natural and synthetic materials are used as roofing materials around the world. The local choice is based on necessity, custom, available materials, material cost, and the anticipated life of the structure. In underdeveloped areas, low-cost and widely available materials such as brush, thatch, or palm fronds may be used. These may be enhanced with clay, mud, or even bitumen. Such organic materials are not expected to have a long life and must be renewed at regular intervals. The low weight of the roof system, however, allows the homes to be constructed using minimal materials, which keeps costs to a minimum.

With increasing urbanization, a desire for more permanent homes leads to the use of heavier-weight materials. More robust homes are capable of supporting a heavier roof structure, and mined earth materials such as slate or flagstone and tiles made of clay or concrete have commonly been employed. Roofing made of metal, which can range from inexpensive corrugated sheets to much more costly, coated modular steel systems, is also very popular around the world. Increasingly, composite roofing materials fabricated of natural and synthetic materials are used because of their lower cost, ease of transport, and greater flexibility of application.

This summary of roofing materials focuses on the opportunities for supplying industrial minerals and rocks to composite roofing manufacturers in North America (as this is where the author has gained his experience). Many of the ideas in this chapter, however, are applicable to markets worldwide.

ASPHALT SHINGLES

Asphalt shingles are the most popular and least costly form of roofing in use today in the United States. In residential construction, asphalt shingles account for nearly 85% of all roofing. Shingles are made to a high standard of quality and are available in a wide variety of styles and weights. Even the least robust shingles are

designed for a life of at least 20 years. Heavyweight, high-end shingles now offer warranties of 40 to 50 years.

Although called *asphalt* shingles, this roofing material is a true composite with asphalt representing an important, although minor, component. By weight, shingles are more than 80% mineral and rock, and shingle manufacturers provide a broad target market for industrial minerals producers. Asphalt roofing shingles are a heavyweight product, so roofing plants are located throughout the United States to avoid high shipping costs. Mineral and rock supply to these individual plants is largely a regional business as well, for the same reason. Previous editions of this volume have focused only on roofing granule production and supply, but many more opportunities for supply to asphalt roofing manufacturers exist, as described in this chapter.

As manufactured in the United States, asphalt roofing shingles are produced in several broad categories. The largest percentage of production is of 3-tab shingles, which are considered the standard of low-cost dimensional roofing. An increasing percentage of production is of what are called architectural or laminated shingles. These new-style shingles offer a dimensional look and are typically of a heavier weight. In addition, many roofing plants still manufacture rolled asphalt roofing and smaller interlocking shingles for use in high-wind areas.

All of these products are manufactured in the same way, using the same basic ingredients. The differences are in the amounts of the ingredients and in the manner in which the shingles are cut at the end of the production line. Asphalt shingles are made in a continuous sheet, up to 60 in. wide. The sheet moves through the machine at speeds as high as 700 fpm, and in just seconds all the materials of the shingle must be applied to build the composite structure while the asphalt is still hot. Granules must be pressed into the asphalt-saturated mat before cooling begins. The sheet is then cooled rapidly and delivered to the cutting machine, which cuts the sheet into standard-size tab shingles or builds a laminated structure for the architectural-style shingles.

Figure 1 shows typical examples of both 3-tab and laminated shingles. At the heart of the shingle is a fiber mat, most commonly made of nonwoven fiberglass, although some shingles are still made with a paper mat. The mat is saturated with mineral-filled asphalt coating, which is applied to both the top and bottom surfaces of the mat. The greatest performance-enhancing differences

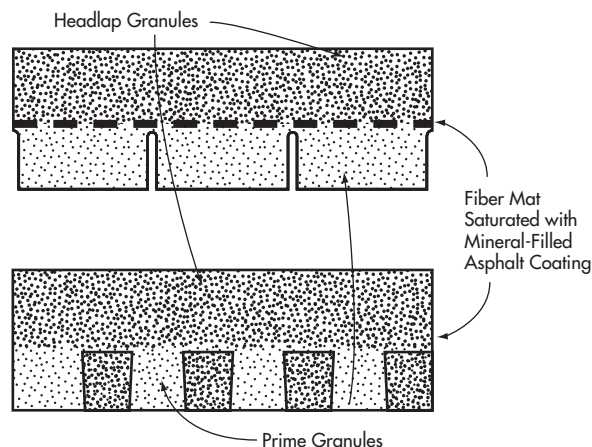


Figure 1. Three-tab and laminated shingle construction

in all the shingles made are in the weight of the mat and in the thickness of the applied asphalt layers. While the asphalt-saturated mat is still very hot, granular rock materials are placed first on the topside of the sheet and later on the backside of the sheet. The granular materials consist of rock granules coated with colored ceramic (prime granules), rock, or slag granules with a similar gradation (headlap granules), and finer silt-sized granules deposited on the backside (backdust).

Top-surface granules give the shingle substantial weight, and prime granules also provide protection for the asphalt, which is the waterproof layer of the composite shingle. Because sunlight's UV rays degrade asphalt, prime granules must be effectively opaque to UV light to shield the asphalt. Today prime granules are colored by a ceramic coating, and nearly a dozen colors are available. These are used either as single colors like white or black, or more commonly as blends of colors, placed on the shingle surface in complex patterns for visual effect. Headlap granules serve little purpose other than to balance the sheet, although they do give weight and substance to the finished shingle.

Because the requirements of roofing plants in the United States and Canada, each requiring significant year-round supply, huge potential opportunities exist for supplying all of these graded rock materials. The greatest opportunity by weight is in supply of fine-grind mineral filler. Individual plants require a minimum of 100,000 t of filler per year. Granules, both prime and headlap, are also used in high volume by each plant, and represent the greatest expense of manufacturing shingles, particularly the ceramic-coated prime granules. Backdust material supply is a smaller opportunity, but can be a lucrative use for mineral fines from aggregate production. Each of these materials is considered in detail in the sections that follow.

TOP-SURFACE GRANULES

The coarse, graded aggregate that is applied to the top surface of asphalt shingles serves several purposes. Colored prime granules provide the distinctive colors and patterns of the finished roof and protect the asphalt layer from rapid degradation by UV radiation. Headlap granules may provide some distinctive appearance in 3-tab shingles, but in laminated shingles these granules exist only to add weight to the shingle and coat the asphalt of the top half of each shingle. Headlap granules offer UV protection only in 3-tab shingles. In all other types of shingles, headlap granules are not exposed on the roof. The growing popularity of laminated shingles has

resulted in many new opportunities for granule supply to individual roofing plants.

Prime and headlap granules share some characteristics but have significant differences in performance requirements. Although in some plants, prime and headlap granules may come from the same quarry, in most cases the two types of granules are likely to be quite different materials. Ideally both granule types should share the same gradation—a rather narrow size range (ASTM [American Society for Testing and Materials] #11)—which resembles coarse sand (12 × 40 mesh, U.S. Sieve Series). For production reasons it is important that both prime and headlap granules have a similar bulk density and roughly the same granule shape. Shingles are made in wide sheets, and these qualities ensure that the weight of applied granules will be equal across the sheet. Both types of granules should be durable and capable of bulk handling without breaking down into smaller pieces. The granules should also be able to withstand multiple freeze-thaw cycles without decrepitation to give the roof a long life.

Prime Granules

Previous editions of this chapter in *Industrial Minerals and Rocks* (Kalyoncu 1994) focused on the potential business opportunity for colored prime granule production. Although the potential profit margin of prime granule production is great, the technical experience and capital expense required to compete with existing granule suppliers is also very high. The days of supplying prime granules to only one or two roofing plants are gone, with most shingle manufacturers now supplying their products nationally from many regional plants. Their desire for uniform products across their manufacturing line precludes entry by startup granule suppliers. Today, most prime granules are produced by only two suppliers, 3M Corporation and ISP Specialty Minerals. Both companies produce uniform colors of ceramically coated granules at multiple plants strategically located across the country.

Although a number of rock types are used as the base rock for coated granules, all are either igneous or metamorphic. The base rock for prime granule production should be inherently opaque to UV transmission and uniform in color. Fine-grained rocks are preferred, and the best granules tend to be made from rocks that, when crushed, have a shape that is not dominated by a strong mineral cleavage.

The shape and natural gradation of granules made from any two rocks will be different and dependent on the type of crushing equipment employed, as well as on the nature of the rock. In practice, the best granules have been made from meta-volcanic rocks, with fine grain size and a relatively light color. These rocks crush uniformly to an approximately cubical shape and can be color-coated thoroughly and consistently. Crushing and screening roofing granules requires considerable experience and care. The desired size distribution (ASTM #11) is narrow, and production of excess fines is undesirable. Waste from the screenings is nearly 50%, and existing granule producers struggle to find suitable uses for the fines.

Color coatings are applied to the base granules in large batches, and the pigmented clay-rich coatings are fired in rotary kilns. Producing consistently coated granules is difficult, and process and batch control are critical for color consistency. Existing prime granule manufacturers employ elaborate storage and shipping techniques to ensure that shingle plants receive consistent supplies of individual colors. The coating must be durable in material handling, as well as stable in application to the shingle.

In humid climates, a small percentage (10% or less) of the prime granules may be replaced by special algae-resistant (AR) granules. These AR granules are made with a layer of copper oxide

beneath the colored ceramic coating. The copper leaches slowly from the coating over the life of the shingle, acting as a biocide to inhibit the growth of algae on the shingles.

Headlap Granules

Traditionally, shingle manufacturers have favored dark-colored granules, with high UV opacity, for shingle headlap. The materials used include both graded rock aggregate and various industrial by-products. Supply has been dominated by specialty companies marketing industrial slags, such as those produced as a by-product of coal combustion in certain old-style power plants. These coal slag supplies have become increasingly scarce because modern coal-fired power plants do not produce a coarse glassy slag. Consequently, the slags have become increasingly costly as many old waste areas have become depleted. At the same time, a shift in shingle style toward laminated shingles without exposed headlap areas has opened an excellent market niche for traditional rock aggregate producers.

Headlap granules are produced to the same physical and gradation standards as prime granules but can be made from many different crushed rocks, and even from coarse sand and gravel deposits. Opacity to UV transmission is not a concern with laminated shingles, and even some carbonate rocks can yield good headlap granules. Consistency of bulk density and granule gradation is of greatest concern to the shingle maker, because the weight of granules per unit area, as applied to the shingle sheet, must be held nearly constant for reliable shingle machine operation.

Granules are typically produced to the rather narrow size range of the ASTM #11 gradation standard (12 × 40 mesh, U.S. Sieve Series). Tolerance for fines in the product is low. Production of such a fines-free sand product from crushed rock can result in significant waste material. A beneficial use for the fines from granule production can mean the difference between a successful operation and a failure. Fines may be added back into a more traditional manufactured sand product or they may be further screened to yield backdusting granules, as described in the following section. Even without a beneficial use of the fines from headlap production, the relatively high cost of headlap can result in a profitable specialty product for a traditional rock aggregate quarry. To compete in the headlap market, a supplier must be able to provide granules at a delivered cost of \$35 to \$45 per ton. Individual roofing plants use upward of 50,000 t of headlap per year, and the largest plants in the United States require 3 to 4 times this quantity.

BACKDUST GRANULES

In asphalt shingles, backdust is used primarily as a parting agent on the bottom or backside of the shingle. Backdust typically consists of fine, sand-sized rock granules that are liberally applied to the hot asphalt coating just prior to the cooling section of the shingle machine. The backdust works to isolate the hot asphalt from the cooling and guide rolls, and also prevents shingles from sticking together when packaged.

Backdust materials are widely varied, both in size range and material properties—ranging from finely crushed talc to crushed carbonate, igneous and metamorphic rock fines, and even crushed glass and slag. Naturally sorted sedimentary silica sand has been the backdust of choice for many years because of its easy handling, ready availability, and low cost. Asphalt shingles have a wide tolerance for these diverse materials, although each shingle process has been optimized for the material in use.

Some backdust materials perform by coating or blanketing the sheet. This is typical with talc or some of the crushed carbonate backdusts, which have a higher percentage of fines. Other backdusts

Table 1. Mohs mineral hardness scale*

Mohs Number	Mineral Name	Common Tool Hardness
1	Talc	
2	Gypsum	Fingernail: 2.5
3	Calcite	Penny: 3.5
4	Fluorite	
5	Apatite	Glass plate: 5.0–5.5
6	Orthoclase	Knife: 5.5–6.0
7	Quartz	Steel file: 6.5–7.0
8	Topaz	
9	Corundum	
10	Diamond	

* Softest = 1, hardest = 10

perform by holding the shingle away from the adjacent sheet or roll. Median grain size of these coarser granular materials will be critical as shingle manufacturers alter the amount of backcoating on the shingle. Thicker backcoating requires a coarser backdust to isolate the sheet, particularly from the cooling section.

Although the shingle process has a wide tolerance for material differences, as with filler, consistency of the backdust is very important to system performance. Suppliers must strive to produce consistently sized materials with consistent bulk density and flowability. This is relatively simple with sand products that are not crushed but produced from loose sediment or disaggregated sedimentary rock. Often these products will not vary much because of the nature of the mined materials. The supplier must tightly control crushed products, such as talc, carbonate, slag or glass, to ensure consistent properties.

One of the high-maintenance areas of shingle manufacture is in the shingle cutting machine. Here the sheet is cut into individual shingles and unique shingle patterns are cut and laminations are assembled. Backdust properties seem to have a considerable effect on the life of materials used in cutting knives in the shingle machines. The difference in the Mohs hardness (Table 1) of the minerals used for shingle backdusts, relative to the hardness of the steel used for the cutting knives, appears to be a major controlling factor. Many shingle lines use silica sand as their backdust, and this material is considerably more resistant to wear than steel. Simply changing to backdust material made from a softer mineral has been shown to result in significantly less wear and lower operating costs. Talc and carbonate backdusts are considerably softer than steel, but even backdusts made from slag or glass offer a hardness advantage over silica sand.

The gradation of backdust sand employed is highly varied throughout the roofing industry. The granule gradation is chosen for its performance as applied to the shingle, and individual plants may make several different specification shingles. Typically the gradations have been fine—a relic of the migration away from using talc and the readily available sand supplies of the coastal plains and river systems of the continent. With thin backcoating on lighter weight shingles, fine-size distributions have worked well; however, heavier-weight shingles require thicker backcoating and a consequent shift to coarser gradations to protect the equipment and prevent sticking of the shingles in the package. The sand must be appropriately sized for the process in which it will be used. Shingle manufacturers may use multiple sands to accommodate the needs of a diverse product line.

The most difficult aspect of producing backdust sand from a crushed rock is obtaining a sufficiently fine sand size without

significant fines (less than 5% to 10% –200 mesh). A target gradation is typically 50 × 200 mesh (U.S. Sieve Series). A dedicated process is needed to produce such a restricted size range consistently. Material removed from the crushed rock at the top end of the sand gradation can be made into a shingle headlap. Headlap granules (10 × 40 mesh) have not traditionally been carbonate rock, but with the production of laminated shingles, carbonate headlap is practical. An effective air classification process should be used to control the tail end of the backdust gradation. Excess fines produced by sand gradation can be added to agricultural lime or landscape pellets.

Backdust Materials

Talc

Talc was more widely used in the past but is now used in only a few plants nationwide. Although talc is the most expensive backdust in use today, less material is needed for each shingle because of the platy nature and fine size of the talc dust. Because talc applies to the shingle sparsely, however, the resulting shingles have a lower weight of backdust and require an increased amount of filled coating. This increases the material cost of the shingle. Concerns about the mineralogical association of talc with asbestos also limit talc's desirability. The low Mohs hardness of talc is a plus; the mineral has no impact on the wear of cutting knives.

Carbonate

Carbonate refers to backdust made from crushed limestone, dolomite, and marble, with mineralogy having little, if any, impact on the performance of the backdust. High-quality backdust can be produced from any hard crystalline carbonate rock, such as those produced by aggregate suppliers for construction and road building. Carbonate backdust is made from crushed rock, and because fines must be controlled, it is fairly expensive to make and somewhat difficult for a supplier to control. The material is dusty and may result in backdust transfer issues, both in manufacturing and in later material handling of the shingles. In certain areas of the country where crushed limestone prices are low, there are distinct advantages to using carbonate backdust, and this material can be very effective in a backdust system. Because the Mohs hardness is significantly less than that of steel, the backdust has considerable less wear potential than silica sand, resulting in greatly reduced knife wear.

Silica Sand

A majority of U.S. roofing plants use silica sand as a backdust. The size distribution and mineralogy of this sand is dependent on the source and somewhat varied. All are predominantly silica (quartz) and inherently hard. Typical minor minerals are feldspar and mica. Although most silica-sand backdusts are from naturally graded sedimentary deposits, these backdusts also have the potential to contain fine, respirable, crystalline silica, which has been identified as a carcinogen. Because all of the silica sands were deposited as sediments, they tend to have rounded grains and great flowability.

Slag

Only a few shingle manufacturers use industrial slag backdust (glass from a refractory process) today, although the use of fairly coarse coal slag sand is increasing and shows good potential because of low material costs. A number of existing slag headlap suppliers could potentially supply useful sand-size slag fines.

Glass Sand

Specialized equipment can crush glass sand from postconsumer-waste bottles to subangular particles. Glass sand can be tailored to a useful gradation, and, in application, compares favorably to silica

sand. Because of the lower Mohs hardness of glass (Table 1), manufactured glass sand offers the potential for significantly reduced wear to the cutting knives of shingle machines. As with carbonate sand, fines in the backdust must be minimized. Producing sand backdust from postconsumer glass is a beneficial reuse for glass, particularly the broken tricolored waste that is typically landfilled today. Many glass recyclers that produce cullet have considerable stockpiles of broken tricolor glass too fine for separation. Cullet for remelting must be of a higher quality than that required for shingle backdust.

Backdust Value

The delivered cost of backdust sand ranges from about \$20/t to a high of nearly \$40/t. Talc is an exception and may cost as much as \$85/t. Talc, however, behaves differently in application than other materials, and it goes much further. Typical sand application rates are about 6 to 10 lb/square of shingles, so individual plants will require upward of 15,000 tpy. It is important to understand the price of competing materials in each market because price depends on a available materials and proximity of supply to the end user. Most sand supplies are delivered by truck, with a typical supply of 2 to 3 days on hand at the shingle plant.

MINERAL FILLER

Fillers or extenders have long been used in the fabrication of asphaltic roll roofing and roofing shingles. Initially the motives were probably purely economic, to incorporate a waste material (roofing granule fines) into the asphalt, extending the filled-coating asphalt and thereby reducing the overall cost of saturating asphalt per unit of roofing. Reducing the cost of saturating asphalt is still the primary motivation for the use of fillers, but the addition of filler material enhances certain performance characteristics of a roofing product, altering the rheological properties of the filled coating and enhancing its resistance to weathering by sunlight.

Early shingles used felt or cellulose for the mat of the shingle, and saturating asphalt had to be nearly pure to infiltrate the mat. Too much (or too coarse) filler was unable to be pressed into the mat, and saturation was incomplete. With the introduction of fiberglass mat (more porous but also stronger) in sheet roofing, an increase in filler percentage was possible, allowing for greatly reduced filled-coating costs. Shingles are made today with filled coating that contains as much as 67 to 68 wt % filler.

When roofing was made primarily at the same location as the surfacing granules, there was little incentive to use any filler other than the rock fines that resulted from crushing and grading rock granules. With the proliferation of roofing plants and the recognition by granule makers that they could profit more from selling colored granules from a small number of large plants, roofing plants sprouted closer to the end-user markets, away from most of the raw material suppliers. This opened the door for manufacturers to try alternate filler materials. Fine-grind carbonate rock is the filler of choice today.

Although dolomite has been effectively used as asphalt filler for roofing, today most manufacturers prefer high-calcium limestone (greater than 91 to 92 wt % calcium carbonate [CaCO₃]). High-calcium filler is believed to result in shingles with higher tear strength, although the mechanism underlying this result is not fully understood. Dolomite is a slightly harder mineral than calcite, and it is likely that the higher-strength shingles result from the interaction of slightly softer filler and the fiberglass mat. Regardless of an explanation for the interaction, manufacturers have come to demand high CaCO₃ content, and consistency of filler chemistry, gradation, and moisture is critical for manufacture of consistent shingles.

Many limestone deposits are quite varied in chemistry, requiring selective mining of the higher-grade, calcium-rich layers. Other variables that may negatively affect filler performance include silica (commonly present as minor chert), silicates that may be introduced in to the ground limestone from included soil, and even insoluble organic material in the limestone.

Carbonate fillers are produced from many different rocks, ranging from marl to marble. Few roofing plants share a filler supply, and many rock and crusher combinations are employed effectively throughout the industry. The best fillers in use are those that are produced as a primary product of crushing, rather than as a by-product of some other crushed stone product. Crushing systems work most efficiently when the mill receives a consistent feed supply, and the resultant filler is likely to have a consistent gradation and chemistry. Material quality control requires routine sampling and testing.

No single filler gradation has been established by the industry. Typically, filler is made to a standard of 60% to 65% passing a 200-mesh screen; however, many roofing plants use finer filler (up to 80% passing 200). Each rock and crusher combination will yield a slightly different size distribution in the ground rock. Typically, roofing plants have learned to work with the material available at a low price and within a reasonable distance of their plant. Filled-coating systems have been adapted to accommodate the available material. Consistency of the material is probably as critical to maintaining a long-term supply contract as the chemical consistency of the limestone.

In general with finer gradations of filler, more material handling difficulties may be encountered in shipment, transloading, and in-plant handling of the filler. Filler must be transferred from trucks or railcars into plant storage silos, which may hold 300 or more tons. The filler must then transfer freely through a filler heater before being combined with the hot asphalt. If the filler has an abundance of superfine particles, or even excess moisture content, it may not flow well through the system and can cause production problems in the shingle plant.

Today mineral filler is the largest component of roofing shingles (by weight or by volume), and having a timely and efficient transportation system in place is a key part of filler supply. Plants require nearly constant supply to their systems, and the most attractive portion of a supply contract may be on the transportation and delivery side. It is common for plants to require 10 to 15 trucks per day, every day of the year. Delivery of filler by rail, which allows material to be sourced at a greater distance from the plant, still requires 400 or more train cars per year. The price that the rock supplier receives for the material and labor typically reflects only about one half of the delivered cost of the product. Here is the biggest problem with filler supply; roofing plants expect high-quality control and consistent material properties, but they want to have rock-bottom pricing. As the demand for more calcium-rich filler continues, the price of filler should increase because of competing demand for the high-calcium stone in flue-gas desulfurization, animal feeds, and other chemical applications.

SUMMARY AND FUTURE TRENDS IN ROOFING MATERIALS

Specialty roofing, such as clay and concrete tiles, metal, and fiber-reinforced tiles of plastic and cement, are typically high-end products with limited or regional markets; however, the market for these traditional and innovative roofing materials is growing. Also, traditional materials such as slate and wood shingles remain in demand in certain areas of the United States. Because of the high initial cost

of installing these specialty roofing materials, however, the demand for asphalt shingles remains strong. The market for asphalt roofing shingles is expected to grow at an annual rate of 2% to 3% for the next several years. This includes both shingles for new construction and re-roofing of existing homes. The industry has seen much consolidation in the last two decades, and there has been a trend toward national markets and less regional supply of shingles. Manufacturing plants have been increasing their capacity, and suppliers of materials have grown to keep up with demand. Innovation in shingle materials and design, along with a continual desire to reduce material costs, offers excellent opportunities for aggregate suppliers to broaden their product lines to include headlap and backdust surfacing granules. Backdust can also help rock crushers to utilize some of their waste rock fines.

Breaking into the supply chain for asphalt shingle manufacturing can be difficult because the industry is conservative and change can temporarily interrupt a high-speed manufacturing process, adding to short-term costs. But the opportunity for both the supplier and the manufacturer is great. Industrial minerals and rocks suppliers should assess the potential market in their areas and consider whether these narrow-specification products can be made with minimal capital additions to their plants. Next, they should find out what manufacturers are located in the region and explore their current supply situations. Production managers should be consulted to see if they are open to change, and if a new material might help them reduce the cost of production or enhance the performance of the process and product. Some readers of this chapter may, however, be coming from the shingle manufacturing side. Manufacturing managers may not be aware of local and regional industrial minerals supply and should take some time to learn what natural rock materials are available locally. Freight costs can easily be as great as material expenses in granule and filler supply, so innovative supply scenarios can cut material costs significantly.

If industrial minerals and rocks suppliers can identify a cost-effective market for their materials and meet the rigid specifications for consistency and quality control needed for roofing material supply, asphalt shingle supply can provide a stable, year-round outlet for high-value, mined-rock products. Breaking into the market might be difficult, but opportunities for success are great.

USEFUL WEB SITES

The following Web sites contain more information about roofing materials:

- National Roofing Contractors Association (NRCA): www.nrca.net
- Monthly publication of the NRCA: www.professionalroofing.net
- A listing of roofing manufacturers: www.roofhelp.com
- Asphalt Roofing Manufacturers Association: www.asphalt-roofing.org
- National Stone, Sand & Gravel Association: www.nssga.org

PERTINENT ASTM STANDARDS

The following ASTM standards pertain to roofing materials:

- ASTM Standard D225-04, Standard Specification for Asphalt Shingles (Organic Felt) Surfaced with Mineral Granules
- ASTM Standard D451-91, Standard Test Method for Sieve Analysis of Granular Mineral Surfacing for Asphalt Roofing Products
- ASTM Standard D452-91, Standard Test Method for Sieve Analysis of Surfacing for Asphalt Roofing Products

- ASTM Standard D1863-93, Standard Specification for Mineral Aggregate Used on Built-Up Roofs
- ASTM Standard D3462-04, Standard Specification for Asphalt Shingles Made from Glass Felt and Surfaced with Mineral Granules
- ASTM Standard D3909-97b, Standard Specification for Asphalt Roll Roofing (Glass Felt) Surfaced with Mineral Granules

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Structural Clay Products

Denis A. Brosnan and J. Gregg Borchelt

INTRODUCTION

Structural clay products are semi vitreous clay ceramic, prismatic-shaped units used in masonry construction and pavements. These products are made by forming moist, earthen raw materials into the desired shape, drying to remove free water, and heating or “firing” to temperatures in the “red heat” range (i.e., temperatures greater than 950°C). Exposure to these temperatures partially fuses the mass so that the bricks, when cooled, are composed of residual minerals bonded with a vitreous or glass phase. It is the vitreous nature of structural clay products that produces their well-known strength and durability.

Other types of masonry units are also used. Concrete masonry units consist of aggregates bonded by hydrated calcium silicate cement (portland cement). Calcium silicate (sand lime) bricks, consisting of siliceous aggregates and sand bonded by lime in a hydrothermal (autoclaving) process, are available in many parts of the world. Adobe bricks are unfired earthen units that are sun-dried and used as such; some adobe bricks are made with portland cement or asphalt admixtures to slightly improve their resistance to rain. (The reader is referred to the chapter on adobe and earthen construction in this volume.) None of these units is heated or processed to high temperatures. Concrete masonry units, calcium silicate bricks, and adobe bricks are thereby differentiated from structural clay products by their lack of a vitreous bond.

Structural clay products (hereafter restricted to and called *brick*) have been produced for at least 8,000 years, and fired bricks have been manufactured for at least 3,500 years. Brickmakers in the Roman Empire were particularly proficient in the firing process, and 1,000-year-old Roman buildings still survive in excellent condition. It was the Roman tradition that led to load-bearing design for brick walls in European buildings—with stucco-covered clay structural (or load-bearing) brick predominating in southern Europe.

Clay facing bricks have been used with clay structural bricks in northern Europe after the Roman tradition. The use of facing bricks and structural bricks was the predominant form of construction in North America until World War II. Thereafter, brick became a popular facing material backed by concrete masonry units (i.e., veneer cladding), or brick veneer is used over wood or steel stud walls in residential or commercial construction (Figure 1). Brick veneer is also used over concrete masonry, concrete, or steel stud backing (the last on framed buildings). In veneer applications, the brick serves as an exterior cladding attached to the backing with a



Figure 1. Bricks are used extensively as facing material for buildings

series of steel anchors. Since 1980, clay paving bricks have gained a large market share in North America.

BRICK PRODUCTION IN THE UNITED STATES

Brick production in the United States rose steadily in the late 1990s to a level of more than 9.2 billion standard brick equivalents by 2004. The brick industry uses the term *standard brick equivalent*, or SBE, as a basis for comparison. An SBE has dimensions of $7\frac{5}{8}$ in. (length) \times $2\frac{1}{4}$ in. (height) \times $3\frac{7}{8}$ in. (thickness). It corresponds to a nominal modular size brick.

Brick production roughly follows residential housing starts. Nearly 80% of bricks produced are consumed in the residential market. Since 1992, the average number of bricks consumed per housing start has been relatively constant at about 5,000 bricks.

In 2003 there were 75 businesses operating at 180 locations (with more than 420 individual kilns) to manufacture clay bricks. They employed 14,199 workers with a payroll exceeding \$430 million. Firms with 500 or more employees represented 8% of the brick manufacturers, and these firms operated 52% of all the brick plants. More information is available from the U.S. Census Bureau (<http://www.census.gov>) and the Brick Industry Association (BIA; <http://www.gobrick.com>).

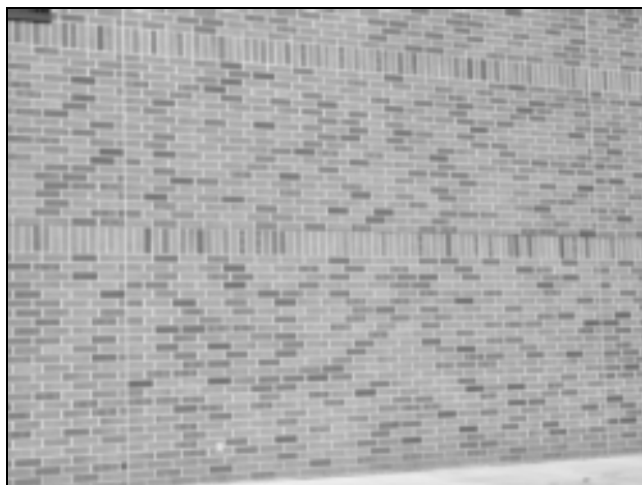


Figure 2. Bricks exhibit ranges in colors and can be blended for an overall visual effect

In the United States, the South Atlantic region (Delaware, Maryland, District of Columbia, Virginia, West Virginia, North Carolina, South Carolina, Georgia, and Florida) predominates in brick production, accounting for 39.0% of the total manufactured while consuming 33.7% of all bricks produced in 2002. The East South-Central region (Kentucky, Tennessee, Alabama, and Mississippi) ranks second in importance in brick manufacturing. This area produced 19.0% of all U.S. brick and consumed 15.5% of the bricks produced. Although virtually all brick manufacturers ship into many states and regions, the geographic distribution varies depending on the size of the producer company. Larger firms are more likely to ship their products throughout the United States, whereas smaller firms tend to ship only to adjacent states or neighboring regions.

The market share for bricks in residential construction in the United States is about 20% for new single-family houses. This share has declined since the early 1970s, but it has held steady since the late 1990s. Bricks are sold directly by producers as well as through brick distributors. Current pricing is available from individual producers.

More than 20 brick sizes are available, with modular brick ($3\frac{5}{8}$ in. wide \times $2\frac{1}{4}$ in. high \times $7\frac{5}{8}$ in. long) accounting for just less than 50% of production. The next most popular size, accounting for 18% of production, is “king size” (3 in. wide \times $2\frac{5}{8}$ in. high \times $9\frac{5}{8}$ in. long). Thousands of uniquely colored and textured bricks are available from producers, allowing consumers to create a unique, personalized appearance for their residences (e.g., Figure 2). The demand for brick is based on the image it creates. Bricks with an antique look have gained in popularity in recent years. Brick remains the preferred facing material on upper end residential structures.

STANDARDS FOR BRICK IN THE UNITED STATES

Brick products must meet standards published by the American Society for Testing and Materials (ASTM, <http://www.astm.org>) if the manufacturer either voluntarily or contractually (in the sale) represents that the product complies with a particular product standard. Several standards relate directly to requirements for bricks:

- ASTM C216, *Standard Specification for Facing Brick (Solid Masonry Units Made from Clay or Shale)*

- ASTM C652, *Standard Specification for Hollow Brick (Hollow Masonry Units Made from Clay or Shale)*
- ASTM C902, *Standard Specification for Pedestrian and Light Traffic Paving Brick*
- ASTM C1272, *Standard Specification for Heavy Vehicular Paving Brick*

ASTM C67, *Standard Test Methods for Sampling and Testing Brick and Structural Clay Tile*, gives testing procedures for brick products. Information on the content of these standards is found in the section titled Key Physical Properties of Brick in this chapter.

ASTM standards for brick are included in building codes adopted by governmental agencies to provide minimum standards for construction. Building codes also provide requirements for masonry construction, and local codes should be consulted for specific requirements.

The *Technical Notes on Brick Construction* series (BIA, various dates) gives design, construction, and maintenance information on brick products.

BRICK MANUFACTURING

Raw Materials

To make brick products, earthen materials obtained by open-pit mining methods are used. These materials must, when processed, contribute plasticity (cohesion) when mixed with water and must exhibit an acceptably broad range of vitrification so that firing may be accomplished in continuous “tunnel” kilns. The plasticity requirement ensures that bricks can be formed and handled for subsequent drying and firing operations.

Raw materials used in brick manufacturing generally are called *clays*, although they may contain only a limited amount of substances considered clay minerals. Clays can vary in chemical composition and mineral origin. Typical raw materials are shale, alluvial clay, and mixtures thereof. Clay minerals usually are members of the kaolin, illite, and smectite mineral groups. Fired brick usually exhibit a chemical analysis of 10% to 20% Al_2O_3 ; 0.5% to 6.0% Fe_2O_3 ; and 50% to 60% SiO_2 . Most of the silica is chemically combined with the residual clay or located in the vitreous phase (i.e., it is not a free or available entity).

The color of fired bricks originates in the intrinsic content of transition metal elements such as iron. Oxidized forms of iron give bricks their typical red color (from hematite, or Fe_2O_3 crystals, held in the vitreous phase). Bricks produced by reduction firing, also called “flashing,” have a characteristic blue-black color from the transformation of hematite into magnetite, or Fe_3O_4 , and the reaction of FeO with silica to form an iron silicate called fayalite (FeSiO_3).

Many brick plants mix clays from different sources to produce unique fired colors. Colorant oxides such as iron oxide and manganese oxide may be added to clays to provide uniform “through body” colors. Many bricks have surface-applied colorants (colorant applied as powdered pigments) or surface-applied slurries of clay and pigments. Glazes containing pigments can be applied to obtain an impervious surface. The surface of bricks can be deformed to provide an antique appearance, and sand can be applied to the surface of the bricks to produce either temporary or permanent textures or colors.

The chapter on clays and shale provides a more detailed discussion of the clay used in brick manufacture.

Clay Processing and Brick Forming

Clay from the mine is crushed and ground to the required particle size. Many plants stockpile or store raw materials to avoid the need to dry the clay during rainy weather. The clay moves through the primary and secondary crushing operations and is screened or “scalped” to about 8 mesh (2.46 mm) and finer sizes.

Forming, Drying, and Firing

Bricks are formed by machines using either extrusion or molding processes. In extrusion, augers push the wet clay mass through an orifice to produce a continuous clay column, which is cut into individual brick units. In molding, a wet clay mass is forced into individual cavities (molds) and subsequently demolded. When producing many molded bricks, sand or water applied to the mold surface prevents the clay from sticking to the wood or metal mold. These bricks are referred to as sand-struck and water-struck brick, respectively. Few manufacturers make traditional hand-molded bricks.

The dry pressing method is used for a minority of clay brick production; the primary method of forming brick is the extrusion method, used for 91.4% of brick shipments in 2002. The machine-molded method is used for 6.8%, and dry pressing accounts for 1.8% of brick production from the reporting companies.

Bricks are dried in continuously fed tunnel dryers, with bricks stacked or loaded on wheeled cars. Kiln cars transport stacked settings of bricks through the kilns. Most bricks are fired in tunnel kilns (Figure 3), where the bricks are exposed to an increasing temperature to a maximum or "soak" temperature condition. More than 90% of the kilns are fired with natural gas. The bricks are then cooled to room temperature for packaging and transport (Figure 4). Waste heat from the cooling section of the tunnel kiln is used in the dryers to maximize thermal efficiency. Some brick plants use periodic kilns: the bricks are loaded in the kiln and remain in a stationary position for the entire firing process. The fired bricks are then packaged "cubed" and strapped for delivery.

Key Physical Properties of Brick

ASTM C216 (for facing brick) and ASTM C652 (for hollow brick) address the following physical properties: compressive strength, boiling water absorption, saturation coefficient, and initial rate of absorption.

Compressive Strength

Compressive strength is the maximum compressive stress the bricks can withstand when loaded on the bed surfaces. Bricks qualifying as Grade SW (severe weathering) must exhibit an average compressive strength of 3,000 lb/in.² (20.7 MPa [or 211 kg/cm²]) for five test specimens, with any individual test result no less than 2,500 lb/in.² (17.2 MPa). Bricks qualifying as Grade MW (moderate weathering) must exhibit an average compressive strength of 2,500 lb/in.² (17.2 MPa) for five test specimens, with any individual test result no less than 2,200 lb/in.² (15.2 MPa).

Bricks usually meet the compressive strength requirement with considerable margin to spare. For example, the average compressive strength of extruded face brick manufactured in the United States exceeds 11,000 lb/in.² (75.6 MPa). Compressive strength is attributed primarily to the quantity of fired bond created in the vitrification process.

Boiling Water Absorption

When bricks are submerged completely under boiling water at atmospheric pressure for 5 hours, they increase in weight (compared to their dry weight) because of water absorption in their pores (small capillaries remaining in the fired product). Boiling water absorption is the percentage increase in weight. For Grade SW bricks, the maximum allowed average boiling water absorption is 17.0% for five test specimens, and any test result on an individual brick specimen must be no greater than 20.0%. For Grade MW brick, the maximum allowed average boiling water absorption is 22.0% for five test specimens, and any test result on an individual brick specimen must be no greater than 25.0%.

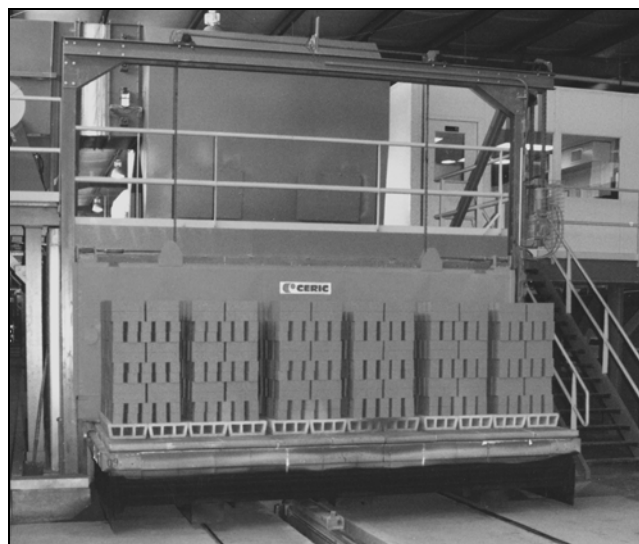


Figure 3. Bricks exit a modern tunnel kiln after firing



Figure 4. Many brick plants use robots in manufacturing

Saturation Coefficient

The saturation coefficient is the ratio of cold water absorption (i.e., the weight percent of absorbed water in bricks immersed in water at room temperature for 24 hours) divided by the boiling water absorption. The average saturation coefficient for five test specimens must be no greater than 0.78 for Grade SW brick and 0.88 for Grade MW

brick, with minimum individual values no greater than 0.80 and 0.90, respectively.

The water absorption and the saturation coefficient reflect the pore quantity and the pore structure, respectively, in the brick after firing. These are influential in giving resistance to freezing and thawing of bricks in cold weather climates. If brick walls become partially saturated with water and then freeze, ice will form within the brick's pore structure behind the face of the brick. When the absorbed water expands on freezing, pressure is exerted behind the face of the brick. Part of this pressure is relieved if ice can expand into larger pores; ice trapped in smaller pores (typically those less than about 2 μm), however, may cause cracks to develop.

Repeated freezing and thawing may result in a fatigue-like failure of the brick, causing spalling or the loss of layers of material more or less parallel to the original face of the brick. The tendency for bricks to fail from freeze-thaw is exacerbated by a high degree of water penetration or the lack of protection on horizontal brick surfaces from pooling water, as in parapet walls, on window sills, on chimneys, on garden walls with inadequate water protection on the face of brick against earth fill, on exposed steps, and so forth.

Bricks qualify as Grade SW in two ways even though they may fail to meet the saturation coefficient criterion. Bricks with an average cold water absorption of 8% or less for five specimens fully qualify as Grade SW under an "Alternate." In addition, bricks passing the freezing and thawing test described in ASTM C67 qualify as Grade SW under the Freezing and Thawing Alternate regardless of the water absorption characteristic.

Criteria for the compressive strength, boiling water absorption, and saturation coefficients were established following extensive empirical research to assure consumers that the brick is durable under freeze-thaw conditions. The criteria do not guarantee that freeze-thaw damage will not be seen in bricks, because many other factors ultimately influence resistance to freezing and thawing. It is also important to note that the freezing and thawing qualification for brick is applied at the point of sale. Testing bricks for freezing and thawing is beyond the scope of the standard after the sale of the product, for example, after removing bricks from a wall or after ambient weather storage.

Initial Rate of Absorption

A brick's initial rate of absorption, or IRA, is the weight gained after the dry brick is laid bedface down to a constant immersion depth of $\frac{1}{8}$ in. (3.2 mm) of water for 1 minute. The weight gain is expressed in grams per square inch of surface area and the results are placed on a common basis of grams of water absorption per 30 in.² of surface area (g/30 in.²-min). IRA is not a specified property for bricks by ASTM standards. The IRA ranges from values of less than 1 g/30 in.² to more than 60 g/30 in.².

Research has demonstrated that the IRA of bricks may be matched to mortar type used in masonry construction to provide the maximum possible flexural bond strength and minimal potential for water penetration (leakage) through the wall. The ASTM standards for facing brick, ASTM C216, and hollow brick, ASTM C652, contain advisory notes that bricks with an IRA greater than 30 g/30 in.²-min should be prewet with water to have their IRA reduced before construction (i.e., before laying bricks). Model building codes for masonry also have this requirement. Additional research has further indicated that strong and watertight joints can be obtained for brick of any practical IRA range.

Other Criteria for Brick in ASTM Standards

Specifications for brick in ASTM standards include sections on efflorescence (discussed in the section on Infrequent Problems Seen

with Brick Masonry in this chapter), materials and finish, sizes and tolerances, and coring and frogging (voids within units). Under materials and finish, limits for cracking and chippage are specified, with a specific viewing distance to observe cracks. The standards also give provisions for sampling and testing. Appearance criteria are determined through the definition of types of bricks. Type FBS for facing bricks and Type HBS for hollow bricks are considered the standard for U.S. production. Tighter limits on dimensional tolerances, chippage, and cracks are applied to types FBX and HBX, respectively, than to other types as defined in the ASTM standards. Bricks with appearance requirements more liberal than the FBS or HBS designations are identified as Type FBA for ASTM C216 and Type HBA for ASTM C652.

Quality Control in Brick Manufacturing

Quality control consists of measuring size, measuring physical properties, and judging appearance using methods in the appropriate ASTM standard for the type of product. Brick color typically is judged at brick plants by comparison of daily production with a standard color panel assembly of bricks. Architects may require contractors to assemble a field-acceptance panel at the job site to compare the delivered product to that specified. Judging compliance to color of field acceptance panels should be done in natural light.

Recycling and Reclamation

Brick plants use essentially all the raw materials brought into the plant. Oversize materials in grinding are reprocessed and used. Extrusion scrap (shaved material) is returned to the extrusion machine. Fired brick scrap is used as grog, or it is crushed and sold as landscaping cover material. Waste products from other sources are sometimes added to the brick body to improve the processing of the clay. Sawdust and bottom ash (the latter from coal firing) are frequently used for this purpose.

Clay pits are usually reclaimed for agricultural use or restored and designated as wetlands or wildlife habitats. Open-pit clay mining usually produces a shallow pit, in contrast to the deeper pits from stone quarrying operations.

USES OF BRICK

Factors Affecting the Quality of Brick Masonry Construction

Bricks are rugged and durable products of commerce, and they are one of the components of a building's wall. The total functionality of the wall system is obtained through the responsibilities detailed as follows:

1. The designer of the wall, typically the architect, must provide design details according to recommended practices, including means for supporting the wall, anchoring the wall to the structure, draining the wall system, placing vapor barriers and flashing, and other details as required by building codes. The BIA's *Technical Notes* series contains recommendations for these components. Failure to provide proper design details can result in performance problems for the wall.
2. The masons who construct the brick masonry have many responsibilities at the job site (Figure 5). The masons and their helpers mix mortar materials according to specifications for the job; they inspect bricks on receipt; they build the wall using wall ties, flashing, weep holes, and so forth, as necessary; they blend bricks (colors) during assembly of the wall; and they strike or tool mortar joints. Failure to perform proficiently in any aspect at the job site can result in an inferior quality wall, creating problems for the building owner, which may include a wall that is not aesthetically pleasing.

3. Laborers who clean brick masonry, typically the contractor's workforce, must clean the bricks according to the brick manufacturer's recommendations. Improper cleaning, with acids, for example, can cause efflorescence or metal staining of bricks. Pressure washing, if performed improperly, can damage surface coatings or the brick itself.
4. The brick manufacturer must ensure that bricks meet ASTM specifications as agreed to by the manufacturer and building owner.

Infrequent Problems Seen with Brick Masonry

Water Penetration

Brick veneer walls are technically classified as drainage walls, where water is channeled to the back surface of the veneer. Water that penetrates the veneer flows downward and away from the building through weep holes over flashing at support locations. Water may penetrate the brick units by normal capillary processes. Such penetration results in a short-term increase in relative humidity in the cavity, or void space between the bricks and the sheathing attached to the building frame. Brick cavities are designed to promote air circulation to maintain average humidity at a level compatible with ambient weather conditions.

Most cases of excessive water penetration of the veneer are the result of inadequate filling of head joints (vertical joints) with mortar. Small cracks may develop between the brick and mortar because of a mismatch between brick and mortar properties (e.g., failure to prewet high-IRA brick) or moving the brick after contact with mortar. These conditions may result in water damage to the inner portions of the walls if the air space between the bricks and their backing is not clear, if there is inadequate flashing, or if weep holes are not used in the wall system.

Freezing and Thawing Durability Failures

Loss of portions of the exposed brick surface, commonly called *spalling*, may occur from repeated cycles of freezing and thawing. Such failures usually are found in locations where a high exposure to water occurs—such as in chimneys, window sills, garden walls, steps, or high places on tall buildings. Freezing and thawing durability failures do not necessarily indicate that the bricks lacked sufficient resistance to freezing and thawing as provided under ASTM standards. Lack of proper chimney caps, lack of flashing on parapet walls, allowance of pooling of water, and other design faults may be the underlying causes of these failures. Inadequate expansion allowance in the wall may result in similar spalling.

Efflorescence

Efflorescence is the deposition of water-soluble mineral salt crystals on a brick surface. Although all bricks contain a very small proportion of soluble salts, only a few contain a concentration sufficient to form visible efflorescence. The process of efflorescence is well known. Water penetration begins the process, dissolving soluble material in the brick over time. Through evaporation and drying, the salts are left on the outer surface of the brick. Drying removes the water from the outer surface and the salt is deposited following evaporation.

The efflorescence test described in ASTM standards is not required for bricks to meet the ASTM specification unless requested by the purchaser. This test exposes bricks to water followed by a drying period to show if the brick units develop efflorescence. The test provides a rating of “not effloresced” or “effloresced.”

Efflorescence frequently is associated with water used in the construction of a building, and it is not recurring as the structure ages.



Figure 5. Masons lay brick using age-old techniques.

When recurring efflorescence is observed, it should be removed by cleaning the surface of the bricks by methods recommended by the manufacturer. Chemical cleaners are used only after thorough saturation of the bricks with water and by strictly following directions for use of that cleaner. Lack of adherence to prewetting and other requirements of the cleaning process can cause an efflorescence problem of increasing severity.

Not all efflorescence is caused by salts within the bricks. Efflorescence may be related to the mortar used in masonry construction. The primary efflorescing species in mortar are calcium compounds that dissolve in water during wetting periods and move through the bricks during drying periods. This type of efflorescence may be white. Saturation of a brick wall with muriatic acid (HCl) is a well-known cause of “mortar efflorescence.” Other sources of efflorescence, particularly with brick pavements, are soluble materials in underlayment or substrate materials, impingement of irrigation water sprays, use of deicing salts, and impingement of fertilizer or herbicide products.

Chippage

Chippage is the loss of small pieces from the edges or corners of bricks. Manufacturers have made major advances in packaging in recent years to limit chippage during delivery to the job site. At the job site, masons should discard bricks exhibiting excessive chippage. ASTM standards for bricks, for example, allow 100% of bricks shipped to a job site to contain chippage to a limited extent. Chippage, however, should not detract from the appearance of the wall. After the wall is built, the manufacturer is not responsible for chippage of the brick units.

Face Cracks

Bricks infrequently exhibit minor cracks across their face, and it is known that these do not reduce the performance of a veneer. To evaluate the presence of “significant” face cracks, ASTM specifications for bricks specify a viewing distance where, if face cracks are visible, the crack may detract from the appearance and functionality of the wall.

Color Variation in Bricks and Mortar Discoloration

Because of the natural variation in clay chemistry and the techniques of brick production, bricks exhibit a natural range in shades

and tones of color. It is the job of the mason to follow the brick manufacturer's instructions for blending different colored bricks at the job site to produce a wall of normal color variation. After construction, bricks may be stained by skilled commercial personnel using inorganic pigment solutions; staining is a widely accepted practice to correct color of bricks in a wall. Staining is usually guaranteed for the life of the structure or 100 years.

A number of factors affect the appearance of mortar. Skilled masons know that mortar joints must be finished, or "struck," within a defined time range after assembly of the masonry, or color variation in the joints may result. Mortars colored with inorganic pigments may exhibit color variations if the concentration of colorant varies from batch to batch of mortar mixed at the job site. Improper cleaning can remove portions of the cement paste and alter the resulting color in the mortar joints. Mortar joints can be stained by skilled personnel to correct color variations.

ENVIRONMENTAL CONSIDERATIONS

Brick Manufacturing

Brick manufacturing emits small quantities of pollutant species into the environment, primarily particulate matter consisting of natural clay dust and dilute acids. The dilute acids are hydrogen fluoride, sulfuric acid, and hydrogen chloride, and their concentration is typically far below the threshold for any type of human health effect. Bricks have been manufactured for thousands of years, and brick plant workers exhibit no greater incidence of disease than the general population.

In 2003, brick plants in the United States became regulated under the provisions of the National Emission Standards for Hazardous Air Pollutants (NESHAP) promulgated by the U.S. Environmental Protection Agency. Even before that time, a number of brick plants had air pollution control devices or "scrubbers" installed to limit emissions from their kiln exhaust. These scrubbers remove acid species from the kiln exhaust. With the implementation of the brick NESHAP, many larger brick plants are likely to use scrubbers.

Brick Products

Extensive studies of brick products show that they do not release hazardous species into groundwater during service. Bricks are considered "green" products that support sustainable construction. The latter is attributed to the long life of brick masonry buildings and to the fact that bricks are recyclable and may be used for other purposes. More information is available from the BIA.

FUTURE TRENDS

The brick industry in North America has undergone significant expansion over the last decade; most new plants use automation. One result is greater uniformity in the physical properties of bricks. Increasing cost pressure on fuel prices represents an important challenge to the industry from a manufacturing perspective.

Brick production will continue to shift to thinner bricks with a greater percentage of void area. These thinner, lighter bricks will provide the appearance and performance attributes of standard bricks but offer savings of materials and energy.

In the marketplace, the trend to use bricks in more expensive residences may continue. The brick industry has recently employed extensive advertising to make the consumer more informed of their choices for residential cladding. Use of brick in governmental, business, and industrial buildings is expected to continue despite the recent availability of numerous competitive materials. Using mixtures of cladding materials for decorative purposes may expand. Growth in the use of brick paving is anticipated.

RESOURCES ON BRICK PRODUCTS

The following organizations offer information on brick products, their production, and their use:

- Brick Industry Association, 11490 Commerce Park Drive, Reston, VA 20191; 703-620-0010; <http://www.gobrick.com>.

The mission of the BIA is to promote clay bricks in order to increase its market share and to safeguard the clay brick industry. It accomplishes this by serving the united interests of the brick industry, primarily to promote the sale and use of clay bricks; to be the authority on brick construction; to render technical assistance to designers and others; to provide education and assistance for the brick industry; to further good relations among brick distributors, manufacturers, and suppliers; to monitor and positively influence governmental actions; to assist in the long-term availability of bricklayers; and to provide member services.

Regional brick associations may be available in certain areas, and these are listed on the BIA Web site.

- The National Brick Research Center, 100 Clemson Research Boulevard, Anderson, SC 29625; 864-656-1094; <http://www.brickandtile.org>.

The mission statement of the National Brick Research Center states that the center will advance the technology of clay brick materials and products, augment the education of ceramic and materials engineering students, and educate and serve individuals in the brick industry with a resultant increase and improved use of structural clay building products. The National Brick Research Center is a component of Clemson University, Clemson, South Carolina.

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Cosmetics

Peter A. Ciullo

INTRODUCTION

Relatively few minerals are used in cosmetics, and their level of use is generally too low to warrant separate statistical consideration compared to major consuming industries. Sales to the cosmetics industry generally are relegated to the category of “Other.” Although tonnage may be relatively small, their use is nevertheless widespread. Talc, kaolin, calcium carbonate, mica, or smectite clay is used in nearly every type of personal care product intended to make the skin look or feel better. The smectite clays and their organoclay derivatives contribute emulsion stabilization, suspension stabilization, and thickening and binding properties, and are used in most product forms offered by the cosmetics industry. Talc, kaolin, and calcium carbonate are used for their inherent physicochemical properties, mainly in decorative cosmetics, whereas the micas, both muscovite and sericite, are also used for their optical properties. Table 1 summarizes the functions and applications of these minerals.

The most common vehicle in the cosmetics industry is the emulsion, which brings water, oils, fats, waxes, and active ingredients to the skin in an effective, homogeneous form. As creams and lotions, emulsions improve the condition of the skin. Functional additives adapt them for specific uses: UV absorbers in sunscreens, alpha hydroxy acids in keratolytics, melanin inhibitors in skin lighteners, and mild abrasives in exfoliants. Emulsions decorate with the addition of pigments and minerals. Decorative or color cosmetics also are made without water (e.g., face powders and nail lacquers), but seldom without minerals. The most mineral-intensive products, clay masks, are based more on what they remove from the skin—oils and impurities—than what they leave behind.

INDUSTRY STRUCTURE

Although the word *cosmetics* is commonly inferred to mean decorative products such as foundation and nail enamel, this chapter adopts the common industry understanding, which includes skincare, hair care, and personal hygiene products as well. On that basis, the worldwide cosmetics industry can claim sales of \$230.5 billion in 2004, fully half of which is accounted for by only 10 companies (Briney 2005). Although six of these are U.S. corporations, North American sales are 22% of the total, third in line after Western Europe at 31% and Asia/Pacific at 25% (Briney 2005). Multinational producers dominate the global cosmetics industry, but private label companies, producing products for themselves and others under various brand names, are regionally significant. It is also an

Table 1. Minerals in cosmetics: Functions and use

Mineral	Function	Typical Application
Talc	Lubricity, skin adhesion, water resistance	Foundation
	Absorption	Foundation
	Fragrance retention	Foundation, dusting powder
Kaolin	Absorption	Foundation, masks
	Matting	Foundation
Calcium carbonate	Absorption	Foundation, masks
	Matting	Foundation
	Opacification	Foundation
Mica	Pigmentation	Foundation, lip colorants, nail enamels
Sericite	Lubricity	Foundation
	Sheen	Foundation
Smectite clay	Thickener/stabilizer	Emulsions, liquid foundation, nail enamels (organoclay)
	Absorption	Masks

industry with a relatively low cost of entry. Nearly anyone with a sales pitch can enter the business and succeed depending on their marketing savvy and the value of their products. Two of the largest U.S. cosmetics companies, Avon and Mary Kay, started as “mom and pop” ventures. Today, aspiring cosmetics moguls take advantage of relatively low cost—low risk exposure provided by the Internet and the somewhat more expensive, but potentially more responsive, television infomercials and shopping channels.

EMULSIONS

The primary function of creams and lotions is to make the skin soft and supple. This is accomplished by inhibiting the loss of moisture already in the skin and by applying additional moisture to the skin. Applying water and then petrolatum or refined oil would work adequately, safely, and inexpensively, but without aesthetic appeal; the emulsion form makes skin care both effective and pleasing.

To formulate an emulsion, two immiscible liquids are brought together with sufficient energy so that one becomes finely dispersed in the other. One liquid is aqueous and the other is “oil.” This oil can be any mixture of liquid, molten semisolid, and molten waxy ingredients. The emulsion consists of both an external or continuous phase

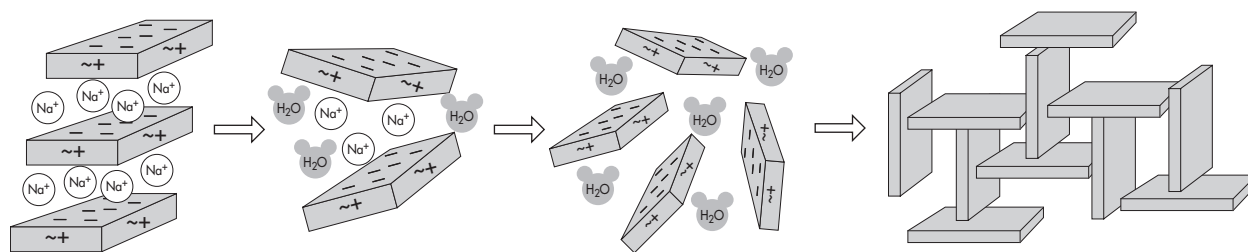


Figure 1. Smectite hydration mechanism

and an internal or dispersed phase. Macroemulsions contain dispersed phase particles ranging from 0.1 to 50 μm . They are opaque, are thermodynamically unstable, and tend to separate. Microemulsions contain dispersed phase particles less than 0.05 μm . They are translucent and thermodynamically stable. They also are limited in the choice of acceptable ingredients and product rheology. Most creams and lotions sold for topical use are macroemulsions, the bulk of which are oil-in-water (O/W) with an aqueous external phase.

The first considerations in designing a cosmetic emulsion are its intended function and its required “feel” properties. For example, a hand lotion should spread without drag, feel silky, and rub in or be absorbed quickly. An O/W emulsion with low oil content is preferred. High water content provides moisture and facilitates quick rub-in. As the water evaporates, the oil phase coalesces into a thin, nongreasy film. Conversely, consumers prefer a heavier residual film from a facial night cream, equating this with increased efficacy. An emulsion of water-in-oil (W/O) can provide this richer residual feel while still providing moisture to the skin.

Requirements for any given product and its performance include ease of preparation, rheology, stability, and economics. These are particularly important when deciding between an O/W and W/O system. O/W emulsions generally penetrate more quickly and are less greasy, less emollient, faster drying, and less expensive to produce. They are chosen when fairly little fatty material is required or when the emulsion is used as a vehicle to deliver water-soluble active ingredients. W/O systems are associated with high emollience or with solvent action (e.g., cleansing creams). They also can be used as alternatives to anhydrous products such as ointments and sticks so that the costs of raw materials can be reduced, and their moisturizing potential can be increased by adding water (Ciullo 1980). Judicious selection of ingredients controls and modifies the actual feel and efficacy of emulsions. The choice of ingredients to provide specific desirable effects represents the merging of science and art by a skillful formulator.

The Water Phase

The water phase contains predominantly water, as expected. The water is preferably deionized, and has low bacteria content. Water is the vehicle for many functional ingredients in topical emulsions. These include emulsifiers (discussed later), water-soluble botanicals, vitamins, keratolytics, and proteins. Most common of the water-phase additives are the *humectants*, which serve a twofold purpose: (1) they inhibit surface desiccation in the container when an O/W product is left uncovered, and (2) they deposit a film that attracts moisture from the air to the skin, or conversely retards the rate of moisture loss from the skin to the air. Glycerin, butylene glycol, and propylene glycol are the humectants used most often in topical emulsions. Sodium pyrrolidone carboxylate and sodium hyaluronate are generally more effective, but because they are more expensive they are less commonly used.

Hydrophilic colloids are used in the water phase to thicken or stabilize the emulsion, especially at elevated temperatures where the oil phase liquefies. They form a colloidal structure that inhibits mobility and coalescence of the dispersed phase. They also participate in the interfacial film that coats dispersed oil-phase particles, providing charge or steric inhibition of coalescence (Lochhead 1994). In practice, hydrophilic colloids often are used as stabilizers to overcome deficiencies in emulsifier performance. They also are used to tailor viscosity, dispensing properties, and application properties of O/W emulsions. A variety of organic colloids, both natural and synthetic, are used in topical products, including xanthan gum, carboxyvinyl polymers, cellulose derivatives, alginates, carrageenans, and various acrylates.

The most widely used inorganic colloid is smectite clay, which is sold under the International Nomenclature Cosmetic Ingredient (INCI) name of bentonite or magnesium aluminum silicate and as sodium magnesium silicate in its synthetic form. INCI names are standardized generic designations applied to every raw material used in cosmetic products. The label of every product has a list of ingredients according to their respective INCI names. Smectite clay is used as an O/W emulsion stabilizer because of its unique colloidal structure. A macroscopic particle of smectite clay comprises many thousands of stacked or overlapped submicroscopic platelets approximately 1 nanometer thick by several hundred nanometers across. Platelet faces carry a negative charge from lattice substitutions, whereas edges have a slight positive charge from broken bonds and cation adsorption. Exchangeable sodium ions balance the overall negative charge.

When the clay is hydrated (i.e., mixed into water), water penetrates the area between the platelets, forcing them farther apart. Exchange ions then begin to diffuse away from platelet faces. Further penetration of water then proceeds in an osmotic manner until the platelets are completely separated. The speed with which platelet delamination occurs is related directly to the amount of energy introduced during hydration. Greater mechanical energy from mixer shear and thermal energy from heated water accelerate delamination. Once delaminating energy is removed, faces and edges of adjacent platelets are attracted ionically, forming a cohesive three-dimensional colloidal structure. Figure 1 illustrates the mechanism of clay hydration and colloidal structure building. The colloidal structure physically inhibits the movement and contact of the dispersed phase. The dispersed phase, stabilized in this manner, can be lipophilic as in an emulsion, solid as in a suspension, or gaseous as in a foam.

Although smectite clay is routinely classed as a thickener, it is relatively inefficient at this task compared to most of the organic hydrocolloids noted. Its utility in topical personal care products derives mainly from its stabilizing properties. By volume, its most common use is as an emulsion stabilizer in treatment, moisturizing, and sunscreen creams and lotions. It also has a long history in liquid foundations where it stabilizes the suspension of pigments and

Table 2. Common oil-phase emollients

Emollient	Functions
Hydrocarbons	
Mineral oils	Major vehicle in most products as emollient, as solvent, or as a diluent for fatty materials; oily feel
Petrolatum	Occlusive emollient; oil-phase thickener; sticky residual feel
Paraffin wax	Occlusive emollient; oil-phase thixotrope; poor oil absorption; sticky/waxy residual feel
Microcrystalline wax	Oil-phase thickener; high oil absorption; promotes occlusive, nongreasy residual films
Squalane	Oily emollient, nontacky skin lubricant
Fatty Alcohols	
Cetyl alcohol	Emulsion stabilizers; emollients; promote occlusive nongreasy residual films
Stearyl alcohol	
Cetearyl alcohol	
Fatty Acids	
Stearic acid (stearic/palmitic)	Soap emulsifier; oil-phase thickener; promotes nongreasy, residual films
Esters	
Isopropyl myristate	Relatively nongreasy liquid vehicles; can promote penetration to reduce oiliness/greasiness of residual films
Isopropyl palmitate	
Octyl octanoate	Emulsifiers; emollient waxes; oil-phase thickeners; semi-occlusive to occlusive
Glyceryl stearate	
Glycol/PEG* stearates	
Glycerides	
Caprylic/capric triglyceride	Bland emollients; promote spreading
Wheat germ glycerides	
Palm kernel glycerides	
Nut and Vegetable Oils	
Almond, corn, coconut, jojoba, olive, rapeseed, safflower, sesame, sunflower, wheat germ	Bland emollients; some prone to rancidity
Lanolin Derivatives	
Lanolin	Occlusive emollient; W/O [†] emulsifier; tacky residual feel
Lanolin alcohols	Occlusive emollient; more hydrophilic than lanolin; W/O emulsifiers; O/W [‡] emulsion stabilizers
Lanolin oil	Occlusive emollient; W/O emulsifier; much less tacky than lanolin; greater solubility in hydrocarbons than lanolin
Acetylated lanolin alcohols	Highly hydrophobic emollient; poor emulsifier; less allergenic potential for lanolin-sensitive skin
Silicone	
Dimethicone	Highly hydrophobic emollient; defoamer; barrier agent; somewhat oily residual feel
Alkyl dimethicone	Less oily feel; better hydrocarbon compatibility

* PEG = polyethylene glycol.

† W/O = water-in-oil.

‡ O/W = oil-in-water.

minerals (in addition to stabilizing the emulsion base), and in mechanical exfoliants where it suspends the abrasive particles. Using synergistic combinations of smectite clay with organic hydrocolloids, particularly carboxyvinyl polymers, is popular for optimum control of stabilization and rheology.

The water phase usually contains the emulsion's preservative system, although some partitioning between water and oil phases will occur. Bacteria propagate preferentially in the aqueous environment, so that water quality and the nature of water-phase ingredients dictate the type and level of preservatives required (Romanowski and Schueller 1995). Commonly used preservatives are methyl paraben, propyl paraben, phenoxethanol, imidazolidinyl urea, diazolidinyl urea, DMDM hydantoin, quaternary ammonium compounds, and isothiazolinones.

The Oil Phase

The oil phase provides emollience, imparting softness and flexibility to the skin while depositing a lipophilic film that inhibits water loss.

The oil phase also can be used for its solvent properties as in cleansing creams, for its protective properties as in barrier lotions, or to carry the actives as in vitamin creams. Organoclay—smectite clay that has been made oleophilic by reaction with a fatty quaternary ammonium compound—is used on occasion to stabilize and thicken W/O emulsions in a manner analogous to that of unmodified clay in O/W emulsions. The cohesion of the colloidal structure formed by delaminated organoclay is based on hydrogen bonding rather than ionic attraction. Table 2 is a very basic listing of common oil-phase ingredients and their primary functions and properties. The current selection of cosmetic-grade lipophiles is considerably more extensive, owing in great part to the proliferation of polyalkoxylated derivatives (PEG and polypropylene glycol) designed to nuance oleophilic and organoleptic properties.

The Emulsifier System

The ease with which the two phases can be emulsified is almost entirely a function of the interfacial tension between the two liquids.

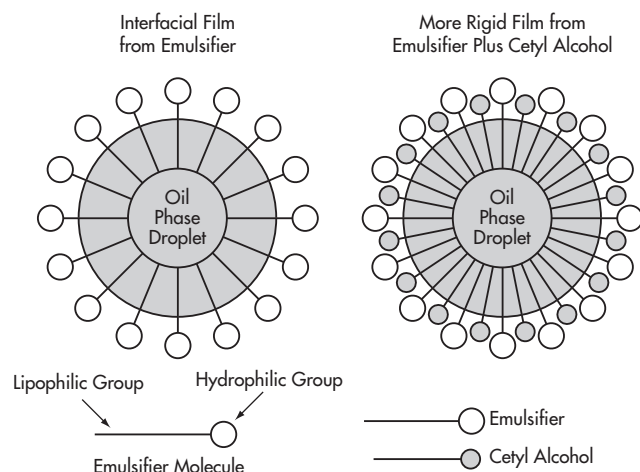


Figure 2. Stabilizing interfacial film in O/W emulsion

Those having low interfacial tension will emulsify easily; those with high interfacial tension will emulsify with difficulty, if at all, and then only with the application of considerable mechanical energy. Introducing emulsifiers into either or both phases alters interfacial tension. Emulsifiers usually contain a polar group attached to a hydrocarbon chain, thus showing both hydrophilic and hydrophobic characteristics. The emulsifiers migrate to the oil-water interface, reduce the interfacial tension, and produce mechanically stable interfacial films. The polar groups are oriented toward the water phase and the hydrocarbon portion is oriented toward the oil phase. Since both oil and water wet the film of emulsifier, a difference in surface tension exists on the two sides of the film, causing it to bend. The side with the higher surface tension assumes a concave shape, and the emulsifier film bends until it completely envelops the particles of the dispersed phase. The nature of the envelope that forms determines whether the emulsion will be oil-in-water or water-in-oil.

Cosmetic emulsifiers are drawn from all four ionic classes of surfactants: an ionic, cationic, ampholytic, and nonionic. Of the anionic emulsifiers, historically the most widely used are triethanolamine stearate soaps, the orthophosphate esters of polyethoxylated fatty alcohols, and sodium cetyl sulfate. Stearate soaps generally are formed in situ, the fatty acid in the oil phase reacting with the organic base or alkali in the water phase. Anionic emulsifiers inhibit coalescence of the oil phase through a combination of charge repulsion and steric hindrance. The latter often is supplemented by incorporation of an oil-soluble polar compound such as cetyl alcohol. This results in a mixed interfacial film with greater rigidity and stability than that of a simple film, as illustrated in Figure 2. The anionic emulsifiers as a class, and especially soaps, tend to be unstable under conditions of low pH and in the presence of polyvalent cations or cationic surface-active agents.

Of the cationic emulsifiers, only quaternary ammonium compounds are used in cosmetic emulsions. Many quaternaries also possess bactericidal properties and adhere to skin and hair, forming lipophilic films. Incorporating a polar hydrocarbon such as cetyl alcohol is usually necessary to obtain a stable system. In general, quaternaries produce O/W emulsions, but various oil-dispersible compounds such as distearyldimethylammonium chloride can be used to produce W/O emulsions. Some quaternary compounds may be skin irritants. As a class, quaternaries are unstable under alkaline conditions. Surface activity and emulsifying power of ampholytic surfactants depend on pH. These compounds are anionic at high

pH, cationic at low pH, and have an isoelectric point at approximately neutral pH, at which they behave as nonionics. At this point their solubility, surface activity, and emulsifying power are minimal. The use of ampholytic and cationic emulsifiers in cosmetic emulsions is not widespread.

In nonionic emulsifiers, the hydrophobic portion, which may be alkyl, alkylaryl, or a silicone, is linked to the hydrophilic portion of the molecule, which can be a simple alcohol group, a polyol such as glycerol or sorbitan, an amino glycol such as diethanolamine, or a polyglycol such as polyethylene glycol or polypropylene glycol. Nonionic emulsifiers range from primarily oil-soluble compounds suitable for producing W/O emulsions to primarily water-soluble compounds for producing O/W emulsions. It is common to use both a hydrophilic and a lipophilic nonionic in an emulsion system for a more rigid interfacial film, therefore achieving the greatest stability. Nonionic emulsifiers inhibit coalescence of the dispersed phase in O/W emulsions primarily by steric hindrance.

Emulsifier Selection

Once the required properties of an emulsion are determined and oil- and water-phase components have been selected accordingly, the most difficult task is to identify emulsifiers that provide ease of emulsification and product stability at minimum cost.

The first and most popular or organized approach to emulsifier selection was the HLB method. The term *HLB* is derived from the expression “hydrophile-lipophile balance.” Any surface-active agent (more strictly nonionics) can be assigned an HLB number that denotes the relative balance of hydrophilic and lipophilic characteristics, thus defining its behavior at an oil-water interface. The HLB number is a direct function of the relative amount of the hydrophilic portion of the molecule, so low values imply poor water solubility but good oil solubility, and vice versa for high values. In general, emulsifiers having HLB values of 3 to 6 will be suitable for W/O emulsions, whereas materials having values of 7 to 18 will produce O/W emulsions. The individual values of given emulsifiers are algebraically additive, so HLB values for mixtures of compatible emulsifiers can be calculated. A shortcut in emulsifier selection is the use of prepared blends of low- and high-HLB emulsifiers and emulsion stabilizers (e.g., glyceryl stearate and PEG-100 stearate). Many are available and serve as a convenience in emulsion formulation. Despite its value as a guide to effective emulsion selection, the HLB method does not necessarily predict which emulsifier system will provide the optimum long-term stability under all anticipated storage conditions. This may explain the widespread use of smectite clay and the organic hydrophilic colloids to ensure product stability.

Emulsion Production

Physically preparing an emulsion involves two basic considerations. The first is the order of addition of the two phases. For W/O emulsions it is preferable to add the water phase to the agitated oil phase. For O/W products the analogous method of adding oil to the water phase is commonly employed, but an inversion method is sometimes preferred. The latter involves adding the water phase to the oil phase slowly, creating a W/O emulsion initially. At a certain water-phase volume, the emulsion will invert to O/W and the remaining water phase can be added rapidly. Emulsions made by this method are usually more stable. It is possible to use less emulsifier, making the technique more economically attractive.

The second consideration is the temperature of the two phases. In typical emulsions, containing waxy or semisolid material in the oil phase, heat is mandatory. Both phases are heated to at least 5°C above the melting temperature of the ingredient with the

highest melting point. The phase that will be added to the other is heated an additional 2° to 3°C to allow for cooling during addition.

Emulsions usually are prepared in jacketed tanks so that they can be cooled rapidly with cold water. For lotions, mixing commonly takes place while cooling to about room temperature. For creams, mixing much below the gelation or solidification point of the oil phase is impractical because of the increase in product viscosity and the increased tendency toward aeration. When cooled without agitation, however, the rate of cooling from the center to the edges of the processing tank can vary considerably. Resultant differences of size and aggregation of oil-phase crystallites or droplets can produce large variations in physical properties within the tank. When this happens, the batch is made uniform by passing through a homogenizer after cooling.

COLOR COSMETICS

Color cosmetics encompass foundations, blushes, eye-area cosmetics, lip colorants, and nail enamels. Table 3 summarizes the forms in which these products are produced and the minerals commonly used therein. Minerals used by the cosmetics industry, including the smectite clays and organoclays used as stabilizers and thickeners, must meet particular standards of mineralogical, chemical, and bacterial purity. Levels of bioavailable (acid-soluble) heavy metals are strictly controlled, typically no more than 3 ppm As and 12 to 15 ppm Pb. Bacteria counts are generally restricted to less than 1,000/g, but much lower levels often are mandated by purchasers. These lower limits are achieved, when necessary, by using bulk sterilizing treatments such as gamma irradiation. High mineral whiteness or brightness generally is required.

Colorants

Several forms of colorant are used in color cosmetics. Dyes are organic compounds that are soluble in the medium to which they are added. They are used sparingly in color cosmetics, other than lip products, to avoid staining skin or nails. Pigments are insoluble in the medium to which they are added. They may be organic or inorganic. Toners are organic pigments made by precipitating water-soluble dyes as insoluble metal salts. *Lakes* are composite pigments made by precipitating the metal salt of a dye onto the surface of an insoluble organic (e.g., rosin, aluminum benzoate), inorganic (e.g., alumina, blanc fixe, titanium dioxide [TiO₂], zinc oxide), or mineral (e.g., calcium carbonate, kaolin, talc) substrate. Organic pigments generally provide clean bright colors; unlike inorganic pigments, however, they have overall poorer chemical stability, lightfastness, and bleed resistance. Pure inorganic pigments tend to be more opaque and subdued, imparting a creamy, rather than sharp, color effect. Those used most commonly in cosmetics are TiO₂ for whiteness and iron oxides (e.g., Fe₂O₃) for earth tones. Nacreous pigments, and powdered aluminum and bronze, often are used for purely decorative effect in nail and eye-area cosmetics.

Nacreous or pearlescent pigments are thin, transparent platelets of high refractive index that partially transmit and partially reflect light. The pearlescent effect is due to specular reflection from the broad surfaces of transparent platelets and the near-parallel orientation of overlapping platelets. Light transmitted through upper platelets is partially reflected by lower platelets. Pearly luster results from the dependence of reflection on viewing angle and the sense of depth created by reflection from successive layers.

The original pearl pigment was derived from fish scales as platy crystals of guanine and hypoxanthine. This pigment remained unrivaled in luster for approximately 300 years, until the refinement of crystallization processes for platy basic lead carbonate in the 1950s. Bismuth oxychloride was developed as a nontoxic alterna-

Table 3. Color cosmetics

Cosmetic	Common Product Form	Mineral Used
Foundation	Emulsion, pressed powder	Smectite, talc, kaolin, mica
Blush	Pressed powder	Talc, kaolin, mica
Eye shadow	Pressed powder, anhydrous cream	Talc, kaolin, mica, organoclay
Mascara	Emulsion, solvent suspension	Smectite, organoclay
Eyeliners	Aqueous suspension	Smectite
Lip colorant	Wax-based stick, ointment	Organoclay, mica
Nail enamel	Solvent solution	Organoclay
Pencils	Wax-based stick	Talc, mica

tive to lead carbonate and is still used in color cosmetics, although its relatively poor light stability may require the inclusion of a UV absorber. Bismuth oxychloride provides a silvery-gray pearlescence, varying from a soft luster to a bright sparkle depending on crystal size. For pearlescent and metallic effects in a range of colors, nacreous pigments are used. These colorants take advantage of the lamellar shape and optical clarity of mica.

White nacreous pigments are made by forming a uniform coating of TiO₂ on mica platelets. Mica serves as a transparent template so that the high refractive index of TiO₂ assumes the required platy shape. Pearlescence is optimal when pigment optical thickness (platelet thickness multiplied by refractive index) is in the 100 nm (blue white) to 140 nm (yellow white) range. Use of thicker platelets produces interference colors; the interaction of reflections from upper and lower surfaces of the platelets creates light interference. A maximum reflection occurs when the wavelengths of light from these two reflections are in phase. A reflection minimum occurs when the wavelengths are exactly out of phase, canceling out each other.

Nacreous pigments provide a two-tone metallic effect. The reflected (specular) color is seen as a highlight. The background color at nonspecular angles is created by the diffuse reflection of the transmission color. The complementary reflection–transmission colors as a function of pigment optical thickness range in a continuous spectrum from blue/white at 100 nm to magenta/green at 250 nm to green/red at 370 nm.

Color effects of nacreous pigments are supplemented by overcoating TiO₂-mica platelets with a thin transparent film of light-absorbing colorant, for example, iron oxide for yellow, ferric ferrocyanide for blue, chromium oxide for green, and carmine for red. The combination pigments thus produced can have matched reflectance and absorption color or they can be two different colors. When colors match, one color is seen at all viewing angles, with metallic highlights at specular angles. A two-color effect is achieved with different colors. Combination interference–absorption pigments are made in the gold to red range by coating Fe₂O₃ directly onto mica.

Minerals

In foundations, skin texture and general aesthetic appeal are improved principally by mineral additives, which serve several important functions:

- Provide a smooth surface
- Facilitate even pigment coverage and adherence to the skin
- Absorb skin oils and moisture to control sheen and prevent caking of pigments
- Provide a uniform optical base for pigments
- Ensure uniform pigmentation

Table 4. Treatments for minerals and pigments

Treatments	Function
Physical Adherents	
Micrometer, submicrometer spheres: silica, nylon, polymethylmethacrylate	Improved lubricity, light diffusion
Surface Coatings	
Silicone oils (dimethicone)	Improved oil dispersibility, color development
Waxes	Improved oil dispersibility, lubricity, powder compressibility
Surface Precipitates	
Amino acids (N-acyl amino acids, N-lauroyl lysine)	Improved skin adhesion, lubricity, powder compressibility
Metal soaps (Zn, Mg, Al; stearates, myristates)	Improved skin adhesion, lubricity, powder compressibility
Lecithins	Silky skin feel, improved powder compressibility
Surface Reactants	
Silicon-based (methicone, alkyl silanes)	Improved oil dispersibility
Titanate esters	Improved oil dispersibility
Fluorochemicals (perfluoroalkyl phosphate, polyperfluoroethoxymethoxy PEG-2 phosphate)	Surfaces are both hydrophobic and lipophobic, resistant to water, perspiration, sebum

Table 5. Composition of O/W liquid foundation

Composition by Phase	Wt %
Water Phase	
Water	62.0
Magnesium aluminum silicate	1.2
Cellulose gum	0.2
Butylene glycol	8.0
Polyalkylene glycol laurate	5.0
Potassium cetyl phosphate	1.5
Preservative	0.4
Pigment Phase	
Talc	5.0
Kaolin	1.3
Titanium dioxide	6.5
Yellow iron oxide	0.5
Red iron oxide	0.3
Black iron oxide	0.1
Oil Phase	
Isostearyl neopentanoate	2.5
Cyclomethicone	2.5
Cetyl alcohol	2.0
Steareth-2	1.0

Only three minerals are routinely used in this way: talc, kaolin, and mica. Talc is, by volume, the most commonly used mineral. It is typically the major component of face powders, blushes, and eye shadows. Talc is naturally oleophilic–hydrophobic and so aids in skin adhesion and water repellency. Cosmetic-grade talc must be pure and white, and it is usually relatively coarse (nominally 200 mesh) so that its characteristic slip and lubricity are palpable. Fragrance retention is also a desirable attribute for anhydrous preparations. Some talcs are better than others in absorbing and holding unchanged the fragrances that are used to add appeal and mask characteristic odors of other ingredients. Water-washed kaolin imparts and maintains a smooth, matte appearance. It prevents shine and pigment caking by absorbing skin oils and perspiration. It also eliminates the slight sheen imparted by some talcs.

Calcium carbonate also provides absorption and a matte finish, along with greater opacification. Milled muscovite mica is used in color cosmetics, but much more in treated form as a pigment than as a functional mineral. Sericite, a naturally fine-grained form of muscovite, is used for its combination of talc-like properties and silky shine.

Cosmetic-grade pigments and minerals are available with a variety of surface treatments (Table 4) that benefit properties in both processing and the finished product (Hollenberg 2002). Treatments generally impart or enhance hydrophobicity, which improves dispersion in nonaqueous vehicles and pressability in pressed powders. In the cosmetic product, the treatments improve lubricity and feel, uniformity of coverage, skin adhesion, optical appearance, water repellency, and wear properties.

Foundation

The functional use of foundation (liquid or powder) is to visually improve skin appearance by covering surface imperfections and uneven coloration. The goal is to provide visually smooth skin with even, but natural-looking skin tone. Its decorative use adds color to either highlight or subdue facial features or contours, or simply to decorate.

Liquid foundations are emulsions, as previously described, in which the pigment phase (pigments and minerals) is suspended uniformly. Selected water- and oil-phase ingredients provide emollience; deliver active ingredients as required (e.g., sunscreens, botanicals, antioxidants); and facilitate smooth and even application, uniform coverage, skin adhesion, and long wear. W/O emulsions are used for greater emollience and water resistance, but foundation emulsions are usually O/W, most of ten using anionic emulsifiers for optimum pigment dispersion, skin feel, spreading, and blending. These products are made by dispersing the pigment phase, often preblended and milled, into the water phase before emulsification. Smectite clay traditionally is used as a stabilizer because it ensures stable and uniform suspension of both the pigment phase and the oil phase. Table 5 gives an example of the composition of an O/W emulsion foundation.

In the past, foundation powders were mostly talc, with just enough pigmentation, and application and adhesion promoters to achieve the desired effect. In most cases, these have been replaced by pressed powders, in which binders, texturizers, emollients, and other additives provide a convenient form with good storage

and application properties. Table 6 summarizes the additives and their functions. It is apparent from this table that some materials used as binders serve other functions as well. Most pressed powders are applied with a dry puff or cosmetic sponge. So-called two-way pressed powders are applied either dry or with a wet cosmetic sponge. These are formulated with surface-treated pigments and minerals, as necessary, to prevent water from penetrating the pressed cake. Pressed powder blushes are similar in composition to pressed powder foundation products, but with a wider range of colors. These are normally applied with a brush, so binders and other additives are adjusted accordingly for proper application. Although foundations are used to make the skin appear as smooth and uniformly colored as possible, blushes are used for more specific optical effects. Blushes harmonize the impact of lipstick and eye shadow and change the apparent contours of the face by highlighting the cheekbones. Pressed powder eye shadows are also similar in composition to foundations, but with more emphasis on color and pearlescence. Pigmentation highlights or subdues eye depth and color. Pearlescent and nacreous pigments are used more often than in other pressed powders. This places added demands on the formulation, because even coverage and durable skin adhesion are essential to a void creasing on the eyelid. Table 7 gives examples of pressed powder formulations.

Other Decorative Cosmetics

Other than mica-derived nacreous pigments, the only minerals routinely used in other decorative cosmetics are smectite clays and their organoclay derivatives. Eyeliners are usually aqueous pigment suspensions used to frame the eye, accentuate eye shadow, and change the apparent shape and size of the eyes. In addition to wetting agents and humectants, they contain smectite clay or an organic gum for suspension stability and a polymeric film former such as polyvinylpyrrolidone (PVP) or polyvinyl alcohol (PVA) to hold the pigment in place after application and drying. Some waterproof eyeliners are pigment suspensions in a hydrocarbon solvent. These are stabilized with an organoclay and contain a solvent-soluble film former. Mascara is used primarily to give the appearance of thicker and longer eyelashes. The most durable and smudge-proof products are typically O/W emulsions stabilized by a smectite clay or organic gum made water resistant with an acrylic, polyvinyl acetate, or polyurethane emulsion polymer. W/O mascaras are offered as waterproof products, as are solvent-based suspension products. The latter are similar to solvent eyeliners, which are stabilized by organoclay, but generally with higher wax content. Because of their proximity to the eye, eyeliners and mascaras must contain suitable preservatives.

Lipstick and lip gloss are essentially pigmented oily suspensions thickened with waxes. Organoclays sometimes are included to ensure uniform pigment suspension during manufacture while the product is in a fluid molten state. Most nail lacquers are based on solvent solutions of nitrocellulose and amino or epoxy resin. Nitrocellulose provides the film, and the resin and plasticizers optimize film adhesion, hardness, flexibility, and gloss. Organoclay, in particular stearalkonium hectorite, often is used in these products to suspend pigments and to improve rheology so that the lacquer applies easily and uniformly without running or leaving brush marks. The “lead” in cosmetic pencils is basically a rigid, pigmented, wax stick with waxy ingredients that thicken emollient oils. “Japan wax” is a common ingredient because of its adhesive properties. An organoclay may be used in the same capacity as in lipsticks. Mica and talc are included in some products to adjust payout onto, and adhesion to, the skin. Cosmetic sticks are produced with colors suitable for eye and lip areas and as alternatives to powder blushes.

Table 6. Additives in pressed powders

Additive	Function
Metal stearate (most often Zn or Mg)	Impart water repellency, improve skin adhesion and smoothness
Magnesium carbonate	Fragrance absorbent/carrier
Texturizer (polymer powders: nylon, polytetrafluoroethylene, acrylates, silicone; boron nitride, starches, surface-treated minerals)	Improve application properties, skin feel and texture
Antibacterial (preservative powders: parabens, imidazolidinyl urea, etc.)	Prevent bacterial growth from skin moisture or water introduced from applicator
Fragrance	Mask subtle odors from other ingredients, impart pleasant odor
Emollient (oils, fats, waxes)	Improve application properties, skin feel and texture, skin adhesion, skin suppleness and smoothness; impart water repellency
Binder (kaolin, micronized smectite, fats, waxes, polymer powders)	Aid ingredient compression and adhesion, enhance pigmentation, allow smooth pickup by applicator, allow smooth transfer to skin, add water resistance

Table 7. Composition of pressed powders, wt %

Ingredients	Pressed Powder Type	
	Foundation	Eye Shadow
Powder Phase		
Talc	63.4	None
Sericite	15.0	10.0
Calcium aluminum borosilicate	10.0	None
Zinc stearate	5.0	6.0
Polytetrafluoroethylene powder	None	3.0
Yellow iron oxide	0.6	None
Red iron oxide	0.7	None
Black iron oxide	0.4	None
Nacreous gold (mica/TiO ₂ /red iron oxide)	None	40.0
Bismuth oxychloride	None	10.0
Ultramarine blue	None	10.0
Chromium oxide green	None	9.0
Preservative	0.4	0.4
Binder Phase		
Sorbitan sesquoleate	0.5	None
Isoeicosane	4.0	7.5
Polyisobutene	None	3.5

Masks

The most mineral-intensive cosmetic compositions are masks. The conventional mask product is the “mud” mask used to cleanse facial skin by means of the absorptive capacity of clays. These products are heavy clay pastes that are coated onto the face and allowed to dry to a mask-like covering. Dirt and oils are absorbed into the clay, which is subsequently rinsed off. A mask of this type provides a tightening effect on the skin (from the contraction of the dried clay film) that the consumer associates with effectiveness. In addition to this tightening sensation and to the actual cleansing, the mask is expected to apply easily, to dry quickly after application, to rinse or wash off without much effort, and to not irritate. Kaolin clay is preferred because it provides good absorption and it has a mild acidic

Table 8. Composition of facial masks, wt %

Ingredient	Clay Mask	Peelable Mask
Water	53	66
Butylene glycol	8	10
Kaolin	30	10
Bentonite	5	2
Oat flour	2	none
Sodium lauroyl sacosinate	1	2
Aloe vera	1	none
PVA	none	10
Preservative	qs*	qs

* qs = quantity sufficient.

pH, which is skin compatible. Although it has a higher absorptive capacity, bentonite typically is used to supplement kaolin rather than serving as the primary absorbent. Bentonite is alkaline, which may cause skin irritation, and its swelling properties generally restrict the amount that can be introduced in to water before the composition becomes too viscous to mix. Bentonite is useful, however, in preventing separation of water from the paste. Talc is sometimes used in relatively small amounts to improve spreading properties while reducing the tendency of the dried mask to flake. Film-forming polymers also are used for this purpose.

The fundamental ingredients for a clay mask are clay and water, which alone would provide an effective but inelegant product. In practice, any number of additives are employed. Humectants contribute plasticity to the dried clay film so that it does not easily crumble off the face. They also facilitate rewetting the film for easy removal. Small amounts of surfactant improve cleansing effectiveness and ease of removal. Botanicals, vitamins, proteins, medications, and emollients may be added to improve skin condition.

Liquid or peel-off masks were developed for neatness and as a more convenient alternative to mud masks. These are based on film-forming latexes or polymers such as PVA or PVP that provide a sensation of skin tightening after the mask dries and the polymer film contracts. Only limited amounts of clay can be used in these preparations so as not to diminish the integrity of the polymer film. Absorptive cleansing therefore is minimized, although it can be supplemented by surfactants.

Mask products are now common for other areas of the body so that the term *mask* is used more conceptually—a product left on the skin (or hair) for at least several minutes to provide treatment, cleansing, or regenerative functions before its removal. These products are typically moisturizing or treatment emulsions that may or may not contain absorptive clay. Table 8 lists examples of facial mask compositions.

REGULATORY CONSIDERATIONS

Regulation of cosmetics production and sales in major global markets directs or guides nearly all aspects of product composition, manufacture, and sale. Purity is the primary issue for raw materials. Considerations are chemical purity and absence of unacceptable residual solvents or by-products, control of heavy metals content, and control of bacteria content. As with all raw materials and all finished products, control of bacteria associated with minerals is paramount. Because minerals do not readily support bacterial propagation, reduction in natural bacteria levels is, if necessary, relatively straightforward and usually is accomplished by heat treatment while milling or with sterilants such as ethylene oxide or

gamma irradiation. A historical requirement is to have fewer than 1,000 organisms/g or mL and the absence of certain staph, *Candida*, *Pseudomonas*, and other gram-negative and enterobacteria in both raw materials and finished product. Raw materials used in cosmetics for the eye area, infant care, and intimate hygiene products must be limited to 100 organisms/g or mL. Cosmetics manufacturers must contend with requirements to improve bacterial control with the smallest possible amount of a limited number of preservatives that are available. The trend is to require raw material suppliers to improve bacterial control to as low as (or lower if possible) 100 organisms/g or mL for all uses.

Although silica is a general concern for most consumers of mineral raw materials, it is not a major consideration in the cosmetics industry because the minerals used by cosmetics manufacturers must conform to a level of purity that minimizes or eliminates residual crystalline silica. In addition, these minerals are not used in compositions that liberate respirable particles.

The use of talc in cosmetics continues to be inhibited to a certain extent by the perception that it is linked in some way to asbestos or asbestiform minerals, which may cause lung cancer if inhaled. Although purity standards for talc preclude the presence of asbestiform particles, the use of talc in dusting powders is not common today. Although unsubstantiated and technically refuted, talc is likewise subject to a persistent association with ovarian cancer.

TRENDS AND OPPORTUNITIES

Consumer interest in “natural” products continues to increase, especially for those used in personal care. Minerals used in cosmetics are fundamentally natural and will continue to be exploited as such. It may be ironic that consumer interest in using minerals that are arguably less natural (i.e., affixed with surface treatments for enhanced aesthetic effects) also continues to increase.

Conventional uses for cosmetic-grade minerals continue to grow along with their major application—emulsion products. Growth in sales of creams and lotions tends to exceed that of other product categories. Opportunities for future growth lie in providing additional functionality and value, as with surface treatments, and more significantly, in the rapidly expanding cosmetics markets in developing economies in Latin America, Eastern Europe, and China.

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Electronic and Optical Materials

Stanley T. Krukowski

In this chapter, minerals for electronic and optical uses are described in two sections—quartz, and minerals other than quartz. Quartz has been used for radio communications since the beginning of the 20th century. Its first major use was in frequency control. With increased interest and study, the physical properties of quartz were exploited in electronics: dielectric, piezoelectricity, and pyroelectricity. Quartz is transparent in both the infrared and ultraviolet ranges of the spectrum. Its high optical activity makes quartz useful in optical instruments. High-quality quartz deposits were eagerly sought; however, when artificial synthesis of quartz crystallization was discovered, an entire new industry emerged.

Contributions made in the fields of electronics and optics by minerals other than quartz also are covered in this chapter. These minerals and their applications are many and given only briefly here; the reader is referred to the commodities chapters of particular minerals for specific uses in these fields.

QUARTZ

The properties of quartz crystal that make it useful for radio communications were discovered in 1918. Since that time, an industry for mining and processing natural quartz crystal has grown, matured, and been replaced almost entirely by new technology. Quartz crystal is still involved, but it is grown rather than mined.

An economic summary of the commercial growing of quartz crystals has a place in a book for the mineral engineering industry because quartz crystals have long been an important commercial mineral. In addition, natural quartz is still the raw material for cultured quartz; that is, quartz crystals grown artificially.

In the first half of the 20th century, nearly all natural quartz crystals used for electronics and optics came from Brazil. The larger pieces that met rigorous standards of quality were used for electronic and, to a lesser extent, optical components. Smaller pieces and fragments were used for vitreous silica. The need for high-quality material in relatively large quantity led the U.S. government to sponsor related research, including exploration programs, in the 1940s. No deposits were found that met the very rigid requirements for electronic-grade quartz, but related projects resulted in the development of a process for the manufacture of beautiful crystals of prescribed shape, size, and quality. Domestic deposits of appropriate quality were identified for use as raw materials in processing cultured quartz.

Development of the cultured quartz crystal illustrates how successfully technology can adapt a mined commodity to increasingly sophisticated uses. This success was foreshadowed by the experiments of Giorgio Spezia (1908), an Italian geologist who studied the relative effects of temperature and alkalinity on the solubility of quartz.

Frequency control in modern radio equipment is achieved most often by the presence in the circuit of a separately added crystal. The initial discovery in 1918 was responsible for the existence and growth of the quartz industry. The quartz is a carefully oriented and prepared slice from a crystal, not a crystal as recognized by a rock hound or seen in a museum.

Quartz belongs to a class of materials called *dielectrics*: substances that do not conduct an electric current but permit electric fields to exist and act across them. Quartz shows the *piezoelectric effect*, which means that when a quartz plate is mechanically deformed against its natural stiffness, one of its surfaces becomes negatively charged and the other becomes positively charged. When the plate is released quickly from the stress, the charges disappear as the plate regains its original shape, but because of mechanical momentum, the plate deforms in the opposite direction (to a lesser amount) and the surfaces correspondingly become charged in the opposite direction. Thinly coating the two surfaces with metal and attaching flexible wires brings these charges into an electronic circuit. If the surfaces are suddenly electrically charged by movement of current through the wires, the converse piezoelectric effect occurs and the plate deforms. An alternating current flowing through the wires responds to this mechanical oscillation. Controlling the thickness of the plate varies its mechanical vibration frequency through a wide range. Cady (1964) and Mason (1964) discuss in greater detail how quartz operates to control frequencies.

One type of quartz plate, the AT-cut, has a precise orientation with respect to the crystallographic axes of the crystal and vibrates on a microscopic scale much as a book would deform when placed flat on a table and the top cover is moved parallel back and forth with the hand. At least 17 other orientations have been studied, some of which have preferred uses in various applications (Cady 1964).

The quartz crystal industry has three main segments (excluding fused quartz and quartz used for optical purposes):

1. *Natural electronic-grade quartz crystals* are mined quartz crystals suitable for fabrication into piezoelectric units. Zlobik

Table 1. Chronology of quartz crystal industry development

Date	Comment
1918	Discovery of the piezoelectric effects of quartz crystal
1921	Application of the piezoelectric effects of quartz crystal in the circuitry of radios
1948	Establishment of a quartz crystal commodity stockpile by the U.S. government
1952	U.S. consumption of natural quartz crystal at an all-time high of 228 t
1958	First commercial production of cultured quartz crystal
1970	Cultured quartz crystal production exceeds imports of natural quartz crystal
1971	Cultured quartz crystal consumption surpasses natural quartz crystal consumption
1976	Surge in the use of quartz crystal, both natural and cultured, because of citizens band radio sales and later decline because of change in technology in citizens band radio circuitry
1977–1990	Continued replacement of natural quartz crystal by cultured quartz crystal to the point that virtually no natural crystal is used in electronic and optical applications. New developments in the use of quartz crystals in all kinds of electronic devices, from watches to microprocessors in automobiles, toys, cellular phones, etc.
1997	Termination of natural quartz crystal mining in the United States
2000	U.S. Geological Survey (USGS) discontinues reporting U.S. cultured quartz crystal production to avoid disclosing company proprietary information
2003	Only two U.S. manufacturers of synthetic quartz crystals continue to operate

(1981) estimated the ratio of suitable commercial-grade quartz crystal to total excavated material to range from 1:1,000 to 1:1,000,000, depending on the deposit.

2. *Lascas* is mined quartz usable as feedstock in the production of cultured quartz. Approximately 0.63 kg of *lascas* is required to produce 0.45 kg of cultured quartz.
3. *Cultured quartz* is produced from *lascas* feedstock in a process in which crystals are grown in an autoclave under controlled conditions of heat, pressure, and time. It is estimated that 0.45 kg of cultured quartz is equivalent to 1.4 to 4.5 kg of natural quartz crystal in yield of commercial quartz suitable for slicing into piezo-electric units.

The chronology of the development of the quartz crystal industry, both natural and cultured, is given in Table 1.

Production and Consumption

Lascas mining ended in Arkansas by the end of 1997. In 2004 no companies reported the production of cultured quartz in the United States, a trend that began in 2001; companies considered production figures to be proprietary information. The capacity for the manufacture of cultured quartz still exists in the United States; feed material, however, consists of imported and stockpiled *lascas*. The year 2000 was the last time that U.S. manufacturers reported cultured quartz production statistics to the USGS. Producers reported fabricating 189 t of cultured quartz crystal in the United States in 2000. Fourteen out of 26 companies responded to a USGS survey intended to monitor cultured quartz crystal in 2003; the USGS withheld these statistics, however, to avoid disclosing company proprietary data. The last time that the USGS reported apparent consumption for cultured quartz was 2000, when operators reported using 146 t to fabricate quartz crystal devices (Dolley 2003).

As of September 30, 2004, the uncommitted inventory—that is, the quantity of mineral material held in the National Defense

Stockpile (NDS)—of natural quartz crystal was 7 t. The amount of committed inventory (materials sold or traded from the stockpile, either in fiscal year [FY] 2004 or in prior years, but not yet removed from stockpile facilities as of September 30, 2004) is 43 t of natural quartz crystal (Dolley 2005). There are 7 t of natural quartz crystal authorized for disposal from the NDS. This refers to quantities that are in excess of the stockpile goal for a material and for which Congress has authorized disposal over the long term at rates designed to maximize revenue but avoid undue disruption of the usual markets and financial loss to the United States. The disposal plan for FY 2004 accounted for 68 t of natural quartz crystal in the NDS, indicating the total amount of a material in the NDS that the U.S. Department of Defense was permitted to sell under the Annual Materials Plan approved by Congress for FY 2004 (from October 1, 2003, through September 30, 2004). For mineral commodities that have a disposal plan greater than the inventory, actual quantity is limited to remaining disposal authority or inventory. Finally, disposals for FY 2004 amounted to 54 t of natural quartz crystal, and refer to material sold or traded from the NDS in FY 2004 (Dolley 2003).

Most quartz crystal is used in piezoelectric and optical applications such as quartz resonators in aerospace, commercial, and military bandpass filter applications requiring high selectivity and very high stability. For many applications requiring only moderate stability, quartz resonators offer a combination of high performance, small size, and low cost. Quartz resonators also are used for less-demanding applications such as timing signals for electronic circuits in automotive, consumer, and industrial products (Dolley 2003).

Exports and Imports

The United States is completely reliant on imports of quartz *lascas* primarily from Asia followed by Brazil, Germany, and Madagascar; Canada is increasingly becoming an important source for natural quartz crystal. Production of cultured quartz has come increasingly from areas outside the United States, particularly from China, Japan, and Russia, as well as Belgium, Brazil, Bulgaria, England, France, Germany, and South Africa (Dolley 2003, 2005). The United States and Japan have been the major importers and consumers of *lascas* as well as major producers, consumers, and exporters of cultured quartz crystals. Little is known of the cultured quartz operations in China, Eastern Europe, and the Commonwealth of Independent States (CIS).

Prices and Trends

Prices of quartz material vary considerably; *lascas* typically sells well below the price of cultured quartz. The USGS (Dolley 2003) reported an average value for as-grown cultured quartz estimated at about \$81/kg in 2003. Also, the reported average value of lumbered quartz, which is as-grown quartz that has been processed by sawing and grinding, was estimated at about \$176/kg.

The electronic-grade quartz crystal industry ranges from the fully integrated producer/consumer (involving base-mineral production, cutting of blanks for piezoelectric units, and fabrication into finished electronic units) to companies that are involved only in segments of the industry. Pricing in the industry reflects this segmented or captive structure depending on where the transfer, or sale, of the mineral takes place.

Demand for quartz crystal devices should continue to grow, and as a result the demand for quartz crystal also should remain strong long into the future. The consumer electronics industry, particularly in the industrialized nations, will continue to foster production on a global scale.

Production of Cultured Quartz

The early history of producing large, high-quality quartz crystals in the laboratory and factory, and the general manufacturing process, was described by Waesche (1960).

Today four operators in the United States have the capacity to produce cultured quartz crystal; one reported in 2003, however, that it was no longer in production, and another reported that it was no longer in business. The production statistics for the remaining two manufacturers were withheld for proprietary reasons. Other countries producing cultured quartz crystal are Belgium, Brazil, Bulgaria, China, England, France, Germany, Japan, Russia, and South Africa.

The manufacturing process involves hydrothermal growth using an aqueous solution at elevated temperature. The process is similar to the hydrothermal action that develops ore bodies and crystal formations in the earth's crust. A vertical steel vessel with suitable internal fittings and pressure gage, safety blow-off valve, thermocouples, and a source of electrical heating is charged with (1) nutrient material (lascas) to about one quarter of its volume; (2) dilute alkaline solution to about three quarters; and (3) an array of seed plates. The vessel is closed, its contents brought to about 350°C, and a high pressure is produced. The heat source is adjusted to provide a temperature differential between the area of dissolution and the area of deposition and growth. Conditions of constant temperature and pressure are maintained for a period of weeks or longer. The status of the growing crystals is monitored using radiography with cobalt-60.

Vessels up to 254 mm I.D. (inside diameter), and capable of operating at up to 275.8 MPa, are in use. Figure 1 shows manmade quartz crystals in an autoclave or reaction vessel.

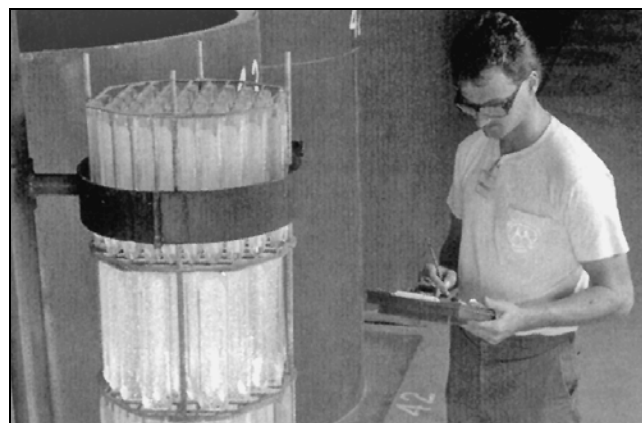
Table 2 compares the growth conditions used in the past by two major U.S. producers (Sawyer Technical Materials, LLC [formerly Sawyer Research Products, Inc.] and Thermo Dynamics, Inc.).

Although no deposits have been mined for natural electronic-grade quartz in the United States (Waesche 1960), high-purity U.S. quartzite (lascas) has been used successfully in producing cultured quartz.

Seed

The earliest seed plate that had considerable attention was a thin plate cut parallel to the minor rhombohedral face, often identified as r or as $\{0111\}$ by Bravais symbols, a face that makes an angle of $38^{\circ}13'$ with the c axis. This seems a reasonable choice because the plate should grow parallel to itself. The AT-cut plate (Cady 1964), whose surface makes an angle of $35^{\circ}15'$ with the c axis, is perhaps the most used for frequency-control oscillators. This choice of seed orientation was patented (Friedman and Tuttle 1951) particularly for promoting rapid crystalline growth. The patent states that this orientation grows "much more rapidly than seed plates cut at other angles." It turns out, however, that in the alkaline mediums used, growth of the minor rhombohedral face terminates prematurely. The major rhombohedral face grows much slower, the prism faces grow at a negligibly slow rate, and the crystal ultimately becomes a more or less square bar (depending on how the seed was supported) elongated in the c direction, lengthening slowly.

In 1954, a newer seed type called the Y-bar seed (Jaffe and Turobinski 1960) was invented: an elongated quartz crystal seed bar with its length extending substantially perpendicular to a crystallographic x axis and substantially perpendicular to the z axis of the crystal; the seed bar is small in cross-sectional dimension perpendicular to its length. In piezoelectric engineering, the x , y , and z axes are mutually perpendicular, the x axis is one of the a axes, and the z axis is the c axis in the hexagonal system to which quartz



Courtesy of Motorola Inc.

Figure 1. Racks of seed crystals are inserted into autoclaves. At the end of the growing cycle, 30 to 45 days later, they are removed.

Table 2. Comparison of growth conditions of two major U.S. producers

Growth Condition	Sawyer Technical Materials, LLC	Thermo Dynamics, Inc.
Solution	0.83 molar Na_2CO_3	1.0 molar NaOH
Percentage of fills, %*	76	80–82
Growing temperature, °C	350	354.5
Dissolving temperature D , °C	+5–20	+26.7–37.8
Pressure, MPa	82.7	158.6
Time, days	42	28–30

Source: Ober 1994.

* Percentage of the internal volume of the vessel not occupied by solid substances when it is being charged.

belongs. This seed type became so successful that it is now the standard seed in the cultured quartz industry.

Growth takes place rapidly in the c direction on this seed (easily growing 1 mm/day under good conditions) and less rapidly in the a direction at right angles. The growth in the c direction does not yield a flat face, but rather a surface composed of many rounded small mounds, occasionally showing growth spirals. The c face or basal face $\{0001\}$ is sometimes seen on the tiny crystals studied as micromounts, but it is not a plane.

Growth on a Y-bar seed proceeds in both the c direction and the a direction. Studies have shown that the highest quality is the c direction growth; hence a modified Y-bar is often chosen as a seed, being long in the direction perpendicular to an a axis and of moderate dimensions parallel to the a axis (Figure 2).

Growth in the c direction is highly satisfactory for producing crystals destined for the relatively small AT-cut oscillator plates and various other units, but the need for longer lengths for frequency filters led to the successful use of relatively large seeds oriented parallel to the minor rhombohedral face $\{0111\}$, a cyclic sweep to the early seed (Lias and Rudd 1969). Figure 3 shows representative man-made quartz crystals.

The Q of Quartz

How does one judge the quality of a find of quartz crystal? A material that has a subtle use may require a subtle test of its useful value. The Q of quartz, a dimensionless quotient, is the mark of electronic

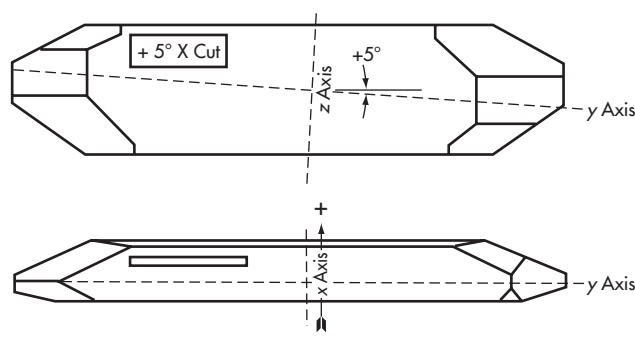
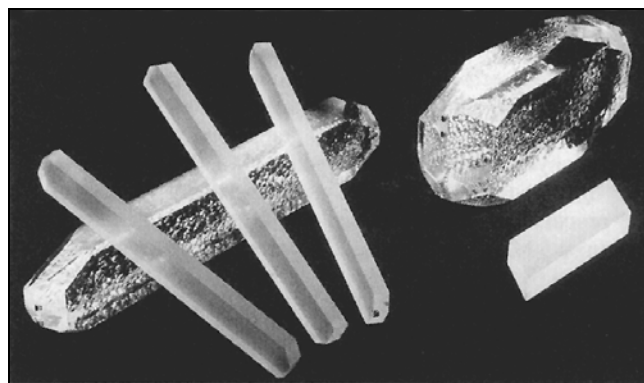


Figure 2. Drawing of cultured quartz crystal slightly modified from standard Y-bar, the seed being cut at 85° to the c axis, as shown, instead of 90° to the c axis. The drawing shows elevation and plan views.



Courtesy of Motorola Inc.

Figure 3. Synthetic quartz crystals are produced in a variety of sizes, then cut to specification dependent on final end use requirements.

quality. It often is called mechanical Q . It is highest when energy loss is slowest in a quartz oscillator because of internal friction. Given a resonator vibrating at resonance frequency while connected to a source of alternating current of that frequency, the instant the current is stopped, the vibration amplitude decays. The Q expresses the slowness of the decay. The diminishing sound of a struck bell is a close analogy. A bell with a long tintinnabulation might have a Q of 250,000; a good quartz resonator has a Q of about 1 million.

Practically, the Q of a resonator can be determined as a ratio,

$$Q = 2\pi fL/R,$$

where quantities are measured for the equivalent electrical circuit (a resonating electronic circuit of the same frequency), f being the resonance frequency, L the inductance, and R the resistance (Heising 1946).

A direct method for observing Q displays the decay of the amplitude of a specially made 5-MHz oscillator on the screen of a cathode-ray tube (King 1959). Still another method involves examining the graph of resistance as a function of frequency (Adams, Kusters, and Benjaminson 1968).

The Q of the best natural quartz (measured at room temperature) lies in the range 1.0×10^6 to 3.0×10^6 , and the usual good cultured quartz is about 1/10 of this range. In the early days of quartz-growth study, Q was much lower, and although the crystals

withdrawn from the pressure vessels were clear and sparkling in their beauty, it was discouraging that the artificially produced crystals could not improve on nature.

At Western Electric Co. (a former quartz crystal producer), quartz finally attained a coveted high Q value with the use of lithium nitrite (LiNO_2), as an additive to the growth solution (Ballman, Laudise, and Rudd 1966). Lithium as lithium fluoride (LiF) improved the Q , perhaps by decreasing the infrared absorption at $2.86 \mu\text{m}$ (or the wave number $3,500 \text{ cm}^{-1}$) (King, Ballman, and Laudise 1962). Adding the nitrite raised the Q , at slow growth rate, into the region of natural quartz values. The anion may be adsorbed onto the growing crystal, decreasing the presence of hydroxyl ion in the quartz.

Sawyer Technical Materials LLC developed ways of growing what it labeled Premium Q Cultured Quartz through slow growth in sodium carbonate solution that, in general, yielded a slower rate than sodium hydroxide solutions (Rudd, Houghton, and Carroll 1966; Sawyer 1972). Sawyer tightened quality control on all pertinent aspects of the growth process, gaining a series of runs that produced 5-MHz 5th overtone Q s consistently higher than those yielded by natural quartz.

Compared to glass, quartz has a considerably widened spectral window, hence the use of vitreous silica for optical components and the use of quartz crystal in spectrometer prisms. Quartz, however, shows a number of absorption peaks in the infrared, certain of which have been identified with impurities—elements and radicals. In particular, hydrogen, which is present in great quantity in the hydroxyl ion in alkaline growth solutions as well as in aqueous solutions in the Earth's crust, is known to be responsible for a characteristic high absorption peak in the wave-number region 3,000 to $3,700 \text{ cm}^{-1}$ (Katz 1962).

A relationship was determined experimentally between the infrared absorption at $3,500 \text{ cm}^{-1}$ and the mechanical Q (Cady 1964). Use of this information led Western Electric (Rudd and Liaison 1967) and Sawyer (1972), to inspect their production of crystals for Q by measuring this absorption with an infrared spectrophotometer. This simple and rapid method has made it easier to monitor programs researching improved Q and to ensure quality control.

Defects in Quartz

Quartz destined for piezoelectric oscillators must be reasonably free from various types of defects affecting the crystalline structure. Defects include twinning, structural imperfections such as slip and screw dislocations, impurity ions, and microscopic inclusions. For a review of defects affecting the quality of quartz for electronic and optical use, see Waesche (1960). For a more general mineralogical view, refer to Frondel (1961).

Quartz may show two types of twinning: electrical or Dauphiné twinning and optical or Brazil twinning. These are displayed beautifully under reflected light on slices etched in hydrofluoric acid, a standard method for checking the quality of natural quartz during oscillator manufacture (resonator plates must not show twin boundaries). Twinning is very rarely seen in the seed, which is carefully chosen in cultured quartz.

When pressure vessel, solution, and seeds are heated at the start of the crystal-growing process, the alkaline solution is likely to dissolve holes and tubes along dislocation lines so that when crystal growth begins, these openings are covered and microscopic bubbles (fluid inclusions) result. If the vessel is cooled and opened after the start of the crystal growing process, the seed plates will show etched pits of characteristic shapes suggesting the density of the defects.

Studies using a special double-crystal x-ray spectrometer technique have disclosed much information on structure defects.

The technique produces a topography of the internal structure and assists in relating defects in structure to other defects such as substitutional impurities (Lang 1967).

When considering growth on the basal plane that yields a cobble texture, the basic mechanism of growth seems to be along screw dislocations; this often results in a spiral pattern visible to the eye or under the microscope. Examination by light interference has produced pictures of great interest and beauty (Joshi and Vagh 1964).

Quartz often darkens in certain areas when irradiated with x-rays, high-voltage electrons, or gamma rays from cobalt-60. This phenomenon was traced to the presence of Al^{3+} substituting for some of the Si^{4+} . The charge compensation for the trivalent aluminum generally is provided by Na^+ , H^+ , or Li^+ if the last has been added intentionally as an impurity (Ballman, Laudise, and Rudd 1966). A broad study of hydrogen in quartz has made some of this behavior evident (Katz 1962).

A powerful method of studying a variety of defects such as substitutional, interstitial, and structural defects is to place a quartz block between metal electrodes, heat the assembly, and apply a direct-current voltage for a period of time. Pfenninger (1961) made a detailed study using electrodes of silver, gold, copper, and platinum; voltages as high as 670; and temperatures to 800°C. Methods of observation included using the microscope, the electron microscope, and infrared spectrometry. A beautiful set of photographs shows veils of defects entering quartz, leaving it, and decorating lines of structural dislocations.

Regrettably, this investigation did not include cultured quartz. For preparing quartz, however, especially stable in a radiation environment, cultured blocks are now free from various defects as a result of this general procedure.

A defect occasionally seen—mostly in earlier, less well-controlled growing operations—is microscopic white particles identified as clumps of acmite ($\text{NaFeSi}_2\text{O}_8$) crystals.

Developments in Quartz Growth and Technology

Low Optical Transmission Loss

Cultured quartz has been examined as a material for transmitting infrared laser light of 1.06 μm wavelength (from the neodymium-doped yttrium aluminum garnet [Nd:YAG] laser). Growth in a silver tube to diminish iron contamination yields quartz equivalent in low optical loss to the best commercial vitreous silica (Lias and Rudd 1969). An interesting correlation was found between H^+ concentration in the quartz and the absorption at 1.06 μm : hydrogen ions seemingly provided charge-compensation for the Fe^{2+} or other divalent ion impurities associated with absorption in that region.

Growth Rate on Basal {0001} Plane

Stemming from an eagerness to grow crystals faster (an economic advantage if characteristics can be maintained), growth studies at 374°C and a pressure of about 275.8 MPa led to a rate of about 2.6 mm/day and a Q of about 1.4×10^6 (Lias et al. 1973). The high growth rate caused by higher expected solubility was anticipated; the excellent Q was a bonus and showed that at the higher temperature, H^+ goes less readily into the growing crystal.

Measurement of Viscoelastic Materials

A device used to study the shear modulus of viscous materials employs a delay line of a suitable mechanically rigid material (e.g., vitreous silica or aluminum) mounted on the end a piezoelectric transducer to generate shear waves. This is typically quartz with frequencies in the range of 1 to 7 MHz, but it also may be a piezoelectric ceramic. The delay line is inserted in the sample and the system is brought to constant temperature to within 0.005°C. Pulses

of waves are sent down the delay line and the echoes are measured for their attenuation and phase shift, from which an accurate calculation can be made of the shear modulus (Hunston et al. 1972).

An ultrasonic impedometer can measure the dynamic mechanical properties of viscoelastic materials (adhesives, paints). It employs Y-cut, shear-wave resonators of 5-MHz frequency attached to the ends of a 10-cm bar of vitreous silica. At its ends the bar is cut at 79°, producing a shape suggesting a bathtub. The bulk shear wave is reflected off the bar's top surface where the material to be studied is spread. The reflected wave returns to the transmitting transducer and an oscilloscope displays the amplified signal. The impedance of the film of material can be monitored while the film is drying (Myers and Schultz 1962). Bradfield (1970) gives further general information on ultrasonics.

Pressure Transducer

Because quartz is piezoelectric—that is, a material that produces an electric field as a response to stress—can it be made into a useful pressure gage? A gage having a range of 0 to 69 MPa and an accuracy of about 0.07 kPa is made using a periphery-stressed resonator as a pressure transducer. The transducer unit is a circular 5-MHz resonator whose edge is integral with a surrounding cylinder of quartz, the axis of the cylinder being identical with the normal through the resonator center. The cylinder and resonator are fashioned from a single crystal of quartz using grinding techniques. The resonator can be either an A-T-cut or some other cut to ensure that the temperature coefficient of frequency at zero pressure is zero at a given temperature in the range of 0° to 100°C (Karrer and Leach 1969).

Pressure Gage for High-Impact Conditions

A study, largely performed at Sandia National Laboratories in Albuquerque, New Mexico, produced a gage technique for studying stresses resulting from shock-wave loading of pressures as high as 6×689 MPa (Ingram and Graham 1972). Based on the piezoelectricity of quartz, the device has been used to study the behavior of quartz and other solids under great impact. A valuable use of this technique is the measurement of forces produced in underground nuclear explosions.

Although stresses of 4 GPa are routinely measured, a tungsten facing on the quartz disk extends the upper stress limit of the experiment to 12 GPa. Ordinarily the stress in an oscillating quartz resonator is probably about 600 kPa.

A projectile in a cylinder is faced with a disk of quartz and another disk is provided at the closed end of the cylinder. In this Sandia quartz gage for impact experiments, the cylinder is a 27-m compressed gas gun that can accelerate the projectile to 510 m/sec. The impact velocity can be measured to 0.01%.

Disks of X-cut (the face of the disk perpendicular to an a axis) cultured quartz are used, which can be 126 mm in diameter and 6.3 mm thick—these dimensions yield about one quarter of an ampere of piezoelectric current at a stress of 1 GPa.

During the study of strains up to 4.3×10^{-2} in these experiments, the data analysis revealed unusually accurate values for linear and nonlinear piezoelectric stress constants, and longitudinal elastic constants up to the fourth order (Graham 1972).

Quartz Thermometer

A quartz resonator with resonant frequency unvarying with temperature has not been made, but the behavior with temperature has been thoroughly studied so that, for a given temperature range, a resonator with a reasonably low, and accurately known, variation could be made. Advantage has been taken of this property to measure temperature differences (Smith and Spencer 1963). A 5 Y-cut

(Cady 1964), operating at 5 MHz, has a temperature–frequency coefficient of about 80 ppm/°C and responds to a temperature deviation of 3.8×10^{-6} °C, indicating a very sensitive device.

Commercial development of the quartz thermometer led successfully, through an analysis of plate orientations, to one yielding a linear frequency–temperature relationship. The available instrument has a range of –80° to 250° C with a maximum resolution of 0.0001°C. A digital readout is used, and with optional amplifiers the sensory probe can be as far as 1,372 m from the measuring equipment (Hammond, Adams, and Schmidt 1965).

Quartz Microbalance

A quartz resonator can be brought to a slightly lower frequency by loading it with a little extra mass, say, from evaporated metal. Hence the change in frequency on loading makes the resonator a mass-measuring device. This idea led to the construction of microbalances reading to about 10^{-12} g for certain unusual applications; for example, the measurement of gases that can be adsorbed in a layer of material coating the resonator, such as a hydrophilic substance for weighing water vapor. The frequency change is directly proportional to the change in mass. A 5-mm-diameter, 15-MHz resonator has a mass sensitivity of 2,600 Hz change per microgram. The resonator is usually an AT-cut. The frequency is also a function of temperature. In one method, a zigzag strip of nickel (to serve as heater, thermocouple, and radio-frequency electrode) is evaporated onto one side of the resonator (an AT-cut crystal) (Saubrey 1964; Stockbridge 1966; King 1969).

Surface Waves on Quartz

Elastic solids can display bulk waves or surface waves. Bulk waves are found in quartz oscillators themselves and in buffer rods or other attachments used for conveying a vibration from an oscillator along a length of rigid elastic solid. A use of bulk waves in such a delay line is described in the section on Measurement of Viscoelastic Materials in this chapter. Bulk waves in quartz have also been used to modulate light.

Surface waves—such as the Lord Rayleigh waves that now find standard application in earthquake study—can be produced on various crystalline solids (Viktorov 1968; White 1970). They can be launched in the x direction (i.e., along an a axis) on a quartz bar by means of electric impulses applied to the surface through two evaporated electrodes having the appearance of two interleaved combs or the illustrative diagram of a multiplate capacitor. Similar electrodes at the far end of the bar can receive the waves and convert them into electrical signals. The bar or plate of quartz can be cut parallel to a plane containing an a axis and the c axis—the Y-cut of the piezoelectric engineer. In one application, the bar is 25.4 mm long. The interesting advantage of using elastic waves in certain electronic circuits is the slowness with which they move: about 1.5×10^3 to 15×10^3 m/sec instead of 3×10^8 m/sec, which is the velocity of electric signals and light. Surface waves move in the lower third of that range. A further advantage of surface waves is that they can be sampled or modified. If the y are accompanied by electric or magnetic fields (when they are produced in piezoelectric or magnetic materials), the passage of the wave and its characteristics can be picked up by a sensing device not in contact with the surface.

Another synthetic crystal of much interest in surface wave applications is lithium niobate.

Miscellaneous Uses

Further uses of quartz resonators have appeared in recent years in color television circuits and in watches. The resonator used in a watch design is not the face-shear mode most used for high fre-

quency, 0.5 to 50 MHz, but a flexural, or wave-shaped, mode operating in the range of 2 to 20 kHz (Cady 1964).

MINERALS OTHER THAN QUARTZ

Crystals large enough to hold in the palm of one's hand are of enormous interest because of the astonishing things that they can be made to do. Naturally occurring crystals are not among these, nor are they likely to be; a modern laboratory, however, can create a material with favorable properties through crystal-growing processes that the solid-state physicist can use for electronic, optical, magnetic, or any combination of circuitry.

Few minerals are found with sufficiently high quality to be employed directly. One special exception is calcite; optical calcite is becoming so difficult to find in sizes that are in demand that investigations are under way to synthesize it.

Natural quartz is becoming less important in the frequency-control oscillator industry; mica and selenite are used in very small amounts in making light-retardation plates as microscope accessories.

If a mineral is observed to have a useful property, the crystal grower can probably reproduce it in an improved crystal that is larger, freer of optical flaws, purer, or conversely, doped with impurities (in either case, to give it an effective property).

Synthetic crystals are, in any case, derived from mined ores that undergo various refining and purifying processes—some rather sophisticated—which leads to growing, cutting, and polishing the crystals into usable shapes.

Many of the currently exploited properties of light and crystals have been known since early in the 18th century. Recently, development techniques using intense light beams, high optical quality crystals, or sensitive measuring equipment have been needed to study and apply them. The technology in optical communication is now on the edge of such an expansion as radio and television experienced in the 1940s. The frequency-control resonator, the diode, and the transistor were among those early achievements. Radio frequencies have given way, along the growing front of research, to ultrahigh frequencies close to and within the visible range of the spectrum.

Minerals of Technological Interest

Table 3 is an alphabetical listing of minerals studied earlier, or in current commercial use. Others are not listed, some are only of casual past interest, and some have been overlooked unintentionally. The mineral name is preceded by the Dana identifying number. The chemical formula and the crystal system are given. It should be noted that this is the system for the crystal at ordinary temperature; at lower temperatures a crystal may move into a less symmetric system, and vice versa. Where appropriate, related or replacing crystals are mentioned; the latter have enhanced new and exciting properties.

The useful mineral, property, application, and device are not easily differentiated in every case, depending on the state of the art. Examples follow:

Mineral	Useful Property	Application	Device
Quartz	Piezoelectricity	Frequency control	Oscillator or crystal
Ruby	Fluorescence	Light amplification	Laser

Some of the listed properties are obtained in enhanced value from water-soluble crystals that are not minerals. Whereas halite and sylvite, for example, are minerals soluble in water, the crystal most phenomenal for ferroelectric and piezoelectric use is Rochelle salt, a rather complex and very soluble organic compound. Other

Table 3. Minerals for electronic and optical uses

Dana No.	Mineral	Chemical Formula	Crystal System	Related or Replacing Crystal	Useful Properties and References	Applications	Devices, Equipment	Growth Studies, References
51.4.3a.2	Almandine	$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$	Iso	$\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG) $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG)	Magneto-optical Fluorescence Hardness, $n = 1.8$ (high)	Microwaves Laser, Nd:YAG (Geusic, Marcos, and Van Uiert 1964) Gem, YAG	Laser, Nd:YAG (Geusic, Marcos, and Van Uiert 1964)	Rudness and Kebler 1959; Makram 1968; Talsdorf 1968
2613	Altaite	PbTe	Iso	PbS	Photoconductivity (Bube 1960)	Pyrometry	Photoconductors; infrared (IR) spectroscopy (Bube 1960); semiconductor laser	na*
41.8.1.0	Apatite	$\text{Ca}_5\text{F}(\text{PO}_4)_3$	Hex	na	Fluorescence with Mn (Ryan et al. 1970) IR spectra (Knubovets, Kislovskii, and Vorobyov 1970)	na	Laser, high gain	Mazelsky, Hopkins, and Kramer 1968
38.4.3	Berlinite	AlPO_4	Hex	Quartz	Piezoelectricity (Stanley 1954) Piezoelectricity (Cady 1964)	Probably none; piezoelectric low	na	na
26.1.7	Boracite	$\text{Mg}_3\text{B}_7\text{O}_{13}\text{Cl}$	Iso	na	Pyroelectricity (Cady 1964)	na	na	Nassau and Shiever 1972
9.1.1.5	Bromyrite	AgBr	Iso	na	IR transmission 0.5–35 μm	na	IR spectrophotometer	na
39.2.1	Brushite	CaHPO_4	Mon KH	${}_2\text{PO}_4$	Piezoelectricity (Cady 1964)	na	na	na
14.1.1.1	Calcite	CaCO_3	Hex	NaNO_3	Strongly birefringent	Polarization of light (Waesche 1960)	Nicol prism; Glan-Thompson prism; etc.	Henisch 1970; Hotta et al. 1971; Liaw and Faust 1972
9.1.1.4	Cerargyrite	AgCl	Iso	na	IR transmission, 0.4–30 μm	na	IR polarizer by reflection	na
269	Cinnabar	HgS	Hex	na	Optical rotation; IR transmission, 1–13 μm	Photoconductors	na	Toudic and Aumont 1971
2616	Clausthalite	PbSe	Iso	PbS	Photoconductivity in IR to 5.6 μm	Detect IR radiation	IR spectrophotometer (Bube 1960)	na
25.1.9	Colemanite	$\text{Ca}_2\text{B}_6\text{O}_{13}\cdot 5\text{H}_2\text{O}$	Mon	na	Ferroelectricity (Cady 1964)	na (1	na	na
8321	Columbite	$(\text{Fe}, \text{Mn})[\text{Nb}, \text{Ta}]_2\text{O}_6$	Rho	na	Piezoelectricity; ferroelectricity; luminescence (Hordvik and Schlossberg 1972)	Electro-optical modulation; hologram recording (Laudise 1968; Stepke 1972)	na	Laudise 1968
4411	Corundum	Al_2O_3	Hex	Sapphire; ruby	High refractive index	Substrate for Si (Cullen 1971); basis for star sapphires	na	Pollock, Bailey, and LaBelle 1972
9.2.1	Fluorite	CaF_2	Iso	na	Fluorescence; reference index low; dispersion low; transmission, 0.12–9.0 μm	Windows; prisms; lenses	Scintillation counter; laser, $\text{CaF}_2:\text{Eu}$ (Garbuny 1965; Nassau 1965)	Nassau 1965
2611	Galena	PbS	Iso	Note altaite and clausthalite	Photoconductivity to 2.8 μm	IR detection (Bube 1960)	na	Laudise 1968
2642	Greenockite	CdS	Hex	na	Piezoelectricity; photoconductivity; photovoltaic; pyroelectricity; electro-optic; linear compressibility	Mixing light beams	Photoconductors; solar cells Acoustoelectric oscillator (Fochs 1970)	Fochs, George, and Augustus 1968; Parker and Pinnell 1968; Nassau and Shiever 1972
9.1.1.1	Halite	NaCl	Iso	NaI	Transmission, 0.2–15 μm	Windows; prisms; lenses	IR spectrometers; x-ray spectrometers	na
28.4.3.1	Langbeinite	$(\text{NH}_4)_2\text{Cd}_2(\text{SO}_4)_3$	na	na	Ferroelectricity (Jona and Shirane 1962)	See columbite	na	na
4.3.3.4	Leushite	NaNbO_3	Orth	Other niobates; see columbite	Antiferroelectricity (Jona and Shirane 1962)	na	na	na
7216	Magnetite	Fe_3O_4	Iso	$\text{ZnNiFe}_2\text{O}_4$ BaFe_2O_4	Low coercive force; high remanence	Ferromagnetic application; replaced by better crystals	Memory devices and permanent magnets	na

(Table continued next page)

Table 3. Minerals for electronic and optical uses (continued)

Dana No.	Mineral	Chemical Formula	Crystal System	Related or Replacing Crystal	Useful Properties and References	Applications	Devices, Equipment	Growth Studies, References
71.2.2a.1	Muscovite	$KAl_3Si_3O_{10}(OH)_2$	Mon	na	Birefringent; good dielectric coefficient; high dielectric strength	Insulation	Capacitors; 1/4-wave plates	na
9.1.3.1	Nantokite	CuCl	Iso	na	Electro-optic; transmission, 0.4–20 μ m	Electro-optic	Light modulator (Murray 1964)	na
4211	Periclase	MgO	Iso	na	na	Insulator	na	Butler, Sturm, and Quincy 1969
7421	Perovskite	$CaTiO_3$	Orth	$BaTiO_3$ (Tet) $PbZrTiO_3$ $STiO_3$ (Iso)	High dielectric coefficient; ferroelectricity (Iona and Shirane 1962); high refractive index	Modulation of light phase (Kaminow 1965) Gem	Phono pickups; many piezoelectric devices (Wheeler 1972)	Nassau and Broyer 1962b; Von Hippel 1963
3212	Proustite	Ag_3AsS_3	Hex	na	Pyroelectricity; photoconductivity; electro-optic	Electro-optical modulation	na	Hulme et al. 1967; Bardsley and Jones 1968; Gentile and Stafsudd 1968
75.1.3.1	Quartz	SiO_2	Hex	No equivalent crystal	Piezoelectricity (Cady 1964; Mason 1964) Transmission, 0.15–3.5 μ m Birefringent Color as grown (Pough 1970; Crowningshield 1972) Fluorescence; high hardness	Frequency control (Cady 1964; 1964); surface waves (de Klerk 1972; White 1970); cultured gems (Crowningshield 1972; de Klerk 1972) Holography; communications	Oscillator or "crystal;" delay lines; transducer filters	na
4411	Ruby	$Al_2O_3:Cr$	Hex	Corundum	High dielectric coefficient, 173; perpendicular to c axis	na	Laser (Maiman 1960; Garbuny 1965)	Nassau and Broyer 1962a
4511	Rutile	TiO_2	Tet	na	na	na	na	Nassau and Broyer 1962b; Farrell and Ling 1972; Rosenberger and Delong 1972
48.1.3.1	Sapphire Scheelite	See Corundum $CaWO_4$	na Hex	na Corundum	Fluorescence; electroluminescence	na	na	na
29.6.3 2621	Selenite Sphalerite	$CaSO_4 \cdot 2H_2O$ ZnS	Mon Iso	na na	Birefringent Piezoelectricity (Cady 1964) Birefringent (Yu and Cardona 1973)	Petrography Light modulation (Buhrer, Bloom, and Baird 1963)	Laser: $CaWO_4:Nd$ (Johnson and Nassau 1961; Garbuny 1965); $CaWO_4:Sm$ 1/2-wave plates	Nassau and Broyer 1962a
7211	Spinel	$MgAl_2O_4$	Iso	na	Optical rotation Good transmission; dielectric coefficient, 8.4	Substrate for Si (Cullen 1971)	na	Wood and White 1968
9.1.1.2 8322	Sylvite Tantalate	KCl $(Fe,Mn)[Ta,Nb]_2O_6$	Iso	KBr, KI Various tantalates; $LiTaO_3$ (Iona and Shirane 1962)	Transmission 0.38–21 μ m Ferroelectric; low birefringence; transmission 0.35–4.0 μ m	Study of color centers Light modulation (Laudise 1968)	na na	na na
454	Tellurite	TeO_2	Tet	na	Piezoelectricity; low-velocity shear wave	Acousto-optic (Bonner et al. 1972)	Light deflector; modulator	Bonner et al. 1972
61.3e.1.10	Tourmaline	$NaFe_3B_3Al_3$ $[Al_3Si_6O_{27}(OH)_4]$ Schorl variety	Hex	Quartz	Piezoelectricity; pyroelectricity (Cady 1964) Slightly electro-optic	na	na	na
14.1.2.1	Vaterite	$CaCO_3$	Hex	na	Strong positive birefringence (Iona and Shirane 1962)	No use noted	na	na
48.1.4.1	Wulfenite	$PbMoO_4$	Tet	$CaMoO_4$	High polarizability (Pinnow et al. 1969) Transmission, 0.45–3.9 μ m	Acousto-optic	Light deflector; modulator	Pinnow et al. 1969
4221	Zincite	ZnO	Hex	na	Piezoelectricity	Acoustoelectric (Kolb 1967)	na	Kolb 1967; Nielsen 1968

Source: Ober 1994.

* na = not available.

important synthetic crystals also not found as minerals are germanium and silicon, the single crystal chemical elements used to make diodes, transistors, integrated microcircuits, or computer chips.

Almandine garnet is listed as the precursor of yttrium iron garnet and yttrium aluminum garnet. Perovskite is so listed for the much-valued barium titanate and lead zirconium titanate. Columbite is listed for the family of niobates. Growers and users of optical crystals have been using niobium instead of columbium for the element of atomic number 41.

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GLOSSARY

The following list contains some of the terms that apply to the use of minerals and various synthetic crystals in electronic and optical technology. Optics texts are mentioned in the references for further coverage of that limited field.

Absorbance: The value of the expression, $I_n(I_0/I)$, where I_0/I is known as the absorbance and is a numerical statement of the absorption of radiant energy by a transparent material: the ratio of the intensity (W/m^2) of the incident light to the intensity leaving. The constitutive equation is

$$I = I_0 e^{-\alpha d},$$

where α is the absorption coefficient and d is the length of light path in the material.

Acousto-optic: A light-modulating device in which an acoustic wave, ultrasonic in frequency, passing through a suitable crystal plate sets up strained layers with its wave fronts such that an entrant light beam is deflected. Ideally the deflection can be controlled through a critical angle, which can be varied at frequencies into the megahertz range.

Beam splitter: A thin sheet of glass or clear plastic with its surface treated to reflect about half the light incident to it at approximately 45° to the surface. In a more advanced type, two right-angle prisms are cemented along the hypotenuse faces with a material having selected reflection properties to control the ratio of transmitted to reflected light or proportion of color.

Delay line: A device used to delay an electrical signal for a short time, usually milliseconds. In one method, a piezoelectric transducer is mounted on an elongated piece of rigid material, for example, vitreous silica or aluminum. A signal is introduced by the transducer and received on reflection or by another transducer at its far end.

Dielectric: A substance that acts as an electrical insulator, a non-conductor of electricity, or a substance with electric conductivity less than 1×10^{-6} mho. The term may refer to a vacuum and many gases and liquids. Many solid dielectrics, mineral and nonmineral, are opaque or absorb all nonreflected light in a very thin layer. Dielectrics useful in optical technology are transparent in the visible or near-visible range of radiation.

Ferroelectric crystal: A crystal that has the ability to become naturally electrically polarized in a restricted temperature range and exhibits hysteresis between polarization and an applied electric field. If the crystal is heated to the transition temperature (Curie point), the crystal becomes nonpolar. (Piezoelectric crystals become electrically polarized when subjected to a deforming stress.)

Fluorescence: The emission of radiation from a substance that is absorbing radiation of higher energy and shorter wavelength. (There are, however, interesting cases of the [apparent] reverse energy relationship.) Often, large crystal size is not important and powdered fluorescent and luminescent crystals, called *phosphors*, are used in cathode-ray tubes, television kinescopes, and

fluorescent lamps. On the contrary, a large fluorescent crystal bar (i.e., ruby, scheelite, or fluorite), is used in the solid-state laser. Crystals do not have the property of fluorescence if they are strictly pure, and the variation in amount and type of impurity yields useful variations in behavior.

Harmonic generation: The combining of two sets of wave motions having different—but not far removed—frequencies, producing an ongoing wave whose frequency is a multiple or submultiple of the input frequency. Long known in radio technology, this effect in optics uses crystals as the medium in which the action occurs. For further information with only slight mention of minerals, see Schlossberg and Kelley (1972).

Holography: A method of producing whole three-dimensional images of objects by means of recorded light wave patterns, often on photographic film. Holography involves dividing a laser beam (a coherent light source, or one that is of a single wavelength or frequency and with all waves in phase) with a beam splitter so that the continuing beam strikes the film; the reflected beam strikes an object and is reflected back onto the film. The two beams, direct and twice reflected, meet, interfere, and record their interference pattern on the film. A three-dimensional view of the object can be seen on the processed film illuminated by monochromatic light. Remarkable features are that no lens is used; the view is not simply two dimensional; a piece of the film will display the same view as the whole; and a large amount of information is stored on the film. A crystal of lithium niobate has been used as the recording medium.

Laser: A device that emits an intense, narrow beam of coherent, monochromatic light as a result of light amplification by the stimulated emission of radiation (Maiman 1960). Originally the laser comprised a ruby rod energized by an intense source of light nearby; after years of investigations, lasers can now be made of glass, liquid, dye solution, or gas. The light from the ruby, at 6300 \AA , is at the infra-red edge of vision; lasers now produce radiation of both longer and shorter wavelengths. Through modulation at the source and demodulation at a receiving station, the laser can transmit as many as 10^{10} channels, each 10 kHz wide (Nassau 1965; Laudise 1968).

Magneto-optic: In certain crystals through which a beam of polarized light is passing, applying a magnetic field with its lines of force parallel to the beam causes a rotation of the plane of polarization: the Faraday effect. This magneto-optic effect can be used to modulate a light beam.

Modulation: The process and effect of adding information to a radio carrier wave or to a light beam. In radio, AM and FM are well known. A light beam can be modulated by altering its amplitude, frequency, phase, or plane of polarization. The modulation can take a digital form, transmitting simply 0 and 1, or an analog form that includes voice and music. The amplitude (or intensity) of a light beam can be modulated, for example, by applying a varying electric field to an electro-optic crystal carrying the beam. The crystal is sandwiched between crossed polarizers to provide the rest of the optical requirement.

Nonlinear: Behavior that does not follow a straight line or proportionality relationship when one variable is altered and a dependent variable is observed. In electronics, for example, the behavior of current through a diode with respect to applied voltage is nonlinear. The optical properties of a medium are linear when the intensity of the transmitted light is low, as is normally the case. Nonlinear refers to changes in the optical properties as the intensity of transmitted light is greatly increased, or when two or more strong light beams are combined in the medium. The study of nonlinear phenomena is the basis of progress in

electronic and optical technology: solar power, transistor, laser, and holography (Schlossberg and Kelley 1972).

Piezoelectric effect: An electric reaction or charge resulting from applying a physical stress (compression, bending, or twisting) to a substance (element, crystal, etc.). The converse effect also applies—the element tends to deform when an electric field or charge is applied. Actual motion or strain is usually involved. The substance, commonly a macrocrystal, can be an assemblage of microcrystals as in a piezoelectric ceramic. That the crystal has no center of symmetry is a necessary crystallographic condition. Applications have included frequency-control resonators of quartz and phonograph pickups of Rochelle salt (not a mineral) and of lead zirconium titanate (related to perovskite).

Property: Relates to any of the principal characteristics of a substance, especially as determined by the senses but also determined by any variety of sophisticated sensing equipment, for example, infrared transparency, laser capability, or semiconduction.

Pyroelectric: The property of a crystal such that electric charges appear on certain faces when it is heated or cooled. Strontium niobate, a synthetic crystal related to columbite, shows such a strong effect that it can serve as a practical infrared detector.

Q-switch, or Q-spoiler: A fast-acting light valve used with lasers to arbitrarily hold back light emission and let it burst forth at the flick of the switch in a high-energy flash. Electro-optic crystals and the Kerr cell using nitrobenzene and a high-voltage pulse have been used for such shutters and require the presence of polarizers on each side in a crossed position. Acousto-optic crystals and solutions of certain dyes also are used.

Resonator: A device or system in which a characteristic vibration can occur involving a continuous exchange between potential and kinetic energy. Examples follow:

- A *piezoelectric resonator* is a rectangular plate (sometimes a disk or bar) of piezoelectric material, commonly quartz, that will vibrate characteristically when placed in an alternating voltage field that has the same frequency as the natural mechanical frequency of the plate. The motion can assume various types or modes: compression, shear, or flexural. Piezoelectric resonators of quartz for frequency control cover the range of about 1 kHz to 55 MHz. A piezoelectric plate can be driven at frequencies different from the resonance frequency.
- An example of an *acoustic energy cavity resonator* is the organ pipe. In microwave technology, a resonator is a metal box or cavity in which electromagnetic energy can be stored; the resonance frequency is determined by the geometry of the enclosure.
- An example of an *optical resonator* is the Fabry-Perot resonator or interferometer; two parallel, partially reflecting mirrors cause the light entering in one direction to oscillate before exiting. In a common application, light is passed through a converging lens to form an interference figure of highly contrasting fringes on a screen. The laser may be called a Fabry-Perot resonator.

Acid Neutralization

Ben Koopman

INTRODUCTION

Because extreme pH values in water are harmful to humans and aquatic life, the pH of drinking waters and treated wastewater effluents is regulated. Extreme pH is also corrosive to water piping systems. The allowable pH range of wastewater effluents that are discharged to receiving waters is typically 6 to 9 or 6.5 to 9.

Reagents used for neutralizing acids are derived from chemical processes such as the electrolysis of brine to produce caustic soda and from minerals such as limestone, which can be used directly for neutralization or can be processed into various forms of lime. Alkaline industrial wastes and metallic iron are also important reagents.

Some of the reagents employed for acid neutralization are also used to remove acid-forming components from flue gases, to purify and soften water, and to pasteurize wastewater sludge. The quantities involved are significant to the minerals industries. For example, almost 1.0 Mt of lime were used in treating water for municipal and industrial supplies in 2001 (National Lime Association, undated [a]). In fact, lime is the most-used chemical in the water treatment industry.

This chapter first describes the commonly used acid neutralization reagents, including chemical nature and primary routes of production, and also mentions some waste-derived materials that

have shown promise. Production and consumption statistics are discussed and trends are noted, and properties and prices of the commonly used reagents are compared. The major environmental applications of these materials are then described.

ACID NEUTRALIZATION REAGENTS

The most common reagents for neutralization are caustic soda and various forms of lime. Other chemicals with important uses include soda ash, magnesium hydroxide, and anhydrous ammonia. Some waste materials, notably the combustion products of coal, have also been suggested as materials for neutralization. Because the common or commercial names for many of the reagents differ from their chemical names, a list of the reagents is presented in Table 1. Representative chemical formulas are also given in the table. Commercial reagent formulations may vary from the pure chemical formula.

Limestone

The term *limestone* has been widely applied to mean rock that is principally composed of calcium carbonate. Many limestones were formed 100 to 500 million years ago from compressed layers of calcareous marine deposits. Other types of limestone include chalk, which is a soft sedimentary deposit of marine calcareous fossils, and marble, which is hard metamorphic rock formed from

Table 1. Common names, chemical names, and representative chemical formulas of acid neutralization reagents

Common name	Representative Chemical Formula	Chemical Name	Other Common Names
Ammonia	NH ₃	Ammonia	Anhydrous ammonia
Caustic soda	NaOH	Sodium hydroxide	
Dolomitic limestone	CaCO ₃ •MgCO ₃	Calcium carbonate/magnesium carbonate	
Dolomitic quicklime	CaO•MgO	Calcium oxide/magnesium oxide	
Half-burnt dolomite	CaCO ₃ •MgO	Calcium carbonate/magnesium oxide	
High-calcium hydrated lime	Ca(OH) ₂	Calcium hydroxide	Slaked lime
High-calcium quicklime	CaO	Calcium oxide	Burnt lime, oxide lime
High-calcium limestone	CaCO ₃	Calcium carbonate	
Magnesia	MgO	Magnesium oxide	
Magnesium hydroxide	Mg(OH) ₂		
Normal dolomitic hydrated lime	Ca(OH) ₂ •MgO	Calcium hydroxide/magnesium oxide	Dolomitic hydrate type N
Pressure dolomitic hydrated lime	Ca(OH) ₂ •Mg(OH) ₂	Calcium hydroxide/magnesium hydroxide	Dolomitic hydrate type S
Soda ash	Na ₂ CO ₃	Sodium carbonate	

sedimentary material. Calcite is the predominant crystalline form of calcium carbonate found in lime stones. Sedimentary deposits of recent origin may contain aragonite, a metastable crystalline form that is gradually converted to calcite over geological time.

Dolomitic and Magnesium Limestones

Some limestone deposits contain both calcium and magnesium carbonates. The mineral dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$) contains equimolar amounts of calcium carbonate and magnesium carbonate. The chemical composition of dolomite by weight is 54% calcium carbonate and 46% magnesium carbonate. According to the National Lime Association, the term *dolomitic limestone* is applied to limestones containing more than 35% magnesium carbonate. Limestones with intermediate contents of magnesium carbonate (5% to 35%) are classified as magnesium limestones.

High-Calcium Limestone

Limestone with a high content of calcium carbonate (and thus a low content of magnesium carbonate) is referred to as high-calcium limestone. The magnesium carbonate for this classification is 5% or less.

Production and Use

In 2002, 978 Mt of limestone and 97 Mt of dolomite were produced in the United States. The leading states for limestone production were Texas, Florida, Missouri, Ohio, and Pennsylvania; their combined production was 40% of the total. Illinois, New York, Pennsylvania, Ohio, and Indiana led in production of dolomite, together producing 65% of the U.S. total. Removal of sulfur dioxide (SO_2) from flue gases consumed 3.0 Mt of limestone. Another 0.17 Mt were used for mine dusting or acid water treatment (Tepordei et al. 2002).

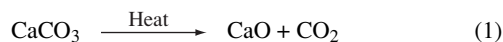
Over the 5-year period from 1998 through 2002, the yearly U.S. production of limestone and dolomite was relatively flat. Use of limestone for sulfur dioxide removal almost doubled during the period, starting at 1.7 Mt and ending at 3.0 Mt. In contrast, application of limestone in mine dusting or acid water neutralization exhibited a slight decreasing trend. A continuing trend toward more stringent U.S. Environmental Protection Agency (EPA) limitations on SO_2 emissions should provide growth opportunities in the limestone flue gas desulfurization (FGD) market.

Lime

Both calcium oxide and calcium hydroxide are commonly referred to as lime. These compounds are also distinguished by the terms *quicklime* and *hydrated lime*, respectively. Other terms for quicklime are *burnt lime* and *burnt limestone*.

Quicklime

Quicklime is manufactured by heating (calcining) limestone at temperatures in the range of 900 °C to 1,300 °C (Moropoulou, Bakolas, and Aggelakopoulou 2001; Georgallias et al. 2002) to drive off carbon dioxide (CO_2), leaving calcium oxide, as shown in Equation (1).

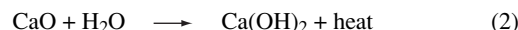


Quicklime is classified chemically according to the calcium carbonate content of the limestone from which it is made. High-calcium quicklime is derived from high-calcium limestone, magnesium quicklime from magnesium limestone, and dolomitic quicklime from dolomitic limestone.

Because the heat of decomposition of CaCO_3 is higher than that of MgCO_3 , the temperature required to drive off the CO_2 from calcium carbonate is also sufficient to drive off the CO_2 from magnesium carbonate. Calcining dolomitic limestone at this temperature yields a product that contains only the oxides of calcium and magnesium— $\text{CaO} \cdot \text{MgO}$. This reagent is referred to as dolomitic quicklime. Calcining dolomitic limestone at a somewhat lower temperature drives off only the CO_2 associated with magnesium, producing a mixture of calcium carbonate and magnesium oxide (e.g., $\text{CaCO}_3 \cdot \text{MgO}$). This reagent is referred to as half-burnt dolomite.

Hydrated Lime

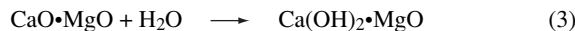
Hydrated lime is a dry powder produced by reacting quicklime with sufficient water to form calcium hydroxide, Ca(OH)_2 , as shown in Equation (2).



It is worth noting that the reaction is exothermic and should be carried out with equipment that can safely conduct away the released heat energy.

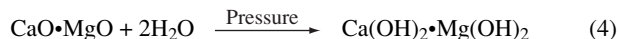
The chemical composition of hydrated lime depends on the composition of the quicklime from which it is made, the hydrating conditions, and the quantity of water used. High-calcium hydrated lime is produced from high-calcium quicklime and generally contains between 72% and 74% calcium oxide and 26% to 28% chemically bound water.

When hydrated under normal (atmospheric) conditions, only the calcium oxide fraction of dolomitic quicklime reacts with water:



The normal dolomitic hydrated lime resulting from Equation (3) is composed of 49% calcium oxide, 35% magnesium oxide, and 16% chemically bound water by weight. Commercial grades of dolomitic hydrated lime will vary in composition.

Hydrating dolomitic quicklime under pressure (and elevated temperature) causes all of the magnesium carbonate, as well as the calcium carbonate, to react with water, as shown in Equation (4).



The pressure dolomitic hydrated lime resulting from Equation (4) contains 43% calcium oxide, 30% magnesium oxide, and 27% chemically bound water by weight. Commercial grades of pressure dolomitic hydrated lime will vary in composition.

Production and Use

U.S. production of lime in 2003 was 19 Mt, compared to an estimated worldwide total of 120 Mt (Miller, Miller, and Wallace 2003). The largest producers were China (23 Mt), the United States, Russia (8 Mt), Japan (7.5 Mt), and Germany (7 Mt). The amount of lime consumed for environmental applications in the United States in 2003 was 5.3 Mt. Most of this was for FGD (65%), followed by drinking water treatment (17%), wastewater treatment (7%), sludge treatment (6%), acid mine drainage mitigation (2%), and miscellaneous applications (2%).

Worldwide lime production has generally trended upward in the past 5 years, increasing from 116 to 120 Mt during this period. U.S. production and consumption rates for environmental applications, however, have been relatively flat. EPA's new interstate air quality rule requires that deep cuts in SO_2 emissions be achieved in

the coming decade. More FGD scrubbers must be installed to comply with the rule, but the implementation schedule could be stretched out as electrical utilities cash in allowance credits banked under the Acid Rain Phase II Program (Miller, Miller, and Wallace 2003). Besides the interstate air quality rule, the acid rain program already in place, incinerator regulations, and upcoming EPA standards for control of industrial hazardous air pollutants are providing growth opportunities in lime's FGD market.

Caustic Soda

Caustic soda (NaOH) is formed along with chlorine from the electrolysis of brine solution. The most common commercial grade is 50% NaOH by weight. Solution of this strength begins to freeze at temperatures below 18°C, so some users prefer more dilute concentrations that freeze at lower temperatures. For example, 20% NaOH freezes at around -10°C (Jones-Hamilton Co. 2004).

In 2001, the U.S. demand for caustic soda was 11 Mt (Kirschner 2003), compared to a global demand of 46 Mt (Shamel and Udis-Kessler 2001). Consumption of caustic soda for water treatment is about 5% of the U.S. demand. The trend in U.S. demand was downward in the 5-year period from 1998 through 2002.

Soda Ash and Sodium Hydrogen Carbonate

Soda ash (sodium carbonate) and sodium hydrogen carbonate (sodium bicarbonate) are produced by refining the minerals trona ($\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot \text{H}_2\text{O}$) and nahcolite (NaHCO_3) or sodium-carbonate bearing brines (Kostick, Milanovich, and Coleman 2003). Soda ash can also be produced synthetically by one of several chemical methods. One of these is the Solvay process, which uses limestone, salt, and ammonia as the raw materials. Disadvantages of synthetic soda ash are its higher cost of production and environmentally deleterious wastes.

The United States and China are the largest producers of soda ash, together accounting for more than half of worldwide production in 2003. Applications of soda ash for FGD and water treatment were equal to 1.2% and 0.7%, respectively, of the 2003 U.S. production of 19 Mt (Kostick, Milanovich, and Coleman 2003).

The trends in soda ash production from 1999 through 2003 were consistently positive in both the United States and around the world. In contrast, soda ash consumption for water treatment during the same period was relatively flat, and consumption for FGD exhibited a downward trend.

Magnesia and Magnesium Hydroxide

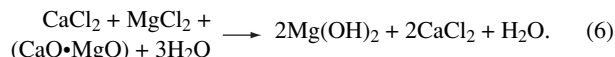
Naturally occurring materials such as magnesite (magnesium carbonate), brucite, dolomite, olivine, brines rich in magnesium chloride, and seawater are used to produce magnesia (magnesium oxide). Conversion of magnesium carbonate to magnesium oxide is accomplished through heating (calcination), which liberates CO_2 :



The temperature of the calcining process influences the properties of the magnesium oxide product. A temperature from 700°C to 1,000°C yields a high-surface-area, reactive material known as light-burned or caustic-calcined magnesium oxide. This is the product that is useful in acid neutralization. Higher calcination temperatures yield materials with lower surface areas and, hence, lower reactivities. Water can be added to produce the hydrate (magnesium hydroxide).

The conversion process for brines or seawater rich in magnesium chloride typically involves adding lime or dolomitic quicklime. The ensuing reaction forms magnesium hydroxide particles in

a solution of calcium chloride. When dolomitic quicklime is added, the reaction is (Martin Marietta Materials 2003)



The magnesium hydroxide particles are collected by gravity sedimentation and washed to remove residual calcium chloride. The magnesium hydroxide can be calcined to produce magnesium oxide.

The U.S. consumption of caustic-calcined magnesia in 2003 was 30,000 t, compared to a production level of 154,000 t (Kramer, Inestroza, and Wallace 2003). Net imports, mostly from China, thus satisfied almost half of the U.S. demand. Water treatment and stack gas scrubbing together accounted for 45% of the caustic-calcined magnesia consumption in the United States. Domestic production of magnesium hydroxide was 217 kt in 2003, slightly greater than the demand of 209 kt. Most of this chemical was used in water treatment.

The trend in U.S. production of caustic calcined magnesia was generally downward from 1999 through 2003, corresponding with expansion of magnesia processing capacity in China. A sharp upturn occurred between 2002 and 2003, however, corresponding to increased environmental applications. The trend of U.S. magnesium hydroxide production from 1999 through 2003 was relatively flat. Use of magnesia and magnesium hydroxide in water treatment is growing as these compounds are increasingly accepted as alternatives to caustic soda. More stringent air pollution regulations should lead to expansion of applications for stack gas scrubbing. As a result, an increasing trend in environmental applications should be expected in the future.

Ammonia

Ammonia (NH_3) is a neutral alkaline, colorless chemical that dissolves readily in water, forming ammonium hydroxide. Steam reforming of natural gas or other light hydrocarbons is the most important process for synthesis of anhydrous ammonia, accounting for 85% of ammonia production worldwide (Appl 1999). Additional ammonia is produced by partial oxidation of heavy fuel or vacuum residue. About 77% of world ammonia capacity is currently based on natural gas, with this feedstock expected to remain dominant over the next half century (EFMA 2000).

World production of ammonia is estimated at 100 Mt yearly, with U.S. production pegged at 14 to 16 Mt yearly (Fee 2003). Most (80%) of the manufactured ammonia is used in agriculture. Of the remaining 20%, wastewater neutralization is the fifth most important application.

Novel Materials

Novel materials for neutralization include alkaline waste materials from industrial processes and zero-valent iron. Industrial wastes that contain high contents of alkaline chemicals can be reacted with acids in a acidic waste streams to accomplish neutralization, thus functioning in similar fashion to the conventional acid neutralization reagents. Zero-valent iron promotes alkalinity-forming redox reactions in the environment.

Alkaline Industrial Wastes

Alkaline wastes considered for acid neutralization include coal combustion by-products (CCBs), steelmaking slag residues, and sludge from bauxite processing via the Bayer process (known as *red mud*). Some 100 Mt of CCBs are generated annually in the United States, of which 25 Mtpy are applied for such beneficial uses as concrete products, structural fill, waste stabilization, and road grade construction. The remaining 75% must be disposed of,

with landfills being the most likely repository (EPA 2000). Types of CCBs include fly ash, bottom ash, fluidized bed ash, boiler slag, FGD ash, and others. These different residues differ in their physicochemical properties. CCBs with high alkaline contents and low exchangeable toxic constituents are suitable for neutralization of acid wastes (Canty and Everett 2001).

Slags from the basic oxygen steelmaking (BOS) process contain large amounts of lime and calcium silicates (Ca_2SiO_4 and Ca_3SiO_3). The alkaline nature of these materials makes such slags possible candidates for acid waste neutralization (Bodurtha and Brassard 2000). Limited amounts of BOS slags are currently used as liming agents in agriculture and as soil conditioners (Lopez et al. 1995).

Red mud is a fine-textured residue from bauxite refining that is currently dumped in holding ponds, which require large areas of land. The principal components of red mud are oxides of iron (Fe), aluminum (Al), and titanium (Ti), which give it high surface reactivity. The liquid phase is primarily a weak solution of sodium aluminate. Its texture and composition confer a high surface reactivity on red mud. It has a high pH (typically 10), is highly alkaline, and forms stable suspensions in water (Altundogan and Tumen 2003; Hanahan et al. 2004).

The potential of alkaline waste materials for acid waste neutralization is accompanied by concerns about the variability in their composition and the contaminants they may contain, particularly heavy metals. Thus, waste-derived acid neutralization agents should be thoroughly characterized as part of the decision-making process in evaluating specific applications.

Zero-Valent Iron

Finely divided metallic iron or, more simply, ground-up scrap iron, has been demonstrated for treatment of halogenated hydrocarbons and heavy metals in groundwater (Matheson and Tratnyek 1994; Shokes and Möller 1999). Iron also exerts a neutralizing effect by promoting chemical and biochemical reduction reactions (e.g., conversion of sulfate to sulfide) that produce alkaline compounds as a by-product (Wilkin and McNeil 2003). Zero-valent iron is attractive because it reacts relatively quickly, has high reduction potential, is nontoxic, and can be obtained from scrap.

ENVIRONMENTAL APPLICATIONS

Acid neutralizing reagents are widely used in the treatment of water for municipal and industrial supplies, purification of municipal and industrial wastewaters, and remediation of acid mine drainage. Significant quantities are also used for the stabilization and dewatering of municipal biosolids and industrial sludges and for FGD. These applications are described in the following sections.

Neutralization of Acidic Wastewaters

The most popular reagents for neutralization of acidic wastewaters are caustic soda and various forms of lime. Ammonium hydroxide is occasionally used for neutralization of industrial wastewaters, and magnesium hydroxide has received attention (Hairston 1996). Factors that should be considered in choosing the optimal reagent include cost, neutralization capacity, reaction rate, storage and feed rate, and neutralization products.

Cost and Basicity

Selected acid neutralization reagents are compared in Table 2 in terms of cost, basicity, and cost per metric ton of basicity. Magnesia is the most expensive reagent, followed by ammonia, caustic soda, soda ash, hydrated lime, quicklime, and limestone. The basicity of the reagents also varies. Basicity is a measure of the alkali available

Table 2. Cost and basicity of selected acid neutralization reagents

Reagent	Price, \$/dry t	Basicity,* metric tons equivalent CaO per metric ton dry reagent	Cost, \$/t basicity
Caustic soda	317 [†]	0.69	459
Magnesia	538 [‡]	1.31	412
Soda ash	169 [†]	0.51	331
Ammonia	411 [§]	1.65 ^{**}	249
Hydrated lime	102 [†]	0.71	144
Quicklime	61 [†]	0.94	65
Limestone	12 ^{††}	0.49	24

* Basicity as reported by Hoak (1950).

[†] 2003 cost from *Chemical Market Reporter* (2003) for truck or railroad-car quantities.

[‡] 2003 cost from Kramer, Inestroza, and Wallace 2003.

[§] 2003 cost from Fee (2003).

^{**} Calculated basicity, metric tons equivalent CaO per metric ton anhydrous reagent.

^{††} 2002 cost from Tepordei et al. (2002) for crushed stone applied in mine dusting or acid water treatment.

for neutralization, relative to pure calcium oxide. This parameter ranges from 1.65 for ammonia to 0.49 for limestone. Caustic soda has a relatively low basicity (0.69) compared to magnesia (1.31) and ammonia (1.65) and thus is the most expensive reagent on a cost per metric ton of basicity basis. The least expensive reagent, both in terms of chemical cost and cost per metric ton of basicity is limestone.

Price volatility is also a factor to consider in reagent selection. As Figure 1 shows, prices for soda ash and magnesium hydroxide powder were very stable from 1999 to 2003, whereas high-calcium quicklime and limestone showed slight increasing trends. Each of these reagents is derived from abundant mineral deposits, which helps to explain their price stability. In contrast, anhydrous ammonia and caustic soda prices have experienced severe volatility. Because ammonia synthesis is highly energy intensive, price swings in this commodity directly reflect energy prices, particularly that of natural gas, which is one of the primary raw materials for ammonia synthesis. Prices of caustic soda tend to mirror those of chlorine, its co-product. Large-magnitude fluctuations in worldwide demand for chlorine in organic chemical synthesis thus lead to wide swings in the price of caustic soda.

Reaction Time, Maximum pH, Sludge Characteristics, and Effect on Total Dissolved Solids

Caustic soda, soda ash, and lime are compared in Table 3 in terms of reaction time, maximum pH, sludge characteristics, and effect on total dissolved solids. Caustic soda reacts almost instantaneously with acids; soda ash and lime are somewhat slower acting. The maximum pH (at 25°C) that could be obtained by adding caustic soda to water is 14, compared to 12.4 with lime and around 11 with soda ash. Sludges produced by neutralization with caustic soda or soda ash tend to be voluminous and difficult to dewater if heavy metals are present. Lime neutralization produces a lower volume, denser sludge that has better dewatering characteristics, even with heavy metals present. Both caustic soda and soda ash produce soluble end products, increasing the total dissolved solids of the treated effluent. Lime produces insoluble calcium salts and can thus decrease the effluent total dissolved solids.

Despite being relatively expensive, caustic soda is widely used because of its uniformity, ease of storage and feeding, rapid reaction rate, and solubility of end products. Soda ash is less reactive than

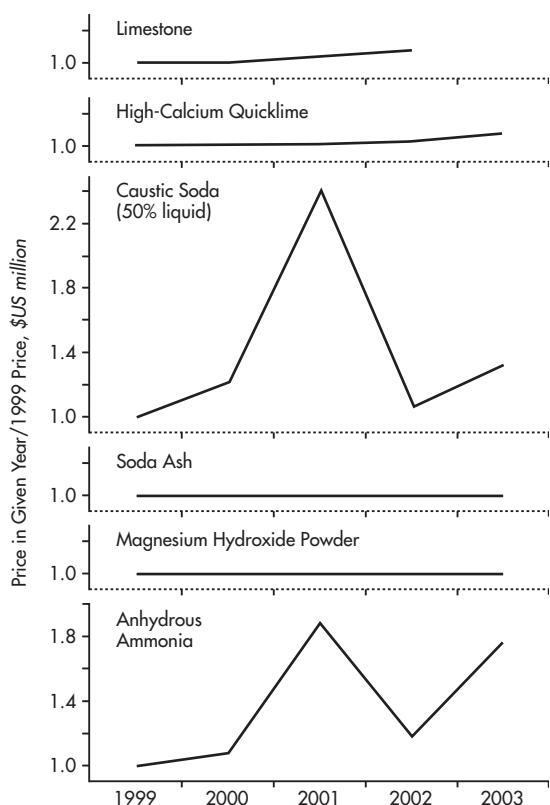


Figure 1. Relative prices of selected acid neutralization reagents between 1999 and 2003

Table 3. Comparison of common neutralization reagents

Reagent	Maximum pH at 25°C	Relative Reaction Rate	Sludge Characteristics	Nature of Salts Produced
Caustic soda	14	Nearly instantaneous	High volume; gel-like if heavy metals present	Soluble sodium salts
Soda ash	>11	Moderately fast acting	High volume; gel-like if heavy metals present	Soluble sodium salts
Quicklime or hydrated lime	12.4	Moderately fast acting	Dense, low volume; good dewaterability, even if heavy metals present	Insoluble calcium salts

Adapted from National Lime Association 2000.

caustic soda and can produce frothing problems caused by the release of CO₂. Quicklime and hydrated lime are attractive because they are low in cost but still possess moderately high reactivity. Handling of these particulate solids is complex, however. Dry lime tends to bulk and bridge in storage, so equipment such as agitators must be installed on silos to ensure reliable delivery. Quicklime must be hydrated on-site, using slaking equipment, before feeding to the neutralization reactor. Lanouette (1977) suggested that hydrated lime could be fed directly from storage to the neutralization reactor, whereas Conway and Ross (1980) recommended that it be fed as a slurry with 15% contained CaO. Slurry feeding of hydrated lime increases reaction rate because the time required for dissolution of reagent in the reactor is eliminated.

Table 4. Reagent requirements for neutralization of waste acids

Reagent	Kilograms Required per 100 kg Waste Acid		
	H ₂ SO ₄	HCl	HNO ₃
Liquid caustic soda (50% NaOH)	164	220	127
Soda ash	119	160	93
High-calcium limestone	110	148	86
Dolomitic limestone	94	127	73
High-calcium hydrated lime	79	107	62
Dolomitic hydrated lime	65	87	51
High-calcium quicklime	60	80	46
Dolomitic quicklime	54	73	42

Adapted from Patterson 1985.

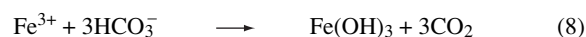
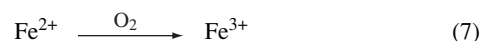
Limestone is most economical in terms of reagent cost, but it has the least reactivity. Pulverizing limestone increases its reaction rate but approximately doubles the reagent cost (Conway and Ross 1980). Limestone-packed beds have proven to be a feasible approach to low-cost neutralization. They are capable of achieving effluent pH 5.0 to 6.5 at appropriate hydraulic loading rates (Bisogni and Vaillancourt 1980). Reaction of limestone with acidic wastewater produces bicarbonates and CO₂. Aeration of limestone reactors or packed beds may be needed to strip out CO₂ so that effluent pH can be raised above 4.3 (Krylenko 1976; Oh sawa 1976). The bicarbonates exert a buffering effect that is capable of achieving near-neutral effluent pH without automatic pH control systems (Pilot 1974). Head loss through packed bed reactors is a major design consideration. Operation of limestone beds in upflow mode has been recommended to flush out fine suspended matter that could blind the bed, as well as to flush out CO₂ (Mezey 1979).

Substantial quantities of sludge can be produced when lime is employed to neutralize sulfuric acid wastes. This results from the formation of insoluble calcium sulfate (gypsum). Use of dolomitic lime can ameliorate this problem, because of the increased solubility of magnesium sulfate relative to calcium sulfate. Because dolomitic limes are less reactive than high-calcium limes, longer reaction times would be required for their application. Neutralization of sulfuric acid wastes with limestone beds can lead to formation of gypsum scale on limestone particle surfaces, reducing the rate of neutralization and increasing head loss. An acid concentration of 5% and surface loading of 12 m per hr were given as upper loading limits for limestone beds treating sulfuric acid waste (Nemerow and Dasgupta 1991).

Reagent Quantities

Quantities of reagent required for the neutralization of sulfuric acid, hydrochloric acid, and nitric acid wastes are shown in Table 4. Use of liquid caustic soda (50% NaOH) requires the most reagent, followed by soda ash, limestone, hydrated limes, and quicklimes. Dolomitic limestone, hydrated lime, and quicklime require somewhat less reagent than the corresponding high-calcium forms because of the lighter atomic weight of magnesium in comparison to calcium.

Ferrous iron salts in acidic wastewaters tend to be oxidized and then form hydroxide precipitates when the pH is raised, for example:



As shown in Equation (8), precipitation of ferric hydroxide consumes alkalinity from the water. Consequently, neutralization of wastewaters from metal plating and ferrous industries can consume several times the amount of base that would be required to neutralize similar wastewaters not containing iron salts (Mac Dougall 1954; Anon. 1968).

Several alkaline wastes have been considered for neutralization of acidic wastewaters. Polat et al. (2002) evaluated coal fly ash as a neutralization/fixation agent for used engine oils. They noted that trace elements and organic components were efficiently fixed within fly ash particles. The neutralization capacity of steelmaking slag residues was examined by batch titration with sulfuric acid (Bodurtha and Brassard 2000). Neutralization profiles revealed two-phased kinetics, in which the free lime, magnesium and silicon oxides, and dicalcium ferrite dissolved almost completely within a few days, whereas weakly bound lime and magnesium oxides dissolved over a period of 10 to 80 days. Although the slag possessed the same neutralizing capacity as limestone, its slow dissolution kinetics and high cost of crushing decrease its attractiveness.

Neutralization of Acid Mine Drainage

The drainage from mines is often rich in sulfide minerals, which are oxidized on exposure to air. Acid resulting from the oxidation can lower the pH of the drainage waters to 2.0 or less (Mill 1972). In addition to high acidity, acid mine drainage typically contains high concentrations of sulfate, suspended solids, and heavy metals. These components are harmful to aquatic life and must be eliminated before drainage waters are released to the environment (Kuyucak 1998). Reagents and processes used for treatment of acid mine drainage are discussed in the following sections.

Lime

Neutralization with lime is widely used for treatment of acid mine drainage. This technology effectively decreases dissolved heavy metal concentrations to below regulated limits. Large quantities of sludge are produced, resulting from the precipitation of calcium sulfate and metal hydroxides and the removal of suspended solids. The sludges tend to have poor dewatering characteristics and often contain less than 5% solids by weight (Zinck and Aube 2000).

Limestone

A denser sludge is obtained with limestone, but this reagent is not effective above pH 6.5 because of its slow reactivity at pH values approaching neutrality. Cox (1998) evaluated the effectiveness of in situ limestone treatment of acid mine drainage. The buffering potential increased as aggregate size decreased, but decreased on repeat exposure to drainage. Cox concluded that limestone aggregate may be a control measure for acid mine drainage produced in spoil piles, tailing ponds, and other surficial settings. Ziemkiewicz et al. (1997) evaluated open limestone channels as a low-maintenance system for acid mine drainage. They found that limestone, after being coated with metal hydroxides (armored), was up to 90% as effective in neutralizing hydrochloric acid solution as unarmored limestone. Limestone channels were considered promising for watershed restoration projects and abandoned mine land reclamation projects that do not have to meet specific water quality goals. Anoxic limestone drains have been used for increasing the alkalinity of groundwater affected by acid mine drainage (Kuyucak 1998). Plastic and clay-soil covers are used to exclude air from seepage interception trenches that have been backfilled with crushed limestone. Because armoring of limestone is associated with oxidation of Fe^{2+} and formation of ferric oxyhydroxides, exclusion of air from limestone drains should improve their effectiveness and

extend their life. Precipitation of iron and other contaminants is usually achieved in a downstream wetland.

Ammonia

Anhydrous ammonia (NH_3) is a gas at ambient temperatures and is compressed and stored as a liquid. It dissolves readily when released into water, behaving as a strong base with peak buffering capacity at pH 9.2. Because of its high reactivity, ammonia may be considered as an alternative to caustic soda (Skousen et al. 1998). Several disadvantages are attendant to the use of ammonia, however. First, it is a hazardous material to handle. Second, because ammonia is toxic to aquatic biota, downstream concentrations must be carefully monitored. Third, oxidation of ammonia to nitrate produces acid and thus can cause pH problems downstream of the injection point. Finally, ammonia is a plant nutrient, both in its original form or as nitrate, and can promote eutrophication in downstream reservoirs or lakes or, ultimately, in the coastal ocean.

Biological Processes

Biological processes for treatment of acid mine drainage depend largely on sulfate-reducing bacteria to produce sulfides that precipitate heavy metals. Net consumption of protons in the reduction reactions tends to raise pH, leading to further precipitation of heavy metal oxyhydroxides and improving the bacterial growth environment. Organic matter required by the sulfate-reducing bacteria is provided by the decay of aquatic plants growing in the wetlands. Additional organic materials (e.g., straw, sawdust, wood shavings, and manure) may be added to supply nutrients to the bacteria, as well as supplemental organic matter (Kuyucak 1998). Passive reactive barriers for treatment of acid mine drainage may depend wholly or partially on sulfate-reducing bacteria. The key parameters of biological systems for treatment of acid mine drainage include temperature, availability of organic matter, loading, and pH. Biological activity depends strongly on temperature; for this reason, the design loading of these systems must take the local climate and seasonal temperature variations into account.

Alkaline Industrial Wastes

Co-mingling of cement kiln dust and red mud with acid-generating tailings was evaluated by Duchesne and Doye (2003). Static and column tests showed that near-neutral conditions were maintained in the fine material layers of mixtures containing 5% or 10% cement kiln dust or 10% of a combination of the two wastes. This significantly decreased concentrations of Al, Fe, Cu, Zn, and SO_4 relative to tailings only. Numbers of viable sulfide-oxidizing bacteria were also decreased.

Coal Combustion By-products

CCBs from processes that add lime or limestone for SO_2 control are good candidates for neutralization of acid mine drainage or mining wastes. Canty and Everett (2001) evaluated the suitability of CCBs for alkaline injection technology. FGD ash and fluidized bed ash had the highest contents of available alkalinity, whereas pulverized coal burner fly ash contained substantially less alkalinity. Toxic heavy metals were associated with all the CCBs. They were most difficult to leach from fluidized bed ash and least difficult to leach from the fly ash. Pozzolanic character is undesirable because it leads to formation of cementitious masses. Fluidized bed ash had the lowest pozzolanic character; fly ash had the highest. Thus, fluidized bed ash was considered most suitable for mine injection. Vondruska, Bednarik, and Sild (2001) used fluidized bed ash for the stabilization/solidification of ferrous sulfate waste generated from production of titanium dioxide. The pH of the waste was initially 1.9. After

mixing equal portions of waste and fluidized bed ash, the pH was raised to 6.5. Heavy metal concentrations in leachate from mixtures that were allowed to harden for 28 days were below detection limits. Zoumis, Calmano, and Förstner (2000) compared the neutralization and heavy metal removal capacity of fly ash, red mud, zeolite, calcium-bentonite, scale arrears, and pine bark. Fly ash and red mud had the highest acid neutralization capacities and gave the best heavy metal removals.

Zero-Valent Iron

Metallic (zero-valent) iron is a reducing agent relative to many redox-labile substances, including hydrogen ions, carbonate, sulfate, nitrate, and oxygen. Metallic anions and cations are reduced by iron in the absence of oxygen (Blowes et al. 2000). Net proton consumption is associated with the redox reactions. Wilkin and McNeil (2003) exposed heavy metal ions from salts of As(V), Ni, Cd, Cu(II), Hg(II), Mn (IV), and Zn to finely divided iron metal under oxygen-free conditions. They noted that the pH of synthetic acid mine drainage containing the heavy metal ions and zero-valent iron increased from initial values of 2.3–4.5 to final values of 5.5–10.0 in the first 24 hours of reaction. Between 1.4 and 225 $\mu\text{mol H}^+/\text{L}$ was consumed. Significant decreases in heavy metal concentrations, with the exception of Mn, paralleled acid neutralization. Remobilization of metals, if it occurred, was associated with exhaustion of acid-neutralization capacity of the iron. Monitoring data from a demonstration-scale permeable reactive barrier containing zero-valent iron showed that the pH of groundwater underwent a sharp increase in pH, from 5.5–6.5 to 9.5–11.0, when flowing through the barrier (Blowes et al. 2000). This was paralleled by an 8 mg per L decrease in Cr(VI) and a 15 to 120 mg per L decrease in SO_4 . The relative magnitudes of these concentration changes suggest that most of the proton consumption resulted from SO_4 reduction (Mayer 1999). Shokes and Möller (1999) noted that colloidal iron was more effective than granular iron in achieving pH increase and metal removal and further noted that sulfate-reducing bacterial populations benefited from the pH increase and contributed to metal removal through production of sulfides.

Acid Rain Mitigation

Combustion of sulfur-containing fuels such as coal and fuel oils produces SO_2 and lesser amounts of sulfur trioxide (SO_3), which are acidic gases (DOE 1999). Hydrochloric acid (HCl) is another product of combustion. SO_2 and HCl are eye and respiratory irritants and contribute to formation of acid rain. Acid neutralization reagents play an important role in decreasing emissions of SO_2 and other acidic gases by FGD. Application of alkaline materials to affected catchment basins is a promising approach to mitigating the effects of acid precipitation.

Calcium- or sodium-based sorbents are commonly employed to control acidic gases from combustion. These materials react with SO_2 and SO_3 to form sulfite and sulfate salts and neutralize HCl to sodium chloride and water. The sorbents can be injected in either dry or wet states. In dry sorbent injection, the dry sorbent is injected directly into the furnace or flue gas duct. There, the dry particles react with the acidic gases and are subsequently removed by particulate control devices. In wet FGD, the sorbent is dissolved in or slurried with water. The flue gas contacts the solution or slurry in a scrubber. Because of their low cost, limestone and lime are the most frequently used sorbents, accounting for more than 90% of U.S. FGD system capacity (DePriest and Gaikwad 2003).

Newton et al. (1996) reported the application of limestone on two tributary catchments to a small lake in the western Adirondack region of New York. Acid neutralizing capacity of the streams was

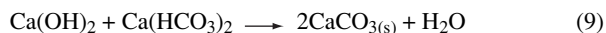
immediately increased as the result of the dissolution of calcite that fell directly into the stream channels and adjacent wetlands. Continued acid neutralization capacity over the next year was attributed to surface runoff and interflow from soil that had received limestone. Better results in one stream than in the other apparently resulted from more extensive wetlands. Sakamoto et al. (2001) considered the ash of coal-biomass briquettes as a source of alkalinity for mitigating the effect of acid rain on soils in the Chongqing City region of China. These briquettes are made using hydrated lime as a binder, and their ash is highly alkaline. Amending soil with 5% ash raised the pH of leachate from 5 to a range of 6.5–7.6. Leachate concentrations of copper were below the environmental standard for irrigation water, but chromium concentrations exceeded the standard during part of the experimental period.

Water and Water Treatment

Water Softening

High concentrations of calcium and magnesium ions in water can be troublesome. These ions tend to combine with soaps or detergents, forming an insoluble scum that stains laundered clothes. Calcium can precipitate with carbonate ions in water, forming deposits of hard scale inside of pipes that reduce flow capacity.

Removal of calcium and magnesium ions from water is called softening. One of the popular, large-scale methods for softening water is to add quicklime (after slaking) or hydrated lime. The lime is mixed with water to form a slurry, which is added to the water in a mixed reactor. Hydroxyl ions from the lime increase the hydroxyl ion activity (i.e., raise the pH) of the water. This converts bicarbonate ions in the water to carbonate ions, which precipitate with calcium. The overall reaction is



This reaction is limited by the concentration of bicarbonate ions in the water. In some cases, sodium carbonate is added along with lime to act as an additional source of carbonate ions. Sodium carbonate is also used as a water softener in laundry detergents.

Coagulant Aid for Removal of Clay Particles

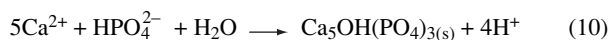
Micrometer-sized clay particles that are washed into surface waters by runoff are difficult to remove directly by separation processes such as sedimentation or granular media filtration. Hydrolyzing salts of aluminum or iron react in water to form aluminum or iron hydroxide complexes and precipitates that coagulate the clays. The resulting flocs settle much faster than the individual clay particles and can be economically removed from water by sedimentation.

Using the addition of ferric iron to water as an example, as shown previously in Equation (8), it is apparent that bicarbonate ions are consumed and CO_2 is produced by the hydrolysis of this metal in water. The same is true of trivalent aluminum. Decreasing the bicarbonate ion concentration and increasing the CO_2 concentration both tend to depress pH, particularly in surface waters having low initial alkalinity. Feeding of reagents such as lime along with the coagulant is therefore commonly required to maintain an appropriate pH range for the coagulation process.

Phosphorus Removal

Phosphorus, which occurs in the form of phosphates in natural systems, is an essential plant nutrient. Excessive phosphorus concentrations can stimulate the growth of microalgae and aquatic plants in surface waters, a process called eutrophication. In watersheds that are sensitive to phosphorus, wastewater dischargers may be required to remove phosphates from their treated effluents.

One of the methods used for removing phosphates from water is lime addition. This raises the pH of the water, converting H_2PO_4^- and HPO_4^{2-} ions to PO_4^{3-} . The phosphate ions, in turn, precipitate with calcium and hydroxyl ions, forming solid hydroxylapatite,



that can be collected as sludge. This reaction occurs simultaneously with the precipitation of calcium carbonate. Because calcium ions are typically present in much larger concentrations than phosphate ions, most of the sludge produced will consist of calcium carbonate.

Alkaline Stabilization of Municipal Wastewater Sludges (Biosolids)

Biosolids result from the treatment of municipal wastewater sludge to substantially decrease vector attraction potential and microbial pathogen content. Recycling of biosolids through land application is widely practiced in the United States and other parts of the world. One of the most popular methods for sludge treatment is lime addition. Addition of hydrated lime to sludge can create pH levels up to 12.4, which destroy harmful microbes and provide a vector attraction barrier. Use of quicklime, in addition to raising pH, also dehydrates the sludge and elevates its temperature, increasing the level of disinfection.

EPA regulations (2005) create two classes of biosolids, A and B. Class B biosolids contain pathogen levels that are low enough for application to agricultural land, providing that public access is restricted. Class B requirements can be met with lime by raising the pH of the biosolids to more than 12 for 2 hr and then maintaining the pH at 11.5 or higher for another 22 hr. Class A biosolids contain pathogen concentrations that are low enough to allow use with few restrictions. Examples include household gardens and nurseries, as well as agricultural land. To meet Class A requirements using lime, the Class B elevated pH requirements are combined with elevated temperatures (e.g., 70°C for 30 min) or other EPA-approved time/temperature processes.

Advantages of lime sludge stabilization are low capital costs and flexibility to produce either Class A or B biosolids. This treatment approach also effectively destroys odors caused by sulfur species such as sulfides and mercaptans (National Lime Association 2000). Ammonia, however, is volatilized through pH elevation, creating ammonia odors that must be controlled. The total quantity of solids for disposal is increased through alkaline stabilization (Oleszkiewicz and Mavinic 2001).

SUMMARY

The commonly used acid neutralization reagents include caustic soda, soda ash, lime, limestone, magnesia and magnesium hydroxide, and ammonia. In addition to their applications for neutralizing acidic wastewaters, including acid mine drainage, these reagents are also employed to soften water, clarify water and wastewater, remove phosphorus from effluents, condition and disinfect municipal wastewater sludges, and remove SO_2 and other acidic gases from combustion flue gases. Novel materials such as alkaline industrial wastes and zero-valent iron have been useful in passive systems for acid mine drainage control. Expanded consumption of the acid neutralization reagents will be needed to achieve environmental quality goals in the future.

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Asbestos Substitutes

Robert L. Virta

INTRODUCTION

Asbestos substitutes are materials that have properties similar to those of asbestos and are used to replace asbestos in manufactured products. Substitutes were used first in quantity in the 1970s when concerns first arose about adverse health effects of asbestos. To replace asbestos, a wide variety of substitutes have been developed that can be fibrous or nonfibrous, organic or inorganic, and natural or synthetic; each has its own unique physical and chemical properties. Lists of asbestos substitutes are given in Table 1 (fibrous and nonfibrous asbestos substitutes) and Table 2 (mineral and organic asbestos substitutes). In most products, asbestos substitutes have been used for a sufficiently long period of time so that they are now considered an integral part of the product and the term *asbestos substitute* is almost outdated.

Differing from asbestos substitutes, *alternative products* replace an entire asbestos-containing product rather than just the asbestos used within the product. For example, cast-iron and polyvinyl-chloride (PVC) pipes are alternative products that are used in place of asbestos-cement pipe.

HISTORY

Serious interest in asbestos substitutes developed during World War II because of possible disruptions of asbestos supplies for strategic wartime applications. In the United States, research focused primarily on using glass fiber and mineral wool. Because supply lines were not disrupted, the use of substitutes did not become critical to national security. The Germans, having been isolated from all asbestos sources during the war, expanded their investigations to include cellulose, glass wool, iron wire, plastics, steel wool, synthetic rubber, and treated paper as potential substitutes for asbestos (Bowles 1959). Serious interest in substitutes waned after World War II because of the large demand for asbestos-based construction materials in postwar Asia and Europe and the stockpiling of strategic grades of asbestos by the U. S. government in the late 1940s (Bowles 1959; Virta 2003).

After a 20-year hiatus, interest in marketing materials as asbestos substitutes returned in the 1970s. By this time, researchers had established a positive correlation between worker exposure to asbestos fibers and respiratory cancer diseases (Selikoff, Chu, and Hammond 1964; WHO 1986; Murray 1990). Companies that mined asbestos, manufactured asbestos products, and eventually installed or used asbestos products began to face an increasing

Table 1. Asbestos substitutes

Acicular to Fibrous Morphology [*]	Nonfibrous Morphology
Aramid fiber[†]	Biotite
Carbon fiber	Calcium carbonate
Cellulose fiber	Calcium silicate
Ceramic fiber	Diatomite
Fiberglass	Fibrillated polypropylene (PP)
Mineral wool	Graphite
Nylon fiber	Muscovite
Palygorskite (attapulgite)	Perlite
Polyacrylonitrile (PAN) fiber	Serpentine
Polybenzimidazole (PBI) fiber	Silica
Polyethylene (PE) fiber	Talc
PP fiber	Vermiculite
Polytetrafluoroethylene (PTFE) fiber	
Polyvinyl alcohol (PVA) fiber	
Potassium titanate fiber	
Sepiolite	
Steel fiber	
Wollastonite	
Wool	

Source: EPA 1980, 1988; Hodgson 1985, 1989; Harrison et al. 1999.

^{*} Dependent on material; for example, wollastonite is acicular, palygorskite (attapulgite) is fibrous, and PTFE can be manufactured in nonfibrous or fiber shapes.

[†] Materials in bold type are more commonly used asbestos substitutes.

number of class-action lawsuits (Butler 2002; White 2002). Public opposition to the use of asbestos also hastened the removal of asbestos from commercial products. As a result, there was a sharp decline in asbestos use, beginning in the 1970s, that was balanced by research for and an increasing use of asbestos substitutes or alternative products (Virta 2003).

PRODUCTION AND MARKETS

U.S. Production

Data on the production and consumption of asbestos substitutes are not available. Substitute materials, such as cellulose, fiberglass,

Table 2. Mineral and organic asbestos substitutes

Mineral	Organic
Biotite	Aramid
Calcium carbonate	Cellulose
Diatomite	Nylon
Graphite	PAN
Muscovite	PBI
Polygorskite (attapulgite)	PE
Perlite	PP
Sepiolite	PTFE
Serpentine	PVA
Silica	Wool
Talc	
Vermiculite	
Wollastonite	

Source: EPA 1980, 1988; Hodgson 1985, 1989; Harrison et al. 1999.

sepiolite, and wollastonite, and alternative products, such as corrugated aluminum sheet, ductile-iron pipe, metallic brakes, and wood siding, were in use before the asbestos health issue arose. Sales statistics by industries manufacturing these materials generally did not indicate if increases in sales after the early 1970s resulted from expansion of existing markets or the opening of new markets for asbestos substitutes. The wide number of substitutes and alternative products available and the many different formulations for products further complicate the estimation process. The magnitude of overall substitute use, however, can be estimated by examining data on asbestos production and consumption (a full review of asbestos data is given in the Asbestos chapter in this book).

Apparent U.S. consumption of asbestos increased through the 20th century to a peak of about 800,000 t in 1973 (Buckingham and Virta 2002; Virta 2003). In 2003, apparent U.S. consumption was 5,000 t (Virta 2004), suggesting that asbestos substitutes and alternative products in the United States replaced sales of roughly 795,000 tpy of asbestos. If it were not for the health issue, expansion of most asbestos markets probably would have continued beyond the early 1970s, with the possible exception of asbestos for automotive brake manufacture. The downsizing of automobiles in North America and the introduction of front-wheel drive in the 1970s resulted in the increased use of semimetallic disk brake pads and non-asbestos organic brakes, both of which did not require asbestos in their formulations (Brunhofer, Aldrich, and Jacko 1980; Jacko and Rhee 1992). This occurred as asbestos usage began to fall out of favor, so it is difficult to assess the exact impact. At a minimum, the shift to brakes that used less asbestos would have slowed growth of asbestos sales in the friction products sector. In general, though, the sharp decline in U.S. sales of asbestos for asbestos-cement pipe and sheet, electrical and thermal insulations, flooring, friction products, packings, plastics, and textiles after 1973 suggests that the asbestos health issue, rather than changing technology, was the most significant contributing factor to the increased use of asbestos substitutes and alternative products.

U.S. Markets

Markets for asbestos substitutes include cement products, coatings and compounds, flooring, friction products, gaskets and packing, insulation, roofing, textiles, and a variety of small-tonnage applications. Estimates can be made for individual U.S. market losses for asbestos and corresponding gains for substitutes and alternative products by using the breakout of U.S. asbestos consumption during

the peak consumption year, 1973, as a guide. In that year, manufacturing used the following amounts of asbestos (Clifton 1975):

- Flooring products—198,000 t
- Unknown or miscellaneous applications—roughly 158,000
- Asbestos-cement pipe—151,000 t
- Roofing products—79,000 t
- Friction products—72,000 t
- Asbestos-cement sheet—58,000 t
- Packings and gaskets—24,000 t
- Insulation—23,000 t
- Asbestos paper products—16,000 t
- Textiles—16,000 t

Under the “unknown” category, an estimated 35,000 t to 40,000 t was probably sold for coatings and compounds. In 2003, the breakout of asbestos consumption was about 1,170 t for coatings and compounds, 2,800 t for roofing products, and 678 t for unknown or miscellaneous products (Virta 2003). These figures represent 30- to 200-fold declines in asbestos use for coatings, roofing, and other uses, and a complete loss of sales for other manufacturing sectors between 1973 and 2003. For all categories, asbestos substitutes or alternative products have replaced most, if not all, types of asbestos.

World Production

Although data on the worldwide use of asbestos substitutes are not available, the impact of the asbestos health issue appears to have occurred at a slightly slower pace outside the United States. World asbestos consumption (assumed to be equal to production until about 1998) peaked around 1975, 2 years after peak consumption in the United States. In 1975, world asbestos production (consumption) was estimated to be about 5.09 Mt, but by 2002, it had declined to 2.13 Mt. Based on trade balance calculations for 2000, asbestos consumption in 2002 was estimated to be less than 2.0 Mt, suggesting that the use of asbestos substitutes and alternative products had reduced annual world consumption of asbestos by at least 3 Mtpy, or 59% since 1975 (British Geological Survey 2002; Virta 2003).

World Markets

Individual markets for substitutes outside of the United States also are not well documented in most countries. Use of asbestos for construction activities (primarily asbestos-cement products but also including caulks, insulation, putties, roofing, sealants, stucco, tiles, etc.) was estimated to be 3.55 Mt in 1974 and 3.83 Mt in 1988. Use in friction products (brakes and clutches) was 310,000 t in 1974 and 152,000 t in 1988. Other uses were 560,000 t in 1974 and 338,000 t in 1988 (Roskill Information Services Ltd. 1990). Based on these estimates, the quantity of asbestos used in friction products and other applications declined 44% between 1974 and 1988 worldwide. Use of asbestos in construction applications, however, increased slightly over this same time period, with overall market share increasing from 80% to 89%. A major contributing factor to the popularity of asbestos-cement products is their cost-effectiveness (Institute for Environment and Health 2000). In 2000 asbestos-cement products were estimated to account for more than 98% of world asbestos consumption, or about 2.0 Mt (Virta 2003). Despite this increase in market share, sales of asbestos for cement products have declined more than 1.7 Mt since 1988, due to the use of asbestos substitutes and alternative products.

Substitutes and Alternative Products

The development of asbestos substitutes and products was accomplished primarily through two methods: the expansion of markets

Table 3. Examples of alternative products

Asbestos-cement pipe	Ductile-iron pipe
	PVC pipe
	Prestressed concrete
	Reinforced concrete pipe
Asbestos-cement sheet and shingles	Aluminum siding
	Cement sheet
	Corrugated aluminum sheet
	Corrugated fiberglass sheet
	Corrugated PVC sheet
	Corrugated steel sheet
	Vinyl siding
Coatings and pipeline wrap	Wood siding and shakes
	Asphalt coatings
	PE films
Floor covering	Urethane tape
	Carpeting
	Dimension stone tile
	Quarry tile
	Vinyl flooring and tile
Friction products	Wood floor
	Metal-bonded ceramic compositions or sintered brakes
	Nonasbestos organic
Packings and gaskets	Semimetallic disk brakes
	Copper, cork, expanded graphite, glass fiber, natural rubber, PBI, PTFE
Roofing	Single-ply membranes

Source: EPA 1980, 1988; Hodgson 1985, 1989; Roskill Information Services Ltd. 1990; Harrison et al. 1999.

of existing products to fill the void left by declining asbestos consumption; and direct substitution of asbestos in former asbestos-based products (Meylan et al. 1978; EPA 1980, 1988; Hodgson 1985; Roskill Information Services Ltd. 1990; Harrison et al. 1999; see Tables 1, 2, 3, and 4). Examples of substitutes include cellulose, fiberglass, PAN fibers, PE fiber, and PVA fibers. Examples of alternative products are ductile-iron pipe, PVC pipe, prestressed concrete, and reinforced concrete pipe (Hodgson 1985; Roskill Information Services Ltd. 1990; Harrison et al. 1999).

Rate of Substitution for Asbestos

Asbestos Substitutes

Although the use of alternative products was readily accepted, the direct replacement of asbestos in products was a more gradual process, because the suitability of the substitutes had to be evaluated prior to their extensive use in any given product. Cost, longevity, performance, and potential health risks were critical factors to consider (Hodgson 1985). The difficulty of replacing asbestos varied for different markets. Of the major U.S. asbestos markets, the rate of asbestos replacement has been much slower for brake markets than for most other products. In 1983, 10 years after peak U.S. asbestos consumption, sales of asbestos for friction products had declined only 33% compared with decreases of more than 75% for other major U.S. end-use markets. Engineers had to overcome problems with glazing of brake surfaces that reduced stopping performance; different heat-resistance characteristics of the substitutes; and moisture absorption that reduced stopping performance until the brakes were applied a sufficient number of times to dry

Table 4. Examples of asbestos substitutes and alternative products

Asbestos-cement pipe	Cellulose fibers, ductile iron, fiberglass, mica, PAN and PVA fiber, PVC pipe, prestressed concrete, reinforced concrete pipe, wollastonite
Asbestos-cement sheet	Aluminum siding, cellulose fibers, corrugated fiberglass panels, corrugated PVC panel, fiberglass, fibrillated PP, PAN and PVA fiber, vinyl siding, wood
Coatings and compounds	Aramid fiber, carbon fiber, cellulose fiber, clay, fiberglass, PE films, limestone, rubber membrane roofing, mica, PE fiber, PP fiber, talc, wollastonite
Flooring	Carpeting, ceramic tile, clay, fiberglass, PE pulp, silica, talc, vinyl compositions, wood
Friction	Aramid fibers, cellulose, ceramic fiber, fiberglass, metal (i.e., brass, bronze, copper, and iron) fibers, palygorskite (attapulgite), PAN fiber, potassium titanate, semimetallic brakes, sepiolite, steel fibers, vermiculite, wollastonite
Insulation	Calcium silicate board, cement board, ceramic fiber, fiberglass, mica, mineral wool, vermiculite
Packings and gaskets	Aramid fiber, carbon fiber, cellulose fiber, ceramic fiber, cork, fiberglass, graphite, mica, metal gaskets, mineral wool, PTFE, rubber sheeting
Paper and paperboard	Ceramic fiber, cellulose, fiberglass, mica, PTFE, vermiculite, wollastonite
Pipe wrap	Nonfibrous minerals, plastic coatings, urethane coatings
Plastics	Aramid fiber, carbon fiber, fiberglass, fumed silica powder, mica, PTFE, potassium titanate, wollastonite
Tape	Carbon-based tape, cellulose, urethane tape
Textile	Aramid fiber, carbon fiber, ceramic fiber, fiberglass, mineral wool, PBI fiber

Source: EPA 1980, 1988; Hodgson 1985, 1989; Roskill Information Services Ltd. 1990; Harrison et al. 1999.

out. There also was brake pad or shoe vibration, which caused “shuddering” of the brake when applied, and rapid wear of many of the early asbestos substitute brakes that manufacturers had to eliminate through design modifications (Lam and Yesnik 1998).

Alternative Products

The rate of replacement depended on the market. In the United States in 1975, cast-iron pipe comprised 75% (by mileage) of water main pipe in place; asbestos-cement pipe, 13%; steel pipe, 6%; reinforced concrete pipe, 2%; plastic pipe, 1%; and other types of pipe, 3%. With sewer mains, the distribution was 67% vitrified clay pipe; 16% reinforced concrete; 5% asbestos-cement pipe; 3% cast-iron pipe; 2% plastic pipe; and 7% other (EPA 1980). The transition to alternative pipe products and cellulose or polymer fiber-reinforced pipe involved only a small portion of the total U.S. water main and sewer pipe markets. This contrasted with the resilient flooring market, where asbestos products accounted for 91% of sales in 1975, and friction product markets, where most brakes were asbestos-based prior to the middle 1970s (Wright 1978; Jacko and Rhee 1992).

PRICES

Prices for asbestos substitutes vary considerably. Mineral substitutes are less expensive than more process-intensive synthetic fibers. Because of the additional processing, substitutes that have been surface treated will sell for a higher value than untreated substitutes. Also, substitutes having narrower specification ranges generally will be more expensive. Average prices for mineral substitutes and synthetic substitutes are listed in Tables 5 and 6, respectively. These

Table 5. Prices for asbestos and mineral substitutes for asbestos, US\$/t

Canadian chrysotile, Group 3	1,030–1,244
Canadian chrysotile, Group 4	710–995
Canadian chrysotile, Group 5	472–655
Canadian chrysotile, Group 6	293–420
Canadian chrysotile, Group 7	144–300
Calcium carbonate, filler	80–200
Diatomite, filler	329 (average)
Graphite	230–750
Mica, ground	200–465
Palygorskite (attapulgitite)	110 (average)
Perlite, filler	410 (average)
Sepiolite, micronized	600 (average)
Silica, ground filler	83 (average)
Talc, filler grade	150–300
Vermiculite, exfoliated	390 (average)
Wollastonite, acicular	170–400

Source: USGS *Minerals Yearbook* (for average prices in 2001 or 2002 when available); *Industrial Minerals* 2002; Geo.net Commodities GmbH 2003; *Rubber World* 2003.

Table 6. Prices for synthetic fibers, US\$/kg

Aramid fiber	9.33–66
Carbon fiber	15.70–73.16
Cellulose fiber	0.19–0.31
Ceramic fiber	1.68–42.71
Glass fiber, E glass	1.12–13.49
Glass fiber, S glass	0.74–36.60
Mineral wool	0.56
Nylon	1.12–2.24
Synthetic organic (PE, PVA, PP, PAN)	0.99–3.15
PBI	33.72–154
Steel fiber	1.35–1.80

Source: Hodgson 1985, 1989; *Chemical and Engineering News* 1994; *Rubber World* 2003; *Chemical Market Reporter* 2004; *Industrial Textiles Association* 2004; *Netcomposites* 2004.

should be used only as a guideline, because prices are negotiated between seller and buyer according to lot size, frequency of purchase, fiber availability, production costs, and so forth.

TYPES OF ASBESTOS SUBSTITUTES

Fibrous substitutes include mineral and organic fibers such as palygorskite (attapulgitite), sepiolite, acicular wollastonite, and PP fibers. Non fibrous substitutes are minerals, mineral groups, or rocks such as diatomite, mica, perlite, serpentine, silica, and talc (Table 1). The natural substitutes encompass minerals and a limited number of organic materials such as cellulose and wool. Synthetic substitutes include fiberglass, mineral wool, synthetic gypsum fibers, synthetic wollastonite, and various polymer fibers (Meylan et al. 1978; Hodgson 1985; EPA 1988; Harrison et al. 1999; Institute for Environment and Health 2000.)

The diversity of materials required to replace asbestos reflects its versatility. To understand what is required of an asbestos substitute, it is best to examine the properties of asbestos. These are fully discussed in the Asbestos chapter in this book.

Table 7. Properties imparted to products by asbestos substitutes

Application	Important Properties
Cement pipe	High green strength, good tensile strength, resists alkali attack, high impact strength, drains well during manufacture, heat resistant
Cement sheet	High tensile strength, heat resistant, resists chemical attack, resists rot and corrosion, and nonflammable
Coatings and compounds	High viscosity, resists sagging, reduced oxidation and deterioration, low cost, thixotropic, heat resistant, resistant to chemical attack
Friction products	Heat resistant, low heat conductivity, durable, low cost
Insulation	Heat resistant, low heat conductivity, durable, low cost, does not deteriorate under exposure to water
Packing and gaskets	Flexible, heat resistant, does not deteriorate under pressure, corrosion resistant, resists chemical attack, low thermal conductivity, tear resistant, dimensionally stable, resists crushing
Paper	Resists chemical attack, dimensionally stable, heat resistant, resists rot and corrosion, nonflammable, high tensile strength, relative low price
Plastics	Heat resistant, increased stiffness, improved dielectric strength, easy processing
Roofing	High viscosity, resists sagging, reduced oxidation and deterioration, low cost, thixotropic
Textiles	Heat resistant, flexible, durable, resists chemical attack, low thermal conductivity, high electrical resistance

Source: Rosato 1959; Sindair 1959; EPA 1980, 1988; Hodgson 1985; Roskill Information Services Ltd. 1990; Harrison et al. 1999; Institute for Environment and Health 2000.

Asbestos Substitutes

Asbestos substitutes are chosen according to their individual properties, how the substitute affects the manufacturing process, and whether the properties imparted to the final product by the substitute make it competitive in cost and performance with other products (Hodgson 1985; Pye 1989). The ideal substitute would serve the same function in commercial products as asbestos (Table 7).

Minerals and Rocks

Minerals and rocks that have been used in place of asbestos include biotite, diatomite, graphite, muscovite, palygorskite (attapulgitite), perlite, serpentine, silica, talc, vermiculite, and wollastonite. The mineral substitutes are chosen for chemical inertness, fibrosity or platyness, flexibility, hardness, heat conductance, reinforcing properties, thermal stability, and/or thixotropic properties (Table 8). Only a small number of the substitutes possess more than a few of these characteristics. For example, diatomite, perlite, and vermiculite do not physically resemble asbestos, but they are used as substitutes because of their thermal stability (Hodgson 1985, 1989; *Industrial Minerals* 1987). In many cases, these minerals were competitors with asbestos before the asbestos health issue arose. As public opposition to the use of asbestos grew, the use of these minerals expanded as they displaced asbestos. It was only then that they became asbestos substitutes. The use of perlite and vermiculite in heat-insulating board and cement products are good examples of competing minerals that began to replace asbestos after concern arose about health issues (Hodgson 1985; Benbow 1987; Kendall 2000).

Sheet Silicates. Muscovite, serpentine, and vermiculite are sheet silicates and have a platy morphology (Deere, Howie, and

Table 8. Selected properties of mineral substitutes

	Density, g/cm ³	Mohs Hardness	Service Temperature Limits,* °C	Particle Shape	Surface Area, [†] m ² /g	pH of Suspension
Calcium carbonate	2.7–2.9	3–4	1,150	Irregular	5–25	9.0–9.5
Diatomite	2.0–2.5	4.5–5.0	1,400	Platy to needlelike	0.7–180.0	6.5–10
Graphite	2.0–2.5	1–2	na [‡]	Platy	6.5–20.0	na
Kaolin	2.58–2.62	2	1,800	Platy	8–65	na
Mica	2.75–3.20	2.5–4.0	1,100	Platy	30	6.5–8.5
Palygorskite (attapulgitite)	2.3–2.4	1–2	800	Fibrous	120–400	6.5–9.5
Perlite	1.2–2.4	5.5	760–1,300	Irregular	1.9	5.5–8.5
Sepiolite	2.0–2.3	2.0–2.5	1,550	Fibrous	240–310	na
Silica	2.65	7	1,450	Irregular	50–400	6.8–7.2
Talc	2.70–2.85	1.0–1.5	950–1,000	Platy	2.6–35.0	8.70–10.6
Vermiculite	2.6	2.1–2.8	800–900	Platy	na	7
Wollastonite	2.85–2.90	4.5	1,540	Acicular	0.4–5.0	9.8–10.0

Source: Hodgson 1985; Cui 1996; Wypych 1999.

* Service temperature for minerals and of products containing minerals is lower.

† Surface area dependent on the degree of grinding of product for most minerals.

‡ na = not available.

Zussman 1966). The platy shape of these minerals provides a large contact area between the particle and the matrix, improving the flexural, impact, and tensile strengths of the product (Trivedi and Hagemeyer 1994). In general, platy minerals do not provide the same degree of reinforcement as asbestos in the product because they are not fibrous. The sheet silicates used as asbestos substitutes are thermally stable at moderate temperatures. At low to moderate temperatures, they lose adsorbed and structural water but do not begin to decompose until temperatures exceed approximately 800°C, with melting points well above 1,000°C (Hodgson 1985). Operating temperatures for products containing these and other minerals are below the melting temperatures of the individual minerals. For example, the working temperature of a nonasbestos high-temperature insulating board product containing talc is about 815°C, below the temperature of 950°C at which talc alters to enstatite and quartz (Cavicchio 1981).

Vermiculite has an advantage over other sheet silicates in that it exfoliates (the individual sheets separate) when heated rapidly to 900°C. The exfoliated product is stable at moderate to high temperatures. Exfoliated vermiculite is an excellent thermal insulator because of the large amount of void spaces in the expanded platelets (Hodgson 1985). Fire ratings above 900°C are reported for some vermiculite products. One company found that working temperatures of glass fiber products that have been coated with chemically delaminated vermiculite increased from 550°C to more than 900°C (Benbow 1987).

As a competitor and also a substitute for asbestos, vermiculite is used as loose-fill insulation and spray-on insulation. It also is used to produce insulation board, fire-resistant plasterboard, and as an additive in cements (Meisinger 1985; Benbow 1987; Hindman 1994).

Mica is used to a much lesser extent as a substitute for asbestos. Its platy morphology and thermal stability enable it to be used primarily in insulating board. Because it is not as effective a reinforcer as asbestos, it is usually supplemented with fibrous additives such as cellulose and fiberglass in substitute applications (Hodgson 1985; Benbow 1987). Mica may be used in brakes as a nonfibrous reinforcer (Jacko and Rhee 1992).

Talc has been used in gaskets, insulating board, and vinyl tile, but its primary use is as a component among many inorganic types

of filler and not as a direct substitute for asbestos (Cavicchio 1981; Hanson and Smith 1981; Lindeman and Andrew 1982).

Lizardite, a form of serpentine, is a sheet silicate with the same composition and many of the same physical properties as chrysotile. It is abrasive, resists chemical attack, and is thermally stable. Lizardite is promoted as a replacement for asbestos in brake pads, insulating board, and a variety of other products (Hedman Resources Ltd. 2004). As with the other sheet silicates, lizardite would not be a direct replacement for asbestos because it is not fibrous.

All of the platy minerals are as resistant to chemical attack as asbestos (Wypych 1999). These minerals are competitively priced with most grades of chrysotile (Table 5) and are widely available (see the individual mineral chapters in this book for details on production and availability of these and other mineral substitutes).

Clays. Palygorskite (attapulgitite) and sepiolite are clay minerals. They are also sheet silicates, but rather than being platy, they have a lath-like structure that is fibrous in appearance (Grim 1968; Hodgson 1985). They are moderately good reinforcers because their fibrous morphology gives them a large surface area, although the fibers are not as long as those of asbestos. Palygorskite and sepiolite lose water from their structures when heated to moderate temperatures (350°C to 600°C) and convert to clinoenstatite above 800°C (Hodgson 1985). They have long been used in products such as caulk, grease, joint compounds, paints, and stucco (Russell 1991). Before asbestos fell out of favor, both competed with asbestos as thixotropic agents and reinforcers. Palygorskite (attapulgitite) has been used as a direct substitute for asbestos in asphalt compounds (Clarke 1985; Russell 1991), while sepiolite is used as a direct replacement for asbestos in some joint compounds (Russell 1991). Research on their use as a replacement in brakes, cement pipe products, and vinyl tile also has been undertaken in the past (Hodgson 1985). Palygorskite and sepiolite are competitively priced with most grades of chrysotile (Table 5) and are widely available.

Graphite. Graphite is a platy mineral composed of carbon (Deere, Howie, and Zussman 1966) and is an excellent nonabrasive lubricant. It is stable at high temperatures, makes excellent packing in its expanded form, and is resistant to chemical attack (EPA 1980; Taylor 1994). Generally mentioned only as a substitute for asbestos

in valve packing applications (Meylan et al. 1978; Parkinson 1986a, 1986b; EPA 1988), graphite is priced competitively with chrysotile (Table 5). Adequate supplies of graphite are available to meet demand for asbestos substitute applications.

Wollastonite. Wollastonite is a single-chain silicate called a pyroxenoid. Stable at temperatures up to 1,540°C (Deere, Howie, and Zussman 1966; Hodgson 1985), it often occurs in a fibrous habit; however, its fibers are not flexible like chrysotile fibers. Wollastonite is fairly resistant to chemical attack but is soluble in strong acids (Hodgson 1985; Bauer, Copeland, and Santini 1994). As with mica and vermiculite, products manufactured with wollastonite are stable at temperatures lower than its melting point. For example, insulation boards containing wollastonite can be used up to temperatures of about 760°C, although wollastonite is stable up to about 1,500°C (Bolger 1998). Priced competitively with asbestos (Table 5), it is already used commercially, so availability is not an issue (Patton 1973; Ciullo 1996; Wypych 1999).

During the 1970s and 1980s, consumption of wollastonite was reported to have doubled for asbestos substitute applications. By 1994, consumption of high-aspect-ratio wollastonite was estimated to be between 35,000 t and 40,000 t for substitute uses. It primarily replaces asbestos in aluminum and asphalt roof coatings, cement board, friction products (brakes), and insulation boards. Wollastonite is used to improve the flexural strength of cement; improve the friction coefficient, green strength, and heat dissipation in brakes; and improve flexural and tensile strengths and heat resistance in insulation board (Fattah 1994). It also improves the tensile strength and the thermal stability of polymers and improves the mechanical strength of paint films (Bolger 1998).

Gypsum. A naturally hydrated calcium sulfate, gypsum also can be synthesized easily in a partially hydrated or anhydrous form. In its partially hydrated form, it is called hemihydrate calcium sulfate, while the anhydrous form is called anhydrite (Jorgensen 1994). In the past, a gypsum fiber product consisting of long, strong, and thin fibers that exhibited good reinforcing properties was used. The fibers were nonabrasive, stable up to a temperature of 1,000°C, and stable in mild acids and bases (Virta 1994). These fibers no longer appear to be available on the market, and their manufacture is believed to have ceased.

Diatomite and Perlite. Two other materials discussed as asbestos substitutes are rocks rather than minerals: diatomite and perlite. Diatomite is a rock composed of amorphous silica shells of diatoms, which are microscopic plants. These skeletal remains range from equidimensional to disk shaped to rod-like, depending on the species. Diatomite has a large surface area, low density, and is stable up to temperatures greater than 1,400 °C (Hodgson 1985; Breese 1994). Because diatomite was used as a filler and extender and in thermal insulations before the asbestos health issue arose, it was first a competitor with asbestos rather than a substitute. Major uses as a substitute are in insulation applications, often in combination with a fibrous reinforcing material such as asbestos (now obsolete), fiberglass, and mineral wool (Hodgson 1985). It has been used as inert filler in non asbestos brakes and millboard (Cavicchio 1981; Lam and Yesnik 1998). Diatomite is priced competitively with chrysotile (Table 5) and is widely available.

Perlite is an amorphous or glassy volcanic rock with a high silica content. When heated, it expands into glassy foam. Perlite has a low density, is chemically inert, and is an excellent thermal insulator (Hodgson 1985; Breese and Barker 1994). Like diatomite, perlite already was used as an insulator (loose fill, pipe insulation, and roof insulation board) and in acoustical tile, concrete, and plaster before health concerns about asbestos became an issue (Hodgson 1985; Breese and Barker 1994). It also has been used as a

substitute for asbestos for filtering liquids (Pye 1989). Because perlite is not fibrous, it often is used in conjunction with fibrous materials in insulation panels (Hodgson 1985). Perlite is competitively priced with chrysotile (Table 5) and widely available.

Organic Substitutes

Organic substitutes are either natural or synthetic. The natural fiber substitutes are animal, vegetable, and wood. Animal fiber normally refers to wool. Vegetable fiber is derived from the bark and leaves of plants such as flax, hemp, jute, and ramie. Wood fiber is obtained by chemically and/or thermally processing wood pulp (Hodgson 1985; Barkalow and Whistler 2000).

Cellulose. Because cellulose is fibrous, it is used to improve tensile strength of many products. An organic material, cellulose has a low density, almost half that of asbestos (Wypych 1999). Cellulose fibers are resistant to alkaline attack and disperse well in suspensions, but they have a lower tensile strength than asbestos, are flammable, and absorb more water than asbestos during manufacturing (Hodgson 1985, 1989).

As early as the 1950s, cellulose was used in combination with asbestos in partition boards and cement products (Hodgson 1985). Cellulose-based roofing felts have long competed with asbestos roofing felts (EPA 1988). As an asbestos substitute, cellulose use has expanded to include adhesives, asphalt compounds, caulking, cement board products, friction products, gaskets, and millboard (Cavicchio 1981; EPA 1988; Annemaier and Graf 1996; Hagens 2003; Merkley and Luo 2004). Cellulose fiber is readily available worldwide, and prices are competitive with those of asbestos (Table 6).

Other Cellulose Fibers. Bamboo fiber, hemp, jute, and sisal are vegetable fibers that have been considered for use in place of asbestos. Their properties are not significantly different from those of cellulose. Because of the wide availability of cellulose derived from wood fiber, however, the use of bamboo, hemp, jute, and sisal fibers as asbestos substitutes is limited (Hodgson 1985, 1989).

Wool. Wool, which is fibrous and can be woven, is the only animal fiber used as an asbestos substitute. It is a good thermal insulator and can withstand short-term exposures to high temperatures without burning. Wool's heat resistance can be enhanced with an aluminized coating. It is widely available but has been used in only a few substitute applications such as heat-resistant textiles (Hodgson 1985, 1989).

Polymer Fiber. Many different types of synthetic or organic materials are used as asbestos substitutes. Organic-based substitutes include fibers composed of polyamide (PA; including aramid and nylon), PAN, PBI, PE, polyester (PT), PP, PVA, and PTFE fiber and sheet (EPA 1980, 1988; Hodgson 1985, 1989; *Materials Engineering* 1987; Harrison et al. 1999; Institute for Environment and Health 2000). These are all polymers or plastics consisting of long-chain organic molecules. Another organic-based substitute is a fiber composed of graphitized carbon (Hodgson 1989; Wypych 1999; Block 2002).

Most polymers are recognized by their commercial names. Kevlar or Nomex are trade names for aramid fibers, which are used to make products such as fire-resistant textiles and bulletproof vests (Hodgson 1985; *Materials Engineering* 1987; Wypych 1999). Nylon is a synthetic fiber used in clothing, while PP is a polymer used to produce building and household materials such as drainpipe, plastic outdoor furniture, and siding. PVA fibers are used in textiles and carpet fibers, and Teflon is an example of a PTFE fiber (Wypych 1999; Block 2002; Carraher 2004).

Most polymer-based substitutes are used to improve flexural and tensile strengths of products when incorporated as fibers. The

Table 9. Selected properties of synthetic substitutes

Type	Density, g/cm ³	Typical Service Temperatures, °C	Thermal Degradation, °C	Tensile Strength, MPa	Young's Modulus, Gpa	Elongation to Break, %
Aramid fiber	1.44–1.45	160–230*	265–425	572–2,790	59–124	2.4–4
Carbon fiber	1.76–1.99	520–3,550	na†	345–4,900	21–550	1–2
Cellulose fiber	1–1.1	200	450	125–500	na	3–30
Glass fiber	2.52–2.68	537–565	na	686–3,400	68–98	4
Mineral wool	2.7	537	na	540–980	68–98	na
PE fiber	0.96–1.0	100	130	290–570	1.7–100	5
PVA fiber	1.3	150	220	690–1,470	12–40	7
PP fiber	0.91	100	170	270–540	1.6–4.8	14–30
PBI fiber	1.43	300	500	380	5.72	30
PAN fiber	1.16	150–200	260–300	230–940	16.5–18	na
PTFE fiber	2.15	200	270–370	97–359	1.31–2.48	400
Potassium titanate	3.3	na	1,350	7,000	na	na
Refractory fiber	1.9–4.84	560–1,800	na	1,400–5,900	72–480	na

Source: Patton 1973; Hodgson 1985; Wypych 1999.

* Fibers may char without losing significant physical characteristics.

† na = not available.

tensile strength of polymer fiber is dependent on the composition and structure of the organic material. Aramid fibers are among the strongest of the organic fibers, approaching the tensile strength of asbestos, and are thermally stable (Hodgson 1985, 1989; EPA 1988). The use of PA, PAN, PE, PT, PP, PVA, and PTFE is limited to situations where temperatures generally do not exceed 200°C. PBI and some forms of PA are thermally stable to about 300°C, although all polymers will begin to soften or char at higher temperatures (Hodgson 1989). All of the organic-based substitutes have low densities. For a given fiber loading, a smaller mass of organic fiber is required than with asbestos (Table 9). Polymers such as PE, PP, and PTFE are resistant to attack by many acids and bases (Hodgson 1989; Institute for Environment and Health 2000). Polymer fibers, which cost more than asbestos, are generally available in sufficient quantities to permit wide-scale use (Hodgson 1985; see Table 6).

Carbon Fiber. Although carbon fiber has a composition identical to graphite, it is a synthesized fibrous material. Certain varieties have an extremely high tensile strength and are excellent additives to improve mechanical strength. Additionally, carbon fiber can be woven and molded into intricate shapes. All varieties are good electrical conductors and can be used at temperatures approaching 3,000°C in inert atmospheres (Hodgson 1985, 1989; Wypych 1999; AZoM.com 2004; see Table 9). Although carbon fibers are readily available, they are more expensive than asbestos (Hodgson 1989; see Table 6).

Nonfibrous Polymer Substitutes. Manufacturers also have investigated the use of nonfibrous organic-based substitutes in some applications. Because they have the same compositions as the fibrous organic materials, they have the same properties. The nonfibrous organics generally are developed for specific end-use markets. Modified PP sheet for use in asbestos-cement sheet and shaped PTFE parts for gaskets are two examples of nonfibrous organic-based substitutes. The nonfibrous materials are widely available (EPA 1980, 1988; Hodgson 1989; *Materials Engineering* 1987; Harrison et al. 1999).

Synthetic Inorganic Substitutes. Fiberglass, mineral wool, and ceramic (refractory) fibers have been used as a replacement for and competitor with asbestos for many years (Meylan et al. 1978;

EPA 1988; Hodgson 1989; Harrison et al. 1999; Institute for Environment and Health 2000). All of these forms are fibrous, with diameters generally ranging from 1 µm to approximately 25 µm. Most forms of fiberglass and mineral wool have relatively low tensile strengths although strengths are greater for specialty fiberglass products (Hodgson 1989; Wypych 1999). A large number of the fiberglass varieties can be woven. Ceramic fibers have higher tensile strengths, with some exceeding those of asbestos. Fiberglass, mineral wool, and ceramic fibers are more brittle than asbestos fibers (Hodgson 1985, 1989).

The resistance of fiberglass and mineral wool to attack by alkaline solutions varies with composition. Those with high silica content are more susceptible. For fiberglass and mineral wool, working temperatures range from 300°C to 500°C, while ceramic fibers can be used at temperatures of 1,000°C to 1,800°C (Hodgson 1989; Harrison et al. 1999; Wypych 1999; AZoM.com 2004). Fiberglass and mineral wool are more expensive than asbestos, particularly for specialty fiberglass products (Tables 5 and 6). Because commercial production of these materials is extensive, availability is not a factor.

Although most fiberglass for substitute applications consists of long fibers, shorter fiberglass lengths also have been used. Essentially the waste stream products from fiberglass manufacture, the short fibers possess almost the same properties as E glass fibers when fiberized but are less expensive. (E glass is a borosilicate glass with high electrical resistivity.) The use of these short fibers has focused primarily on plastics applications. The shorter lengths allow the fibers to be more easily mixed with the polymer and allow for higher loadings than with other fiberglass products. This reduces costs by displacing more expensive components, and the short fiberglass has been shown to improve creep resistance, flexural modulus, and thermal stability (Lancaster Fibre Technology Group 2004).

Potassium titanate whiskers are another synthetic inorganic fiber used in substitute applications. Hard and abrasive, the whiskers have diameters of 0.2 to 1 µm and lengths of 10 to 20 µm. Potassium titanate is used primarily in brake manufacture where it improves the coefficient of friction, heat resistance, tensile strength, and wear resistance of disk pads and brake linings. Because of the

Table 10. Properties of fibrous asbestos substitutes

Heat Resistance		
Poor (less than 200°C)	Moderate (200°–400°C)	Good (above 400°C)
Cellulosic fiber	Aramid fiber	Mineral wool
PE fiber	PVA	Refractory fiber
PP	PTFE	Potassium titanate
	PBI	All minerals
	PAN	Steel fiber
	Carbon fiber	
	Glass fiber	
Reinforcing Strength		
Poor	Moderate	Good
All minerals	Cellulosic fiber	Aramid fiber
PTFE	Gypsum fiber	Carbon fiber
	PP	Potassium titanate PVA
	PAN	Glass fiber
	Refractory fiber	Steel fiber
	Mineral wool	
Chemical Resistance		
Poor	Moderate	Good
Cellulosic fiber	Aramid fiber	PBI
	Gypsum fiber	PAN
	Steel fiber	PTFE
		PVA
		PP
		Carbon fiber
		Potassium titanate
		Refractory fiber, except in alkalis
		Most minerals

Adapted from Hodgson 1985.

health controversy of fibers, the use of balled, platy, or powder forms appears to be preferred. These offer the same friction characteristics and heat- and wear-resistance properties as the whisker form. The nonfibrous forms generally are mixed with a fibrous organic material such as aramid or with metal fibers. Generally the nonfibrous form of potassium titanate is treated with a silane or phenolic resin to improve adhesion to the matrix (Kesavan and Burmester 1999; Hikichi, Haruta, and Horiguchi 2003). Potassium titanate whiskers are also used in heat insulation products and plastics.

Table 10 summarizes some of the important properties of the fibrous asbestos substitutes.

Alternative Products. Many manufacturers, instead of searching for an asbestos substitute, choose to replace the asbestos-containing product with one that never had asbestos (Table 3). For example, ductile-iron pipe and reinforced concrete pipe have been used in place of asbestos-cement pipe. Aluminum, vinyl, or wood sidings and cement board have been competitors with asbestos-cement shingles for many years (Meylan et al. 1978; EPA 1988; Pye 1989). Ceramic, nonasbestos organic, and semimetallic disk brakes are other common alternative products (Jacko and Rhee 1992). Alternative products are practical for many applications, because they usually are existing products and do not require the manufacturer to develop a new asbestos-free product. The major concerns of customers and manufacturers when selecting an alternative product are cost and performance (Hodgson 1985; Pye 1989).

To summarize, the ideal asbestos substitute would be composed of fibers that are flexible, have a high tensile strength, have a large surface area, and can be woven. The substitute also would be a good electrical insulator; resistant to degradation when exposed to high heat or chemicals; widely available; competitively priced with asbestos; and not a carcinogen. Products manufactured using substitutes and alternative products need a proven reliability record, must be easy to use or install, and pose little health risk in manufacture and use. While none of the substitute materials possess all of these qualities, through proper engineering, substitutes have been able to replace asbestos in a majority of commercial applications, particularly in Europe and North America.

PRODUCTION METHODS

Production of mineral substitutes for asbestos is straightforward. In most cases, open-pit mining is used. The ore is crushed and milled, typically with simultaneous drying and air classification, to produce multiple products based on particle size, shape, and other physical or chemical properties. Calcination, density and magnetic separation, exfoliation, flotation, thermal expansion, and surface treatment with silanes or titanates may be required for some minerals (details of mining and processing of minerals are given in the individual mineral chapters in this book).

Fiberglass, mineral wool, and refractory (ceramic) fiber are produced from a molten state. They are manufactured from molten glass that is dripped onto a rotating disk and spun off into long strands, dripped into a stream of air or steam and stretched into long glass strands, or forced through multiple nozzles forming continuous fibers. Glass for fiberglass is manufactured using various mixtures of quartz, feldspar, soda ash, kaolin, and specially selected oxides to produce fiberglass with specific compositions. Rock, usually basalt or diabase, and furnace slag may be melted to manufacture mineral, rock, and slag wools. Refractory fibers are made from glass melts rich in alumina, boron, silicon, and zirconia (Mohr and Rowe 1978; EPA 1985; Hodgson 1985; Skinner, Ross, and Frondel 1988; Institute for Environment and Health 2000; McMahon and Wenzel 2001). Potassium titanate whisker and powder may be synthesized by reacting hydrated titanium dioxide and potassium hydroxide at 160°C to 170°C (Kesavan and Burmester 1999).

The manufacture of polymeric fibers is much more complex because the organic starting compounds are derived from petroleum. The entire process involves reacting two or more organic compounds under heat and pressure to obtain the appropriate compounds, which are then polymerized. These polymers may be dissolved and extruded through dies into a chemical bath where the extruded compounds solidify into fibers. Alternatively, the melted polymer may be passed into an air stream to form fibers. The polymer fibers may be stretched to further orient the polymer chains in the fiber and improve strength. Fiber texture also may be modified to improve the characteristics of the fiber for a particular application (Block 2002; Carraher 2004). To produce carbon fibers, PAN, pitch, or nylon thread are carbonized and then graphitized at high temperatures (Skinner, Ross, and Frondel 1988; Hodgson 1989). Cellulose fibers are obtained through the chemical processing of wood fiber (Hodgson 1985). Details of the process to obtain organic fibers are beyond the scope of this chapter but are available in references on chemical manufacturing. In general, the energy and technology required to manufacture organic fibers account for their higher prices compared with minerals and inorganic fibers.

TECHNOLOGY

Much of the difficulty with asbestos substitutes was not the development of entirely new substitute materials for asbestos, because

many materials possessed some of the same chemical and physical characteristics as asbestos. The task was to determine how to manufacture equivalent asbestos replacement products while compensating for the deficiencies of the substitute materials compared to asbestos. This has been accomplished in most cases through the use of a mixture of asbestos substitutes and alternative products (Meylan et al. 1978; Dupré 1984; Hodgson 1985, 1989; EPA 1988; Pye 1989; Virta 1994; Institute for Environment and Health 2000; and patents accessible through the U.S. Patent Office Web site [2005]).

Cement Products

Cellulose fiber has become a common substitute for asbestos in concrete pipe, although fiberglass, PAN, and PVA fibers also are used (Hodgson 1985, 1989; EPA 1988; Pye 1989; Institute for Environment and Health 2000). Because some substitutes lacked certain properties of asbestos, it was necessary to make compensations. For example, because most fiberglass is not resistant to alkali attack, an alkali-resistant fiberglass must be used in cement products. To ensure adequate reinforcing properties in cement products, high-quality cellulose must be used, and a modified curing process for pipe products had to be developed to avoid degrading the cellulose fiber. Compensation also had to be made because cellulose absorbs more water than asbestos during the manufacturing process. Poor adhesion of fiberglass and PP fibers to matrices was another problem in some of the earlier fiber-reinforced-concrete products. This necessitated modification of the cement formulation or surface treatment of the fibers to solve the problem (Hodgson 1985; Pye 1989; Institute for Environment and Health 2000).

A common substitute product for asbestos-cement pipe is PVC pipe for small-diameter pipe, and ductile-iron and concrete pipe for large-diameter pipe. Vitrified clay pipe also may be used (EPA 1988; Pye 1989). Calcium silicate, cellulose, ceramic fiber, fiberglass, mineral wool, and PP are used in sheet products (Institute for Environment and Health 2000). Fibers of alumina, aramid, carbon, cotton, hemp, jute, kraft, PVA, ramie, and sisal also have been investigated for use in sheet products (Johnson and Melling 1983). Because PP is hydrophobic, it must be surface treated and mixed with other fillers to enhance its adhesion to and dispersion with the cement matrix (Pye 1989).

Substitutes used in asbestos cement often do not offer sufficient heat resistance, so fillers such as mica, vermiculite, and wollastonite may be added (Institute for Environment and Health 2000). Concrete mixes containing nylon, PE, and PP fibers, which typically are used for driveways, floors, sidewalks, and walls, have been available for many years to control plastic shrinkage, crack growth, and permeability. Polymer mesh products also are used as a supplement to reinforcing rods in some cement products (Concrete Fibers, Inc. 2004; NPC Inc. 2004).

Coatings and Compounds

Coatings and compounds require substitutes that are nonreactive, are thermally stable at elevated temperatures, add resistance to cracking, improve fire-resistance, control viscosity, can be dispersed easily in the matrix, bind with the matrix, and/or improve weathering properties (Meylan et al. 1978; EPA 1988; Hagens 2003).

Several substitutes used in place of asbestos in paints and sealants are aramid fiber, bentonite, calcium carbonate, cellulose, ceramic fiber, fiberglass, kaolin, mica, palygorskite (attapulgite), PE fiber, PAN fiber, PP fiber, silica gel, talc, and wollastonite. Mixtures of these substitutes often are used to obtain the desirable properties (EPA 1988; Pye 1989; Wypych 1999). As with cement, adjustments must be made with coatings and compounds. For example, cellulose is not thermally stable under acid conditions, so

asphalt compound chemistry must be adjusted to be more alkaline. Also, compensation must be made for different oil absorption properties of fiber fillers in asphalt compounds, compared to asbestos (Hodgson 1985; Hagens 2003).

Flooring

In flooring, the asbestos substitute should provide a durable, smooth, and resilient surface, and make the flooring dimensionally stable (Rosato 1959; Meylan et al. 1978; EPA 1980, 1988).

For flooring felts, substitutes such as cellulose, fiberglass, PE fiber, and PP fiber, often in combination, have been used in place of asbestos. Alternative flooring products with modified vinyl composition and foam backings also have been used to compensate for the removal of asbestos (EPA 1988). Flooring primarily to replace vinyl asbestos tile has been made from modified vinyl compositions and may contain mineral fillers such as calcium carbonate, clay, fiberglass, mica, PE pulp, talc, vermiculite, and wollastonite (EPA 1988). Alternative products for flooring include carpeting, ceramic tile, and wood flooring (EPA 1980).

Friction Materials

Substitutes for friction materials should be heat resistant and have low thermal conductivity, a low noise coefficient, and high strength. They also should be moisture resistant, nonabrasive, long wearing, and bond tightly to, and disperse well in the matrix (Hodgson 1985; EPA 1988; Pye 1989; Jacko and Rhee 1992; Kobayashi 2002).

Aramid fiber, carbon fiber, cellulose, ceramic fiber, fiberglass, metal fibers (brasses, bronze, copper, and iron), mineral wool, palygorskite (attapulgite), potassium titanate, tremolitic talc, vermiculite, and wollastonite are used in various combinations to replace asbestos in brakes (Meylan et al. 1978; EPA 1980; Hodgson 1985; Jacko and Rhee 1992). Aramid fiber appears to be the predominant fiber substitute in brake and clutch applications (Pye 1989; Institute for Environment and Health 2000).

Substitution for asbestos is difficult in semimetallic drum brakes, primarily because of the curvature of the lining. Brake shoes using substitutes absorb moisture and perform poorly until the shoes are dried through use. These problems resulted in some manufacturers stopping production of semimetallic drum brake linings (EPA 1988). The use of semimetallic disk brake pads, however, has not experienced manufacturing and performance problems; in 1986, they accounted for about 85% of original equipment disk brake pads on light-to-medium-weight vehicles (EPA 1988; Jacko and Rhee 1992; Kobayashi 2002). The market share for semimetallic disk-brake sales has declined, and nonasbestos organic brakes are now the most common type of friction materials used in brakes and clutches (Kesavan and Burmester 1999).

Gaskets and Packings

Substitutes for gaskets must be resistant to heat, tears, and chemical attacks, and be nonabrasive and resilient. Packings, which are used to form a seal between two moving parts, must be heat and chemical resistant, have low thermal conductivity, and seal liquids. Packings can be made with loose fiber, woven into braided products, and be made using yarns (EPA 1988).

Depending on the particular application, aramid fiber, cellulose, ceramic fiber, clay, copper, cork, diatomaceous earth, fiberglass, mica, mineral wool, PTFE, rubber, talc, vegetable fiber, and wollastonite have been used as asbestos substitutes in gaskets and packings. Also, carbon fiber, cellulose, ceramic fiber, expanded graphite, fiberglass, PBI fiber, and PTFE are used in packings (Corbett 1986; EPA 1988; Pye 1989; Shelley 1993; Harrison et al. 1999; Institute for Environment and Health 2000).

Insulation Materials

Insulation materials, including felts, millboard (a heavy cardboard product), paper, and wools require that substitutes be resistant to heat, corrosion, and chemical attack. Additionally, they should have a high strength, low thermal conductivity, and be moisture resistant for millboard and paper applications. Specific uses include electrical insulations in appliances and electrical panels; equipment protection when handling molten glass or metal; fireproofing for safes; durable, chemical-resistant gaskets; heat insulation for automotive mufflers, furnaces, kilns, steam lines, and stoves; paneling for garages; and even partitions for offices (Rosato 1959; EPA 1988).

The most common substitute is fiberglass for moderate-temperature, low-cost insulation. Higher-temperature applications require the use of ceramic fiber (Meylan et al. 1978; EPA 1988). A variety of other substitutes, including calcium silicate, cellulose, clays, diatomaceous earth, mica, perlite, silica, talc, vermiculite, and wollastonite, can be used in millboard and papers (Cavicchio 1981; Hodgson 1985; Benbow 1987; EPA 1988; Pye 1989).

Plastics

Filler materials improve the impact and tensile strength, stiffness, resistance to deformation when exposed to heat, and electrical resistance in plastics (Hodgson 1985; EPA 1988).

Aramid fiber, carbon fiber, cotton, fiberglass, PTFE, potassium titanate, and fumed silica powder are used in place of asbestos in plastics (Meylan et al. 1978; EPA 1988; Pye 1989). Calcium carbonate, clays, mica, talc, and wollastonite also are used as inert fillers in plastics to improve strength and stiffness (Virta and Barsotti 2000).

Roofing

Roofing materials must be flexible yet dimensionally stable and resistant to rot, fire, and heat (Meylan et al. 1978; EPA 1988). In roofing felts, cellulose and fiberglass are used as substitutes for asbestos. Fiberglass- or cellulose-reinforced shingles, metal roofing, roof tile, single-ply membrane, slate, and wood shakes are alternatives to asbestos-reinforced shingles (Hodgson 1985; EPA 1988; Pye 1989).

HEALTH ISSUES

A full review of the health issue is beyond the scope of this chapter, and readers who seek more details are referred to the abundant references available in the public domain. As with almost any material, most substitutes pose some risk to humans from exposure to dust (Douglas 2001). For most of the substitute materials, exposure limits to dust have been set to reduce the risk of pulmonary disease (NIOSH 2004).

Organic fiber substitutes generally are not thought to pose a serious health risk because the fibers are not easily respired (Elmes 1989; Harrison et al. 1999; Institute for Environment and Health 2000; Douglas 2001). Also, no serious health issues have arisen with cellulose despite the fact that it is durable and does not dissolve in the lung (Institute for Environment and Health 2000).

Laboratory animals developed intraperitoneal or intrapleural cancers when glass wool, long-fiber palygorskite (attapulgitite), titanate fibers, refractory ceramic fiber, rock wool, silicon carbide, special-purpose glass fiber, and potassium titanate fibers were implanted in them; however, intratracheal cancers were not observed. In animal inhalation studies, either cancer or mesothelioma was observed using long-fiber palygorskite (attapulgitite), refractory ceramic fibers, silicon carbide fibers, and special-purpose

glass fibers. The results were inconclusive with potassium titanate fibers (Osinubi, Gochfeld, and Kipen 2000; Douglas 2001).

Carcinogenicity to humans is probably the most important consideration in the use of any asbestos substitute, given the carcinogenic nature of asbestos. Through the review of animal testing or epidemiological studies, the International Agency for Research on Cancer (IARC) has determined that some of the substitutes are carcinogenic (IARC 1997, 2002). Some implanted and injected materials were carcinogenic in animal studies, but there were conflicting results in inhalation studies using animals and in epidemiological studies (IARC 1997, 2002; Osinubi, Gochfeld, and Kipen 2000).

Materials such as diatomite (not containing quartz), graphite, mica minerals, perlite (not containing quartz), potassium titanate, pumice (not containing quartz), serpentine (not containing asbestos), talc (not containing asbestos), and vermiculite (not containing asbestos) have not been reviewed by IARC. Recommended exposure levels, however, have been established for these lung irritants (NIOSH 2004).

Of the materials reviewed by IARC, respirable cristobalite (typically found in many calcined products) and quartz are classified as Group 1 (human carcinogens; WHO 1987; IARC 1997). Although diatomite is composed of amorphous silica, deposits usually contain crystalline silica. Also, calcined diatomite may contain cristobalite.

Specialty E glass fibers, "475" glass fibers, and refractory ceramic fibers are classified as Group 2B (possible human carcinogens; IARC 2002). Palygorskite (attapulgitite) with lengths greater than 5 μm also is listed by IARC as Group 2B (IARC 1997).

Glass wool for insulation, continuous glass filament, rock (stone) wool, and slag wool are classified as Group 3 (not classifiable as to their carcinogenicity to humans) by IARC (IARC 2002). Also classified as Group 3 are wollastonite (recognized as a lung irritant), short-fiber palygorskite (attapulgitite), and diatomite (IARC 1997; NIOSH 2004).

Vermiculite typically poses little carcinogenic risk, but vermiculite mined in the past from a deposit near Libby, Montana, contained asbestos. As a result, the vermiculite industry has been under intense scrutiny (EPA 2004). In 2000, the National Institute for Environmental Health Sciences (NIEHS) investigated talc as a possible carcinogen. The agency concluded that data were inadequate to make a ruling and, as of June 2005, was still reviewing this issue (NIEHS 2001).

Questions have been raised about the health and safety risks posed in the manufacture of some of the alternative products, particularly with regard to volatile organic compounds released during the manufacture of plastic products and during metal casting.

Another health concern with substitutes is that their use has occurred mainly during the past 20 years. Given the 20- to 30-year latency period for asbestos-related diseases (Gross and Braun 1984), many still believe that an inadequate period of time has elapsed to establish the effects of long-term exposure to asbestos substitutes on human health. These issues, however, have not discouraged the use of substitutes or alternative products.

FUTURE TRENDS

In the United States, Western Europe, parts of Eastern Europe, and a few other locations, asbestos consumption has declined enough to see that the efforts to substitute for asbestos are almost complete. In these locations, substitutes probably will experience little growth that can be attributed directly to the replacement of asbestos. In fact, many asbestos substitutes have been in use for a sufficient

period of time that they should no longer be labeled as substitutes, but can now be considered an essential component of the product.

There is still sufficient asbestos use elsewhere, however, to permit a considerable expansion in sales of substitutes or alternative materials. Most of this growth will be in asbestos-cement products, which account for more than 98% of world asbestos usage. Based on growing worldwide opposition to the use of asbestos and the increasing rate at which countries are now considering bans on the use of asbestos, the displacement of asbestos by substitutes and alternative products will continue. Some specialty applications will probably remain (where it is not feasible to replace asbestos) but in most cases substitutions will be made.

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Clay Liners and Barriers

Robert Trauger

INTRODUCTION—CLAY AS A BARRIER

Containment is a fundamentally important concept in environmental and civil engineering. Effective containment preserves quality of life and protects valuable environmental resources. Engineered clay barriers have been used for several decades as technically suitable, cost-effective solutions for containing water, wastewater, landfill leachate, and gas. Before the introduction of synthetic liner materials in the early 1980s, clay liners were the only available option for most containment applications. Thanks to the more recent development of cost-effective thermoplastic barriers (geomembranes), the quality of containment systems can be appreciably enhanced. Clay liners still play a major role in water and waste containment, however, and are often used with geomembranes.

This chapter examines the many types of clay barriers that can be used in environmental containment applications. It covers the engineering properties of these materials and the regulatory criteria used to establish the performance of clay barriers. Information on the design of these clay barriers highlights the most important concepts required to meet modern containment performance criteria. Given the breadth and complexity of this subject matter, only an overview is possible; added details can be found in the referenced documents listed at the end of the chapter.

Types of Clays Used as Barriers

Clay or clayey soils are used as barriers primarily because their particle size is small enough to limit the flow of fluids. For this reason, engineered clay barriers are rarely categorized by clay mineral species. As discussed in the section on Engineering Properties in this chapter, hydraulic conductivity is the most important property of any soil evaluated for its barrier properties. In fact, soil barriers are often described as “clay liners” even if they are not strictly clays as defined by any common classification systems, because the hydraulic conductivity of a sandy or silty soil with some clay content is often acceptable as a barrier.

The result of this performance-oriented identification is that many kinds of clay minerals have been successfully used in engineered clay barriers. Illite, kaolinite, and smectite rank among the most common species in terms of barrier clays (Goldman 1988), but often this is due as much to their ready availability as to their desirable properties. The existing literature is incomplete with respect to identifying specific mineral species in a soil used as a

barrier. Engineers have historically specified only the required performance properties of the soil and the completed liner, leaving it to the contractor to demonstrate that these properties will be achieved. Consequently, the relationship between mineral species and engineered barrier properties is not well understood.

Smectite clays, specifically montmorillonite-bearing bentonite, are also commonly used in barrier applications. Bentonite is used as an admixture to existing soils to fill fluid-conducting void spaces. Because of its water absorption and volumetric swelling properties, a small percentage of bentonite (usually less than 10% by weight) can significantly decrease the hydraulic conductivity of a porous soil. Bentonite is also used in geosynthetic clay liners (GCLs), another type of barrier that has largely replaced the practice of using bentonite as an admixture. Bentonite and attapulgite are also used in vertical cutoff barriers, applications that are less common than conventional containment barriers but are still important technologies in contaminated site remediation.

Types of Barriers

This chapter categorizes clay barriers as “horizontal” or “vertical.” Horizontal barriers are constructed by placing and compacting clay soils, or by unrolling clay-based geosynthetic products. Vertical barriers are constructed by trenching into existing soils and then backfilling the trench with clay-bearing soil or cement mixtures.

Compacted Clay Liners

Compacted clay liners (CCLs) are the most prevalent type of clay liner. A CCL is a discrete layer of soil placed on a subgrade to serve as a barrier to fluid flow. The CCL can be placed on subgrades of varying slopes, although it becomes more difficult to compact the layer as slope steepness increases beyond 3H:1V. The CCL may range in thickness from 150 mm to 1,500 mm, depending on the application and the relevant regulatory requirements. The most common CCL thickness is 600–1,000 mm.

A wide range of clay species can be effectively used as a low-permeability barrier. Few regulatory or engineering restrictions guide the appropriate mineralogical makeup of the soil used or its physical properties. This means that a clay liner can be built using any available soils, as long as the finished product achieves the relevant hydraulic conductivity requirement, which is typically 1×10^{-9} m/sec.

For these reasons, there is no “standard” clay liner with a certain mineralogical composition and a specific range of engineering properties. The soils used to construct a CCL are often extracted from the site where the liner is to be located to minimize the cost of excavating and transporting suitable clay soils from an offsite borrow area. Thus, the mineralogy of clay liners varies significantly, relating more to local geology than engineering and regulatory requirements. In fact, very few data are available identifying the mineralogy of specific clay liners. Although the performance (hydraulic conductivity) of these liners has been exhaustively studied, their composition has been studied only occasionally (Kovach 1991; Millard 1995).

Soil-Bentonite Liners

Liners are often built in locations with unsuitably porous or rocky in situ soils, so clay soils must be brought to the project site and then placed on a prepared foundation. Instead of importing the full volume of clay soils needed for the liner, it can be more economical to import bentonite clay, which is then mixed with the existing soils. Sodium bentonite, with its ability to swell significantly when wetted, can fill large pore spaces in sandy or other well-grained soils and thus reduce permeability to a required level. The end result is a soil-bentonite liner (SBL). These liners have also variously been called “mixed blankets,” “bentonite-amended liners,” and “bentonite-enriched soils.”

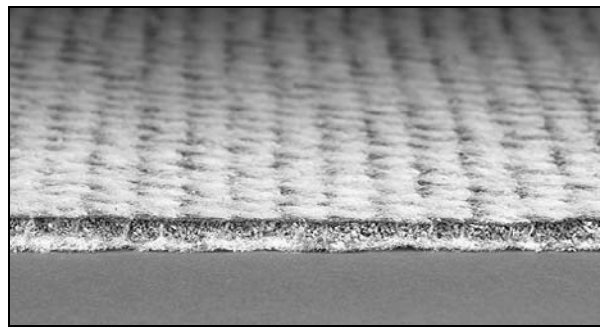
SBLs are constructed in one of two ways. Bentonite can be deposited directly on the soil and tilled into it to a prescribed depth; or when more application control or a thicker liner is needed, the bentonite is mixed with soil using a pug mill. This mixture would then be placed and compacted on a prepared subgrade. Like CCLs, SBLs have also been effectively used for several decades. But with the growing ease of use and regulatory acceptance of geomembranes and geosynthetic clay liners, SBLs are not as prevalent as they were in the early and mid-1960s, 1970s, and 1980s.

Geosynthetic Clay Liners

GCLs are the newest class of clay liner; they were invented in 1982 but did not achieve commercial success until the early 1990s. A GCL is essentially a hybrid of geosynthetic materials (geotextiles and geomembranes) and sodium bentonite clay (Figure 1). A GCL uses the impressive barrier properties of sodium bentonite to form an effective hydraulic barrier in a convenient package (5–10 mm thick) that can be unrolled on a prepared subgrade. Any clay mineral could be incorporated into a GCL, but sodium bentonite has the unique ability to form a monolithic gel structure when wetted. In this form, it has a very low hydraulic conductivity (1×10^{-10} m/sec to 1×10^{-11} m/sec) and does not require mechanical compaction. Because sodium bentonite is a swelling clay, the hydration process results in very few interparticle pathways that conduct flow.

GCLs are typically used as alternatives to CCLs and are often compared to CCLs to ensure that the performance objectives for the liner system as a whole can be achieved. This comparison is known as an “equivalency” demonstration and has been the focus of much research and discussion among engineers, regulators, and GCL manufacturers.

The several varieties of GCLs all have a few common elements. First, they all contain sodium bentonite because it is the only material proven to possess the hydraulic properties needed for lining applications. Second, they all include one or more geosynthetic materials. The most common GCL configuration is a “sandwich” of bentonite and geotextiles that are laminated or needlepunched together. Other GCLs are produced with a layer of bentonite adhered to a geomembrane.



Courtesy of CETCO.

Figure 1. Typical needlepunch-reinforced GCL

Cutoff Walls

If CCLs, SBLs, and GCLs constitute the category of horizontal clay barriers, then cutoff walls represent the category of vertical clay barriers. Cutoff walls are used almost exclusively in environmental remediation projects where it is necessary to contain a migrating subsurface contaminant plume. These barriers can also be used to control the local groundwater gradient at a contaminated site, allowing more efficient use of remedial groundwater treatment technologies.

Cutoff walls present a completely different set of practical and engineering challenges than horizontal barriers. The presence of groundwater (often contaminated), unstable soils, unfavorable terrain, and other commonly encountered obstacles and site conditions make cutoff walls difficult to build. But they are often essential to the successful remediation of a contaminated site, and much research has been performed to overcome site challenges and optimize their effectiveness.

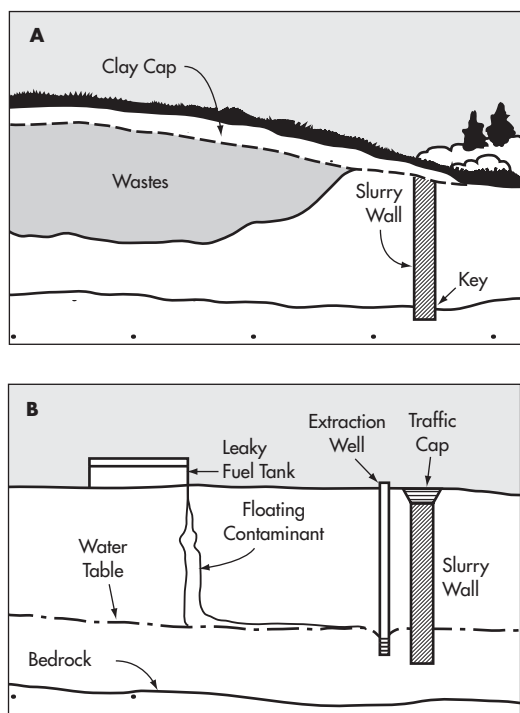
Cutoff wall construction involves trenching into the subsol around a site to a prescribed depth, usually such that the wall can be “keyed” into a low-permeability clay strata or aquitard. “Hanging” cutoff walls, which are not keyed into such an aquitard, can be built if the contaminants of concern are less dense than water (Figure 2).

A bentonite slurry holds the trench open during construction. The slurry is denser than water and thus offsets the hydrostatic pressure on the sidewalls of the trench. The bentonite also forms a “filter cake” on the sidewalls that itself is a barrier to flow and further contributes to trench stability. Using bentonite slurry in this fashion has resulted in the name “slurry wall,” but “cutoff wall” is preferred when describing barrier applications of this construction method.

A cutoff wall is constructed with simultaneous excavation and backfilling. Excavation at one end of the trench is followed by backfilling at the opposite end. The exposed trench is always filled with bentonite slurry or backfill. This keeps the disturbed area to a minimum and optimizes the use of slurry. The nature of the backfill determines the type of cutoff wall constructed during this process.

Three types of cutoff walls contain clay: soil-bentonite (SB), cement-bentonite (CB), and soil-cement-bentonite (SCB). Many other materials can be used in cutoff walls, however, including concrete, plastic membranes, steel sheets, and porous reactive media. This discussion focuses only on those types of cutoff walls containing clay.

SB Cutoff Walls. The bentonite in an SB wall decreases the hydraulic conductivity of the backfill soil just as it does in horizontal SBLs. Soil, bentonite, and water are mixed at a predetermined ratio necessary to ensure uniform slump into the bottom of the trench while still providing low hydraulic conductivity.



Source: Spooner et al. 1985.

Figure 2. Conceptual view of (a) keyed-in and (b) hanging cutoff walls

CB Cutoff Walls. In a typical CB wall, a 2%–10% by weight bentonite-to-cement mixture is used to backfill the trench. A CB wall will possess significant compressive strength, which may be necessary to ensure the stability of nearby structures or topographical features near the construction site. The inverse relationship between strength and hydraulic conductivity means that the amount of bentonite added to the mixture must be enough to form a barrier but not so much as to excessively reduce the compressive strength of the wall.

SCB Walls. As the name of this barrier implies, an SCB wall uses soil, cement, and bentonite to achieve a certain combination of barrier and strength properties required for a specific project. One advantage of an SCB wall over a CB wall is that the excavation spoils can be incorporated into the backfill, thus reducing waste (Inquip 2004).

Clay Barrier Applications

Clay barriers are used in any application that must contain water or waste. A brief discussion of the four broad classes of clay barrier applications prefaces a presentation of detailed engineering properties of clay soils that relate to these applications.

Surface Impoundments

The term *surface impoundment* describes any structure designed to contain water: decorative ponds, reservoirs, fire ponds, sedimentation/retention basins, dams, canals, and wastewater lagoons. Even engineered wetlands would fit into this broad classification of water containment structures.

Surface impoundments are the earliest applications of clay barriers. The need to control the flow of water is among the most basic needs of an industrialized civilization, and clay soils played a critical

role in doing so long before the advent of other impervious materials. Using clay soils in engineered surface impoundments is much more recent, however. When mechanical earthmoving equipment began to replace human labor (about 1900 in the United States), the ability to shape the earth greatly improved. Manipulating soils for various engineering projects became the subject of intense focus, thus beginning the clay liner era. It is interesting to consider the difficulties that must have been present when lining projects were built around the turn of the 20th century. There were no formal soil classification systems, no standard construction practices or specifications, and, perhaps most important, no laboratory tests or test equipment to measure the hydraulic conductivity of clay soils.

The construction of a reservoir in Baltimore, Maryland, in 1908 illustrates the difficulties of these working conditions (Beatty 1912). For this reservoir, a cutoff wall was installed under the toe of a dam to prevent seepage under the dam face. The cutoff wall was composed of compacted ("rammed") clay placed in many 3-in. lifts. The water tightness of the clay layer was tested by embedding perforated pipes in the clay and then pressurizing the pipes. Visual observations of the clay wall were made to see if seepage occurred. Indeed, it was discovered that water seeped through the interlift boundaries of the clay layer, a phenomenon noted decades later by Daniel (1991). Further studies on the suitability of the clay were made by digging small pits into the surface to observe whether the water level decreased. Beatty (1912) also describes the quality control procedures in place for placement of the clay, whereby inspectors required that all lumps be "broken to the size of an orange, and all larger stones rejected."

It is clear that although clay has a long history of use as a liner, a truly engineered clay barrier did not emerge from its application in surface impoundments. The more likely origin of the engineered clay barrier is the waste containment industry.

Landfill Covers

Early municipal waste landfills were seldom installed with any kind of engineered barrier system. Municipalities located garbage dumps on the basis of convenience, close to urban centers, in old quarries or gravel pits, or on "unproductive" land such as swamps. Pre-industrial era household refuse was not likely to be especially harmful, but solid and liquid wastes from industrial sources were proven in the 1960s and 1970s to be a significant cause of long-term environmental contamination. Modern environmental legislation forced the closure of these dump sites, and new scrutiny was applied to developing suitable barriers to the inflow of precipitation. The era of the engineered clay liner had begun.

Placing a clay layer on an existing landfill serves several functions. Most important, it limits the infiltration of precipitation that would otherwise percolate into the waste mass and then out the bottom of the dump into groundwater. The clay cap also contains gases generated as organic matter decomposes in the waste. In so doing, the clay reduces offensive odors, which are a common nuisance to nearby residents. Finally, the clay is a buffer between environmental receptors (plants, animals, and humans) and the potentially harmful waste itself.

Landfill Liners

Inadequate containment of landfilled waste causes environmental problems that the U.S. Environmental Protection Agency (EPA) Superfund cleanup program is still working to resolve. Thousands of national and state-led cleanups of old landfills and dump sites were completed over the past 25 years, many of which consisted of placing some form of cap over the waste.

With the hindsight provided by these contaminated sites, more research was undertaken to ensure that new landfills were designed

to minimize the threat of leakage. Governments instituted various measures, such as banning the disposal of liquid wastes, imposing siting restrictions, and restricting the disposal of hazardous materials. Additional work was done to develop liner performance requirements in this newfound era of environmental responsibility.

EPA's report to Congress in 1974 concluded that existing waste management practices in the United States at the time were "generally inadequate" and that better control of the wastes was necessary to protect public health and the environment. Congress agreed and passed the Resource Conservation and Recovery Act of 1976, authorizing EPA to establish waste management controls and regulations (Haxo et al. 1984). Research into the effectiveness, compatibility, and durability of lining materials accelerated to improve waste management practices.

Knowledge of clay liners had accumulated over several decades of experience in water containment applications such as dams, reservoirs, and canals. This experience was not wholly relevant to waste containment, where possible chemical interactions with the liner must be considered and where seepage from the liner is potentially hazardous. Therefore, new information and research were needed to ascertain the effectiveness of clay liners in waste containment applications.

One of the first and most important research programs evaluating the compatibility of clay liners with chemical contaminants was summarized in an EPA document, *Liner Material Exposed to Hazardous and Toxic Wastes* (Haxo et al. 1984). This report offered a comprehensive investigation into the performance of both clay and synthetic membrane liners (new at the time) after long-term exposure to both real and laboratory-prepared liquid wastes. The study, performed from February 1975 through July 1983, found a wide range of performance variations depending on the materials and wastes used. This report set the stage for even more research into the use of clay barriers for waste containment, discussed later in this chapter.

Mining Applications

Clay liners are used in many types of mining applications, including stormwater detention, process water collection, heap leach pad lining, and final closure or remedial closure. The function of the clay in these mining projects is the same for the other applications described herein: containment of water and leachate. The only difference is that the leachate to be contained in mining projects has a much different chemistry than that in waste containment.

Heap leaching is a mineral processing technology in which large piles of rock are percolated with chemical solutions that extract valuable minerals. The largest heap-leaching operations involve copper mining, where copper-bearing rock is flushed with a weak sulfuric acid solution. This solution dissolves the copper from the mineral and is carried in the leachate to a collection system resting on top of a liner. An electrowinning process extracts copper from the solution, and the leachate is then recirculated to the ore pile. Gold is extracted in much the same fashion, except that the leaching solution contains low concentrations of cyanide. The hazardous solutions used in heap leaching require a robust liner system. Leach pad lining practices vary worldwide, but commonly a geomembrane (such as high-density polyethylene [HDPE] or polyvinyl chloride [PVC]) is the primary liner and a clay barrier may be used as the secondary liner.

ENGINEERING PROPERTIES OF CLAYS FOR BARRIER APPLICATIONS

Civil engineers evaluate several different properties to assess a soil's suitability as a liner material. It is rare that a candidate soil

will possess superior attributes across the complete spectrum of desirable properties; in fact, usually any one desirable attribute is offset by one that is undesirable. For example, a highly plastic clay that possesses beneficial strain behavior is not likely to be sufficiently compactable. The engineer must identify an acceptable "window" of properties that allow a clay soil to function as a barrier. This design approach ensures that performance requirements can be achieved yet still allow the variability that is inherent with natural soil materials.

Hydraulic Conductivity

Hydraulic conductivity measures the intrinsic capability of a soil to convey water. This term is often used interchangeably with *permeability*, although, in the strictest sense, permeability applies to all liquids inclusive of organic chemicals and aqueous chemical solutions. This distinction is rarely applied in engineering parlance, and so this chapter uses hydraulic conductivity and permeability interchangeably.

Hydraulic conductivity is by far the most commonly specified and required property for a soil liner. In fact, permeability and thickness are often the only properties ever specified or required. Taken together, permeability and thickness can be used to theoretically estimate the total amount of flow (leakage) expected for a saturated soil layer under a specified hydraulic head pressure.

During the period from 1855 to 1856, Henry Darcy worked to identify the relationship between flow and permeability. Darcy's law resulted from a series of experiments in which he subjected a column of soil to a constant hydraulic force and measured the water flow rate through the soil (Figure 3). The flow rate was found to be directly proportional to both the hydraulic head and a numerical constant he designated as "*k*." The value of *k*, in units of meters per second or centimeters per second, has become the defacto indicator for a soil's relative ability to transmit water. Mathematically, Darcy's law is:

$$Q = kA(\Delta h/L) \quad (1)$$

where

- Q = volumetric flow rate (cu m/sec)
- k = hydraulic conductivity (m/sec)
- A = flow area perpendicular to L (sq m)
- h = hydraulic head (m)
- L = flow path length (m)

Equation (1) can be simplified by noting that the term $\Delta h/L$ is actually the change in hydraulic head from the top to the bottom of the liner. Assuming that the liner leaks into an unsaturated zone, the head pressure at the bottom of the liner is zero and $\Delta h/L$ becomes equal to the *hydraulic gradient*, which is $(h + L)/L$. The gradient is usually designated as *i*, and the lined area A can be made equal to 1 sq m to obtain a flow rate per unit area (q). Thus, Darcy's law is reduced to $q = ki$. For example, for a clay liner with a permeability of 1×10^{-9} m/sec and a thickness of 0.6 m, leakage at a head of 3 m would be calculated by applying the simplified version of Darcy's law,

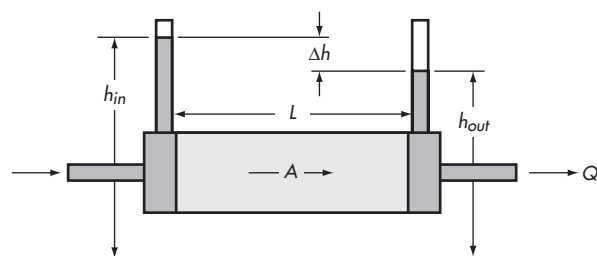
$$q = ki, \quad (2)$$

where

- q = unit flow rate (cu m/sec)
- k = hydraulic conductivity (m/sec) = 1×10^{-9} m/sec
- i = hydraulic gradient = $(h + L)/L = (3 \text{ m} + 0.6 \text{ m})/0.6 \text{ m} = 6$.

Therefore,

$$q = (1 \times 10^{-9} \text{ m/sec})(6) = 6 \times 10^{-9} \text{ cu m/sq m/sec or } 5,184 \text{ L/ha/day.}$$



Courtesy of Glenn Brown, <http://biosystems.okstate.edu/Darcy>.

Figure 3. Water flow model used in the development of Darcy's law

Table 1. Typical permeabilities of various soils^a

Group Symbol	Description	Typical Permeability, m/sec
GW	Well-graded clean gravels, gravel-sand mixtures	2.5×10^{-4}
GP	Poorly graded clean gravels, gravel-sand mix	5×10^{-4}
GM	Silty gravels, poorly graded gravel-sand-silt mix	$>5 \times 10^{-9}$
GC	Clayey gravels, poorly graded gravel-sand-clay mix	$>5 \times 10^{-10}$
SW	Well-graded clean sands, gravelly sands	$>5 \times 10^{-6}$
SP	Poorly graded clean sands, sand-gravel mix	$>5 \times 10^{-6}$
SM	Silty sands, poorly graded sand-silt mix	2.5×10^{-7}
SM-SC	Sand-silt clay mix with slightly plastic fines	1×10^{-8}
SC	Clayey sands, poorly graded sand-clay mix	2.5×10^{-9}
ML	Inorganic silts and clayey silts	5×10^{-8}
ML-CL	Mixture of inorganic silt and clay	2.5×10^{-9}
CL	Inorganic clays of low to medium plasticity	5×10^{-9}
OL	Organic silts and silt-clays, low plasticity	$>5 \times 10^{-9}$
MH	Inorganic clayey silts, elastic silts	2.5×10^{-9}
CH	Inorganic clays of high plasticity	5×10^{-10}
OH	Organic clays and silty clays	1×10^{-9}

Source: NAVFAC 1971.

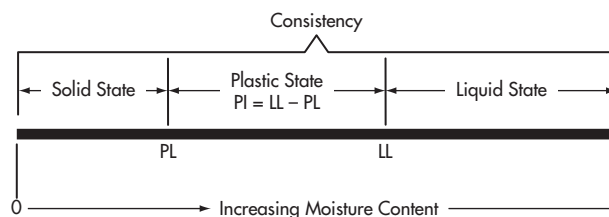
^a Note the trend of decreasing permeability with decreasing grain size.

As would be expected, soils with smaller particles have a lower permeability (they will allow less flow) than granular soils. Table 1 lists soil types and their typical permeability values. Only those soils with some clay fraction achieve the permeability values required to be considered suitable for a liner (as defined by a permeability value of 1×10^{-9} m/sec or lower). Small particles create a "tortuous path" of interconnected pores through which water passes only very slowly. This results in a low permeability value if the soil is placed and compacted correctly.

Some clay soils can achieve permeability requirements more easily than others. The relative ability of a soil to be compacted as a functional liner depends on a combination of many properties, including moisture content, density, and of course particle size. The effects of these other variables are discussed in the section on Compacted Clay Liners and Soil-Bentonite Liners in this chapter.

Particle-Size Distribution

All naturally occurring soils contain a range of particle sizes. Soils used for liners have a significant fraction of very small particles, or



Courtesy of CETCO.

Figure 4. Schematic of moisture values relating to the Atterberg limits of soil

"fines," that reduce the ability of the liner to transmit flow. The fines content of a soil is usually defined as the weight fraction of a sample having a particle size of less than 0.075 mm (corresponding to the amount passing a 200-mesh sieve). With a preponderance of small particles, the permeability may be low enough for the soil to function as a liner. This means that the particle size of the remaining 70% of the soil can vary widely and even include stone or gravel particles without affecting liner performance. Shakoor and Cook (1990) found that it was possible to achieve a permeability value approaching 1×10^{-9} m/sec even when the stone fraction in a soil was 50%. Beyond this point, however, permeability values increased several orders of magnitude. In practice, this means that there can be tremendous variability in particle size for a soil liner, but it can still function effectively as long as the fines content is 30% or greater (Benson, Zhai, and Wang 1994).

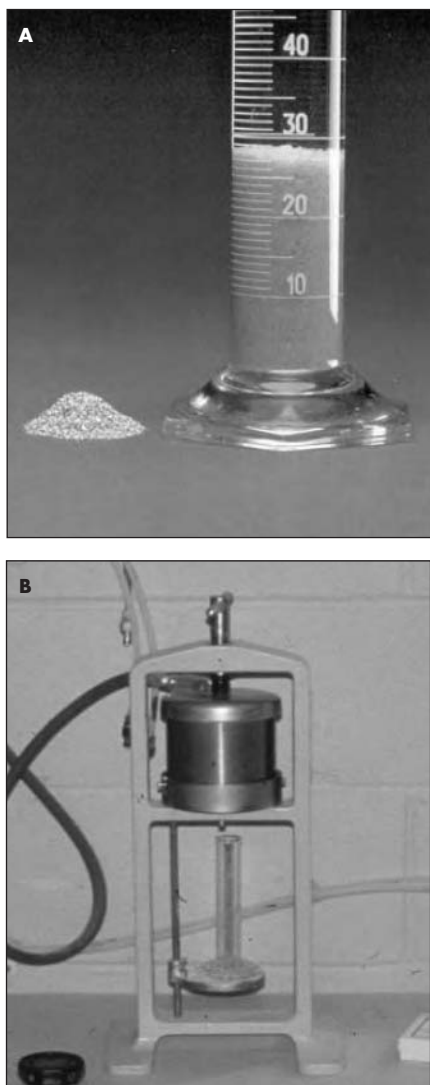
There will always be uncertainties relating to the maximum allowable particle size in a clay liner. Although a single large stone or rock may not lower overall performance, the presence of multiple large rocks most likely will increase its permeability. Therefore, the maximum particle size is often recommended not to exceed 25–50 mm (Daniel 1990). Screening the soil before placement controls particle size but this adds cost to the project and can be a source of controversy between quality control personnel and the contractor.

The grain size distribution of a soil determines its classification. In the United States, the Unified Soil Classification System (USCS) predominates, although there are dozens of different classification schemes worldwide. This system, whose nomenclature is used in Table 1, defines soils by particle size, gradation, plasticity, and compressibility. Geotechnical engineers use the USCS most often because these parameters have a strong relationship to the properties of soil structures such as dams, embankments, and liners. Other classification systems, derived from formation mechanisms or geographical location, are not descriptive of engineering considerations.

Another advantage of the USCS is its ability to classify soils through visual observation, with added laboratory testing for confirmation and complete description of the soil. When constructing a liner, it is helpful to have a third-party quality assurance inspector (one experienced in the classification process) monitor soil placement activities to determine if the soil is within the range of classifications that allow for the construction of an adequate hydraulic barrier.

Atterberg Limits

The Atterberg limits describe transition points in the consistency of a given soil throughout its full range of moisture content from zero to complete saturation (Figure 4). The plastic limit (PL) is the boundary moisture content at which a soil transitions from a plastic



Courtesy of CETCO.

Figure 5. Free swell (a) and fluid loss (b) testing of bentonite

to a nonplastic and noncohesive state. The liquid limit (LL) is the moisture content at which the soil transitions from a plastic, cohesive mass to a viscous fluid. The difference between the LL and the PL is known as the plasticity index (PI), which defines the complete moisture range over which the soil is considered to be in a plastic state.

In a general sense, the larger the PI, the more suitable the soil as a barrier. This is because the PI is really an indirect measure of particle size. Clay particles can absorb water, thus imparting plasticity. Moreover, a plastic soil can accommodate tensile strain better than a nonplastic soil. There is a trade-off, however, between plasticity and compaction. A soil with an extremely high PI may not be compactable to the extent needed to make it structurally sound and to achieve the density needed for low permeability. Benson, Zhai, and Wang (1994) evaluated PI data for 67 landfills in North America and found that acceptable permeability values were achieved when the PI exceeded 7. The lowest permeabilities were achieved with the PI ranging from 10 to 30.

Moisture Content and Density

The most important performance parameter for the completed clay liner is its permeability. Many researchers (Rogowski 1990; Shaktour et al. 1996; Benson, Daniel, and Boutwell 1999; Alba et al. 2000) have shown that the in situ permeability of clay liners can be orders of magnitude higher than the design value. These results demonstrate the need for a better understanding of the soil properties and accompanying construction techniques to achieve acceptable field performance.

The moisture content and the compacted density of a soil exert primary influence on its hydraulic properties. Moisture, when added to a dry soil, facilitates compaction by lubricating adjacent particles, allowing them to slide against each other into a tighter arrangement. As a result, the density of the soil increases, its porosity decreases, and its in situ permeability decreases. Proctor's work in the 1930s laid the groundwork for understanding soil moisture–density relationships. Mitchell, Hooper, and Campanella (1965) demonstrated how compactive effort affected clay soil permeability. Finally, in 1990, Daniel and Benson performed landmark research to extend these relationships to predict permeability. The most important aspect of this work was the introduction of the concept of an “acceptable zone” of moisture contents and densities that could be measured in the field and would relate to the ultimate performance criterion of permeability. The discussions of design later in this chapter give more information on this concept.

Bentonite Free Swell and Filtrate Loss

Sodium bentonite as an admixture to porous soils improves their workability and decreases their permeability. If the bentonite is effective in filling voids in such soils, bentonite admixtures can be very effective liners. Bentonite also is the barrier component of GCLs. The primary properties of bentonite that affect its performance in both SBLs and GCLs are free swell and filtrate loss (Figure 5).

A free swell test measures the ability of bentonite to swell in an unconfined state. In this test, 2 g of powdered bentonite are slowly distributed into a graduated cylinder filled with deionized water. After 16 hr, the interface between the swollen clay and water is recorded as the free swell. For bentonite used as an admixture, the typical required value is 16 mL; for bentonite used in GCLs, the typical required value is 24 mL.

A fluid loss (or filtrate loss) test comes closer to evaluating a clay's ability to form a hydraulic barrier, although the oil exploration industry developed it to evaluate bentonite-based drilling fluids. In drilling applications, bentonite mixes with water to form a viscous slurry that suspends drill cuttings, lubricates the drill bit, and forms a protective coating on the interior of the borehole. This coating prevents water from entering the borehole and thus prevents its collapse during drilling operations. The fluid loss test mimics the ability of the bentonite to form this layer. A bentonite slurry is subjected to a pressure of 690 kPa (100 psi) and then forced through a filter paper. The fluid loss of the clay is the direct measure of the volume of water that percolates through the filter cake. A high-quality bentonite will form a low-permeability coating and will possess a low filtrate loss. In oil exploration, a value of 15 mL is desired. In GCLs, the industry has established a baseline requirement of 18 mL. The fluid loss test is also important in cutoff wall applications, where a bentonite slurry supports the open trench (see sections on quality control in this chapter).

The origin of these free swell and fluid loss requirements is somewhat uncertain. Olsta, Daniel, and Chung (2004) evaluated bentonite clays of varying free swell and fluid loss values to determine what relationships, if any, they had with respect to permeability.

Interestingly, there was very little correlation between free swell and permeability, especially for free swell values exceeding 18 mL. This value appears to be a threshold above which the bentonite is capable of hydrating into a monolithic mass with few flow pathways. There is a better correlation between fluid loss and permeability; a fluid loss of 18 mL is the upper limit for GCLs required to possess a permeability of 5×10^{-11} m/s. Still, there was considerable scatter in these data, indicating that other clay properties may affect permeability test values.

Although both tests are useful in assessing the quality of the bentonite for a GCL or SBL, neither test alone is a reliable indicator of bentonite's potential as a barrier. There is still a need for a short-term bentonite test that can serve as an indicator for GCL permeability tests, which can take as much as a week to perform.

Contaminant Transport

Clay barriers are used extensively in waste containment applications and therefore should effectively mitigate the flow of waste materials, not just clean water. Landfill leachate is the liquid formed when water percolates through waste. Chemicals and particles in the leachate may eventually contact the liner system, with the potential to cause degradation. In wastewater containment applications, municipal or industrial process water may also contain deleterious chemicals that can affect the liner. Understanding contaminant transport is necessary when evaluating clay liner materials.

Advection

Advection refers to the direct mass flux of contaminants contained in a waste liquid. Advection is quantified by multiplying the flow rate (flux) by the contaminant concentration. Thus, the permeability and flux of the clay barrier completely control advective contaminant flow. Although it is a simple matter to calculate the amount of a specific contaminant being released from a clay barrier, actual flux values are likely to differ significantly from advective flux calculations. The effects of concentration variation, contaminant attenuation, soil liner saturation, and diffusion all complicate the task of modeling contaminant transport.

Goldman's (1988) report for the EPA is an authoritative source for detailed information on the permeability behavior of clay liners with many chemical contaminants. The results of many different studies were assembled to demonstrate that clay soils are affected to varying degrees by different chemicals. It was also found that various clay-chemical interactions can influence permeability and thus advective transport. For example, a chemical can modify the soil "fabric" (its arrangement of particles) by dispersion and flocculation. A chemical that disperses the clay particles (such as sodium in the presence of montmorillonite) can decrease permeability. A chemical that flocculates or collapses the clay particles (such as calcium in the presence of montmorillonite) can increase pore size and increase contaminant flux significantly.

Other chemicals such as strong acids or bases can literally dissolve the clay fabric and thus increase its permeability. Finally, pores can be physically blocked by precipitated metals or microorganisms, leading to a beneficial decrease in permeability.

Diffusion

Diffusion is the movement of contaminants through a liner owing to the presence of a concentration gradient. Advection and diffusion can occur together, but they are totally different transport mechanisms. Whereas advection relies on a hydraulic gradient, diffusion depends on a concentration gradient. Net movement of contaminants will be from areas of higher concentration (above the liner) to

Table 2. Comparison of contaminant transport mechanisms

Feature	Advection	Diffusion
Governing equation	Darcy's law $q = k i C$	Fick's law $q = D^* n (\Delta C/T)$
Transport driving force	Hydraulic gradient (i)	Concentration gradient ($\Delta C/T$)
Intrinsic soil property	Permeability (k)	Coefficient of diffusion (D^*)
Limiting assumption	Saturation of liner	Saturation of liner

areas of lower concentration (below the liner). Table 2 gives a conceptual comparison of these mechanisms.

It is extremely difficult to quantify diffusion, partly because every soil has a unique coefficient of diffusion for each contaminant of concern. The time dependency of the diffusion process is another complicating factor. A great deal of research has been performed to understand how diffusion occurs and to assess its significance as a contaminant transport mechanism. Various researchers have adapted Fick's law to predict contaminant flux. While the means and methods of this research vary, a generally supported conclusion has been that diffusion can be a significant transport mechanism, especially for thin barriers such as plastic geomembranes and GCLs. For CCLs, advection appears to be the dominant transport mechanism when the in situ permeability of the clay is less than 1×10^{-9} m/sec. Refer to works by Brown and Thomas (1998); Foote, Benson, and Edil (1999); Katsumi et al. (2001); Kim, Edil, and Park (2001); and Foote (2002) for detailed discussions of these issues.

Attenuation

Attenuation refers to the ability of a material to absorb or otherwise impede the movement of contaminants. Because clays have a high cation-exchange capacity (CEC) relative to other soils, it has been theorized that clay barriers can serve not only as physical barriers but also as "treatment" media that actively remove contaminants as liquids flow through them.

Early research by Griffin and Shimp (1978) performed when clay barriers were the only widely available option for waste containment focused on known contaminants, such as dissolved metals, in municipal landfill leachates. Column studies revealed that most clays could moderately attenuate K, NH_4 , Mg, Si, and Fe. The same study found that the clays strongly attenuated heavy metals such as Pb, Cd, Hg, and Zn, but organics were not attenuated. Edil, Park, and Heim (1993) also found that volatile organic compounds such as methylene chloride and trichloroethylene were not significantly attenuated. The pH of the leachate and the effects of other solutes in the leachate also altered the attenuation capabilities of the liner materials.

Thornton, Lerner, and Tellam (2001) found that heavy metals were attenuated by sorption and precipitation of metal sulfide and carbonate compounds near the top of the liner. Adequate reserves of sulfates and carbonates are needed for these processes to occur. Ammonium was attenuated by ion exchange but was detected in effluent flow when the exchange capacity was exhausted. They also found that some metals may not be attenuated if they occur as stable complexes with organics in the leachate.

In general, the mechanisms of advection, diffusion, and attenuation are potentially important contaminant transport issues, yet it is difficult to make any general statements regarding the predicted behavior of a clay liner. The type and concentrations

of contaminants, the surrounding chemical environment, the interrelationships of other contaminants, and the unique composition and construction of the clay barrier itself all combine to create a unique “signature” related to its performance in contaminated liquids. For this reason, past research is helpful in understanding the mechanisms by which clays can be affected by chemicals, but it certainly is not predictive with respect to a specific clay liner and specific chemicals of concern.

ENVIRONMENTAL REGULATIONS FOR CLAY BARRIERS

Like clay soils themselves, the regulatory environment for clay liners varies significantly from state to state within the United States and from country to country around the world. Although there are common prescriptive clay liner standards, the requirements set forth by individual regulatory entities vary. The concerns of regulatory personnel, past experience with clay barriers, and the geography within a regulated region all combine to demand a project-specific approach to liner design and construction.

U.S. National Regulations

National rules for clay liners in the United States, which were promulgated by the EPA, exist only for landfill bottom liners and final covers. States regulate clay liners used in other facilities (water and wastewater storage lagoons, etc.). U.S. landfills can be used for the disposal of either “solid” (nonhazardous municipal) or hazardous waste. The rules for the containment of solid waste are understandably less stringent than those applicable to hazardous waste disposal facilities. In both cases, however, the clay liner requirements are similar, varying only in the thickness required for each type of facility.

Solid Waste Landfills

The national regulations for solid waste landfills appear in 40 CFR 258 (also known as Subtitle D; EPA 1988). EPA provides the states with considerable latitude in implementing these rules because they are risk based. This means that a landfill is permitted only when it will not exceed groundwater quality criteria at its boundaries. These criteria are drinking water standards for which numerical limits are derived from toxicological studies designed to identify the relative risk of exposure to various contaminants. Thus, the primary intent of 40 CFR 258 is not to provide detailed landfill design instructions, only to ensure that human health is protected regardless of the design selected. In this way, EPA allows the use of any type of liner system if it can be shown to protect groundwater.

Recognizing that there may be insufficient data to develop a detailed design based on this approach, EPA offers an optional approach in which specific liner design criteria are listed. 40 CFR 258.40(a)(2) indicates that a composite liner, consisting of a geomembrane and a clay layer, is an acceptable alternative to the risk-based design approach. According to this section, the clay component of the composite liner must be 2 ft (600 mm) thick with a permeability not to exceed 1×10^{-9} m/sec (EPA 1988). For a final cover on a solid waste landfill, 40 CFR 258.60(1) requires a soil cover less than or equal to the permeability of the bottom liner, but at least 450 mm thick with a permeability not to exceed 1×10^{-7} m/sec. Interestingly, these are the only prescriptive performance standards for clay liners for any application regulated by EPA.

As might be expected, states that administer their own solid waste disposal programs prefer these specific prescriptive standards. Although the need for a composite liner system in, for example, Nevada, might be less than that in Florida, regulatory entities prefer to adopt the prescriptive approach to guarantee their compliance with national regulations. This means that any liner system not

specifically meeting the prescriptive standard must be evaluated as an “alternative” design and therefore subject to careful scrutiny as a potential replacement for the geomembrane and clay composite system mentioned in Subtitle D.

Hazardous Waste Landfills

The EPA regulations for hazardous waste landfills are codified in 40 CFR 256 (Subtitle C; EPA 1988), with liner criteria specified in Section 264.301(c)(1)(B). The liner must be at least 900 mm thick with a maximum permeability of 1×10^{-9} m/sec. For final covers, the regulations in Section 264.310(a)(5) mirror the solid waste regulations with respect to thickness and permeability requirements. Final covers on hazardous waste landfills must contain a compacted soil liner with a thickness of 900 mm and a permeability no greater than 1×10^{-9} m/sec.

Furthermore, hazardous waste landfills require a “double composite” system in which two independent composite liners are installed with a leak detection system between them. Interestingly, some states (Florida, Michigan, and New York) have also adopted this rigorous standard for their solid waste landfills.

Thickness Requirements

The default soil liner thickness is 2–3 ft, or 600–900 mm. In almost any country or state, these thickness requirements rarely differ. What is the rationale behind a thickness requirement of 600–900 mm? Although its origin is unclear, the requirement has been in existence at the state level since the 1970s. It was not until many years later that research verified the adequacy of this thickness range.

Benson and Daniel (1993a, 1993b) researched the hydraulic performance of clay liners of varying thicknesses. They concluded that there is little improvement in performance when the thickness of a clay liner is increased beyond 600–900 mm (4–6 lifts). Because clay liners are installed in lifts that are 250–300 mm thick, the performance of the liner relates to the performance of the lifts rather than the liner as one continuous layer. Benson and Daniel found that four to six lifts provide a liner with the redundancy needed to minimize the potential for preferential flow pathways to penetrate through the entire liner. In other words, there is a point of diminishing returns when landfill liners are more than 900 mm thick, and the performance benefits seldom justify the expense of building a thicker soil liner. Thus it appears there is sound technical justification for the currently adopted liner thickness regulations, even if the thickness rules predated the supporting data.

Hydraulic Conductivity Requirements

In almost all U.S. and international regulations, the hydraulic conductivity requirement for a clay liner is 1×10^{-9} m/sec. Although occasional exceptions to this value are based on environmental risk levels specific to different locations and applications, it is clear that the generally acceptable clay liner must achieve a permeability of 1×10^{-9} m/sec in both laboratory and field quality control (QC) testing.

There is no known precedent for the universal selection and adoption of this value. In all likelihood, a permeability of 1×10^{-9} m/sec represents a performance standard that is a compromise between achieving maximum containment and achieving reasonable cost and construction feasibility. In other words, higher permeability requirements (such as 1×10^{-8} m/sec) could result in unacceptable levels of environmental contamination, whereas lower requirements (such as 1×10^{-10} m/sec) may not be possible to achieve with many soils and would create undue technical and

financial burdens associated with identifying clay materials that could achieve this value.

GCLs in National Regulations

Although GCLs constitute a large and growing fraction of landfill liner and cover systems built in the United States, they are not mentioned in any Subtitle C or D rules, because the rules were written long before GCLs were commercialized and used in landfills. The first landfill use of a GCL was in 1985 when Claymax was installed into an industrial waste disposal cell in a Chicago, Illinois, landfill. The GCL was sandwiched between two geomembranes and served as a secondary component of the liner system that was not required under Illinois law at the time. GCLs were then installed in 1986 in two municipal landfills in Pennsylvania, again to supplement, not replace, the clay component of the liner system required by law. Other than these uses, GCLs did not gain widespread commercial use until 1992–1994, about 1 year after Subtitle D was finally issued.

Because EPA rules do not cover GCLs, a great deal of research has compared them to the clay prescriptive standard. If it can be shown that a GCL is equivalent to the CCL, then it may be approved for use. Koerner and Daniel (1993) authored a comprehensive equivalency review of GCLs and CCLs. The review covered all major design, performance, and construction issues that might be of concern to regulators tasked with evaluating whether a GCL could be considered “equivalent” to a CCL (and thus acceptable for use in a Subtitle D-compliant landfill liner or cover system).

They concluded that GCLs were indeed equivalent and often superior to CCLs in most aspects of comparison. Using this and other equivalency concepts, GCLs have emerged not only as acceptable but often as preferred alternatives to CCLs, as is explained in the section on Geosynthetic Clay Liners in this chapter.

State Regulations

For landfills, liner systems are regulated at the state level assuming that the state solid waste management program is in general compliance with the national rules in Subtitle C and D. In many cases, the state regulations are virtually identical to the national regulations already discussed. Many states, however, have adopted more or less stringent liner design rules based on their specific geographical situations. States in humid climates have more stringent liner regulations than those in arid climates. Florida, for example, requires a double composite liner system containing two geomembranes and two clay components. Wyoming, on the other hand, requires only a single liner system consisting of a CCL, a GCL, or a geomembrane. This is exactly what EPA intended in promulgating risk-based standards in stead of an overall requirement that might place an unreasonable burden on some states or may not be sufficiently protective of human health in others.

States also have liner regulations pertaining to wastewater storage lagoons. The most widely recognized regulations are adopted from the Great Lakes–Upper Mississippi River Board of State and Provincial Public Health and Environmental Managers (1997). This group developed the so-called “ten-state standard” that contains clay liner design requirements for wastewater storage facilities. The ten-state standard is expressed in terms of a maximum leakage rate of 500 gal/acre/day, or 4,695 L/ha/day, at a depth of 6 ft (1.8 m). Assuming a thickness of 600 mm, this equates to a permeability of 1.8×10^{-9} m/sec, which is slightly higher than the de facto standard appearing in other regulations.

Not all states have adopted this standard. As with landfills, states developed wide-ranging liner performance criteria depending on specific issues relevant to each state. It is beyond the scope of this chapter to list all the different state level rules for such facilities.

Other Regulations

The United States has influenced liner system design and regulation worldwide. Although countries vary significantly in clay liner requirements, many adopted the EPA’s prescriptive standard liner system. Koerner and Koerner (1999) summarize worldwide landfill liner system regulations. In general, more developed countries have more stringent regulations than those that are less developed.

The European Union adopted a clay liner requirement of 1 m thickness and 1×10^{-9} m/sec permeability; this rule applies to both landfill bottom liners and landfill covers (CEC 1999). For hazardous waste landfill liners, the thickness requirement is 5 m and the same permeability value of 1×10^{-9} m/sec.

COMPACTED CLAY LINERS AND SOIL-BENTONITE LINERS

Although CCLs and SBLs are constructed in different ways, the general design issues discussed herein are applicable to both types of liners.

Design

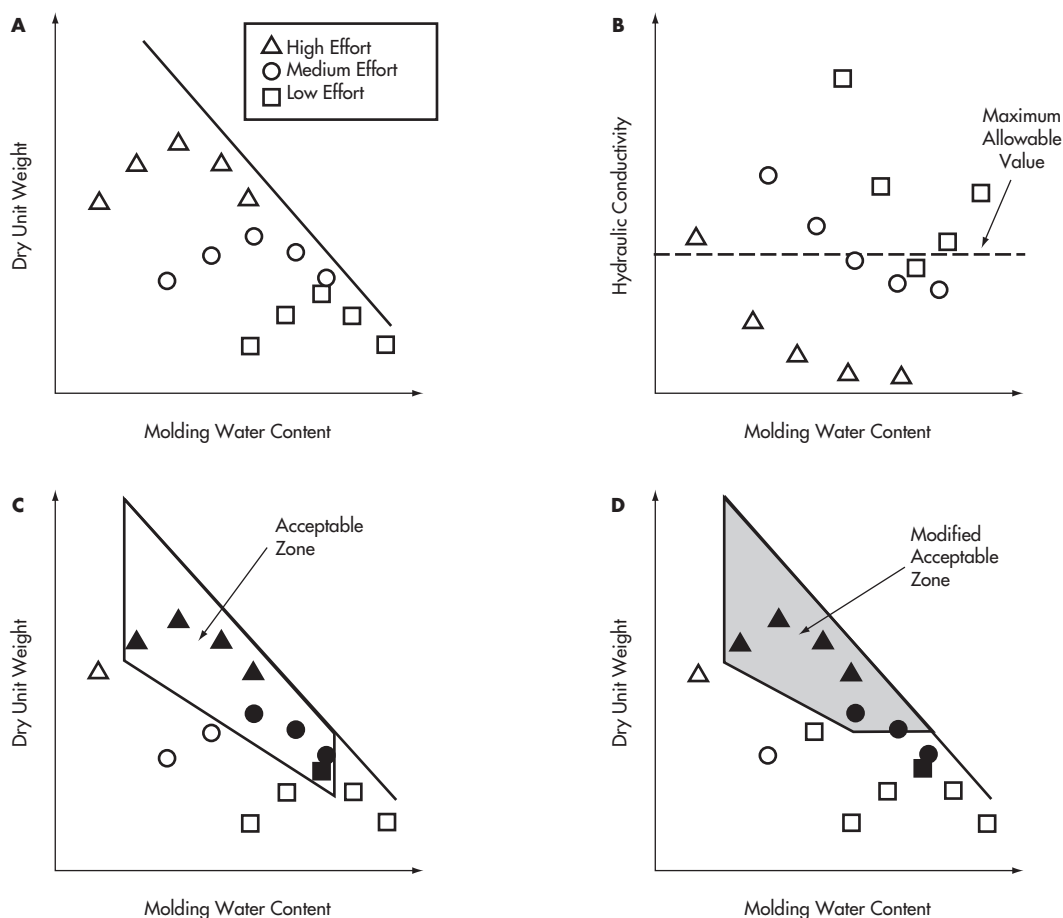
The design of a clay liner requires detailed knowledge of the soil properties such that a technically appropriate specification can be written. A designer is interested primarily in moisture-density relationships, water balance models, time of travel, and slope stability.

Moisture–Density Relationships

The hydraulic performance of a clay liner depends greatly on properly determining the relationship between soil moisture, density, and permeability. The designer must identify acceptable clay soil sources for the project. Determining whether these sources contain soils that can achieve the required permeability values is best accomplished with a four-step process, as described in Daniel and Benson (1990):

1. Obtain representative samples of the candidate soils and compact them in the laboratory using standard, modified, and reduced effort to achieve compaction curves (plots of density versus moisture content), as shown in Figure 6(a).
2. Perform permeability tests on the samples and plot the resulting permeability versus moisture content. Also plot the maximum acceptable permeability (typically 1×10^{-9} m/sec) to distinguish between acceptable and unacceptable samples, as shown in Figure 6(b).
3. Highlight all the data points with “acceptable” permeability values (falling below the permeability pass/fail line from step 2) on the plot from step 1. Draw an “acceptable zone” on this plot, with the zero air voids curve as the outer border and the acceptable permeability data as the inner border, as shown in Figure 6(c).2
4. Modify the acceptable zone, as shown in Figure 6(d), to account for other design criteria such as realistic water content and shear strength. These are project-specific modifications that are made to derive a single acceptable zone for the soil in question.

Using this four-step procedure, a designer can identify the range of acceptable moisture and density values that must be achieved in the field to obtain the required permeability value. This information is used not only to qualify candidate soils but also to facilitate the construction quality control (CQC) and construction quality assurance (CQA) processes. Moisture and density can be measured rapidly and inexpensively in the field, whereas permeability tests are slow and relatively expensive. The moisture and density data then can be used to ensure maximum probability that the ultimate performance criterion—permeability—will be reliably achieved.



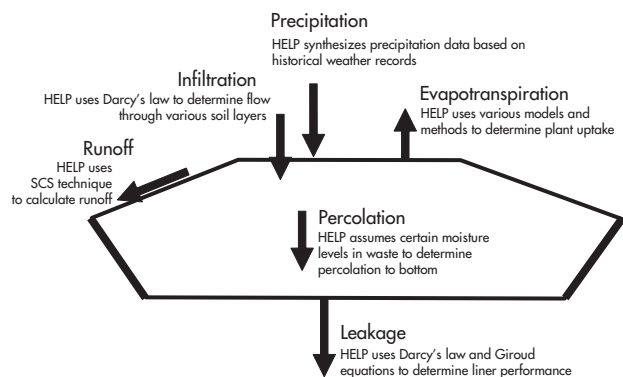
Courtesy of David Daniel.

Figure 6. The process for determining a zone of moisture and density values that will result in acceptable permeability values

Water Balance Models

Mathematical water balance models are often used to demonstrate that the liner system, consisting of multiple layers of soils and geosynthetics, will meet applicable regulatory performance criteria and will not allow harmful levels of contaminants to escape a waste containment facility. Many different models are available, but the most popular and relevant model is known as the hydrologic evaluation of landfill performance (HELP). The HELP model is actually a compilation of several smaller models that simulate precipitation, runoff, percolation through various soil layers, and ultimately the amount of liquids that penetrate into or through a landfill system (Figure 7). For CCLs and GCLs, the model uses Darcy's law to calculate leakage performance (Schroeder et al. 1994).

Designers use the HELP model to determine whether a proposed or existing landfill could allow enough leachate to flow into and contaminate groundwater. If the modeling results are unfavorable, the designer can alter various input parameters such as increasing the slope of the landfill final cover, adding a barrier layer, or decreasing the spacing of leachate collection drains. Although the simulation requires numerous simplifying assumptions, the HELP model is a valuable tool to the designer because it demonstrates how various landfill design parameters can ultimately influence its environmental performance.



Courtesy of CETCO.

Figure 7. Conceptual schematic of the HELP model

Time of Travel

Theoretically, a clay liner behaves as a perfectly monolithic barrier with uniform hydraulic characteristics from top to bottom (the "plug flow" concept). This is seldom the case, as is discussed in the section on Performance of Clay Barriers in this chapter. It still may be useful to the designer, however, to evaluate CCLs in terms of

how long they will ideally contain a leachate of concern. Assuming that the liner is perfectly constructed, it will not allow contaminants to be released until the leachate front progresses from the top of the liner to the bottom. Various analytical methods have been proposed for estimating this time as a means to justify the design life of a waste containment facility (Horton, Thompson, and McBride 1988; Goode 1990; Benson and Charbeneau 1991), but the basic concept of travel time involves knowledge of the soil's permeability and *effective porosity*. Effective porosity is the fraction of total porosity that is capable of conducting flow. This is a difficult parameter to measure and renders accurate time of travel estimates difficult. Moreover, with real-world construction problems such as clods and interlift flow zones influencing flow (refer to Performance of Clay Barriers section in this chapter), the time of travel calculation is not as relevant as once believed.

Slope Stability

Sloping surfaces, whether they are lined with a CCL, a GCL, or some combination of natural and synthetic materials, must be proven to be stable. Assessing the stability of a lined slope is perhaps the designer's greatest challenge because it requires knowledge of the materials of construction, testing methods, and stability modeling. Many methods exist for calculating the stability of sloping liner systems, ranging from simplified sliding-block analyses to sophisticated finite element analyses. There is no single "best" analytical method; the most appropriate method depends on the type of liner system, the type of forces to which it may be exposed, and the relative skill and expertise of the designer. The reader is referred to works by Koerner (1994) for a more detailed discussion of the various techniques that can be used in assessing slope stability.

With respect to CCLs and GCLs, the designer is interested in measuring the shear strength of the clay internally as well as the strength of the interfaces between the liner and adjoining materials. With this information, rational analyses can be made to determine overall stability under the normal and shear loads expected for the system. Internal shear strength refers to the strength of the clay itself and whether interparticle interactions are sufficient to resist movement when shear stress is applied. Compacted clays are usually fairly strong in this regard, although "fat" clays with high moisture contents must be evaluated carefully. GCLs, with hydrated bentonite, may have very low internal shear strength unless the GCL itself is reinforced. Designers should be careful to consider the internal strength of a GCL whenever it is proposed for use on slopes.

The interface between the clay liner and adjacent materials is another potential failure plane. For example, a smooth geomembrane placed on a smooth, compacted clay surface constitutes a low-strength interface that presents considerable limitations for designers seeking to maximize slope steepness. By assessing the strength of all relevant interfaces in a liner system, the designer can identify the weakest interface and propose alternative materials that may be needed to demonstrate stability with an acceptable factor of safety.

Construction

After the designer identifies proper materials, the field performance of a clay barrier depends on the quality of its construction. Several decades of experience, research, and trial and error have led to knowledge of which construction variables influence performance and how to manage these variables in the most favorable way possible.

Equipment Requirements

Because the success of a compacted clay barrier depends on achieving the proper level of compaction, a fundamental require-

ment for proper construction is heavy compaction equipment. Daniel (1990) recommends compactors with a minimum weight of 15,000–20,000 kg (30,000–40,000 lb) equipped with footed rollers whose foot length is at least 20 cm (7.5 in.). The combination of high weight and footed rollers produces a "kneading" action that delivers high compactive energy to the soil and promotes bonding between individual lifts of the liner.

Even with these parameters specified, adequate compaction still may not be achieved unless the compactor makes a minimum number of passes over the soil. Daniel recommends at least six passes to achieve uniform compaction and density. Multiple passes also break up clods that can cause excessive flow through the liner.

Moisture Control

The acceptable zone of moisture and density determined in the design phase must be maintained consistently during the construction process. Water must be added to the soil (especially for a bentonite-admixed soil) before compaction. This is accomplished using a water truck equipped with a spray bar that can pass over each lift of precompacted soil.

Physical Processing

Depending on the quality of the soil, a screening system may be necessary to remove stones larger than the design requirements (typically 50 mm). A suitable "borrow" soil would require no further processing except where bentonite is used as an admixture. In this case, bentonite can be added in one of two ways. The simplest method, suitable for smaller projects with thin liners (<300 mm), is to place the bentonite on the surface of the subgrade and blend it with the soil using a tiller. Water is added to the SB mixture before compaction. The second method is to use a pug mill (Figure 8) to blend the soil and the bentonite together continuously. The mixture is then delivered in trucks to the working area where it is placed, spread to the specified loose lift thickness, and compacted.

Quality Control

The construction process must be continually monitored to ensure that the CCL or SBL meets the applicable permeability requirement. A properly engineered liner construction project will have a comprehensive CQC and CQA program that includes third-party inspection and testing, as described in Table 3.

The QC program should also contain provisions to deal with a failing test result, and the typical procedure in such instances is to retest the sample. If another failure results, the area from which the sample was obtained is reworked, recompacted, and resampled until passing results are achieved.

To verify the overall adequacy of the design and construction procedures intended for the liner, a test pad is often specified. A test pad is a small section of liner built specifically for testing. If passing results are obtained from the test pad, it can be presumed that the project can continue without any modification in materials or methods.

Economics and Market Trends

It is difficult, if not impossible, to make any conclusive statements regarding the economics and market conditions of clay liner construction. Based on the author's experience and market knowledge in the United States, Europe, and Asia, the following tentative statements can be offered as a general assessment of the clay liner market:

- It is conservatively estimated that at least 500 engineered landfill liners are built in the United States each year, and that at least double this number (1,000) clay liners are built for



Courtesy of CETCO.

Figure 8. Trailer-mounted pug mill (a) and close-up view of mixing blades (b) for combining bentonite with screened soil

ponds and lagoons. There is no way to verify the accuracy of these estimates, and no information is available on the world size of the highly fragmented clay liner market.

- The typical installed cost for a CCL with a thickness of 600 mm is \$4.50/sq m to \$5.00/sq m. The cost of a CCL varies significantly by region, based on materials availability, land costs, hauling costs, labor rates, and professional services. A CCL installed in the Northeast and West Coast are as of the United States would be more expensive than this range, whereas the same liner installed in the Midwest and Southeast would likely be less than this range.
- As GCLs become more commonly accepted alternatives to CCLs, the number of CCLs constructed each year will decrease, especially in waste containment applications (landfill bottom liners and covers). CCLs are typically more economical than GCLs only when clay soil is located at the project site.
- SBLs represent a small fraction, less than 5%, of all clay liner systems constructed worldwide.
- For facilities with engineered liner systems, QC costs are approximately \$250/ha.

This information is based on general market knowledge only. There are no authoritative sources for such information nationally or internationally.

Table 3. Summary of QC procedures for a CCL or SBL

QC Category	Required Activity	Desired Result
Raw materials	Set Atterberg limits and PI	PI > 10%
	Establish maximum particle size	25–50 mm
	Establish maximum gravel content	<20%
	Establish minimum fines content	>30%
Equipment	Ensure adequate compactor weight	>15–20,000 kg
	Ensure adequate footed roller	>20 cm
Compaction	Establish minimum number of passes	>6
Liner lifts	Establish maximum loose lift thickness	25 cm
	Establish maximum compacted lift thickness	15 cm
	Ensure previous lift surface is scarified	Yes
	Measure in-place density	Within acceptable zone
	Measure in-place moisture	Within acceptable zone
	Measure lab permeability	Below minimum requirement
	Measure in situ permeability	Below minimum requirement
	Protect against desiccation cracks	Yes

Adapted from Daniel 1991.

GEOSYNTHETIC CLAY LINERS

GCLs represent an interesting subset of clay barriers. Part geosynthetic material and part bentonite clay, these unique hybrids are growing in popularity as partial or complete substitutions for CCLs because of their attractive price, ease of installation, and high performance under demanding site conditions.

GCL Types and Production Methods

GCLs consist of a layer of bentonite clay bonded to one or more geosynthetic materials such as geotextiles or geomembranes. GCLs are separated in to two broad classes based on their internal shear-strength properties:

- **Unreinforced**—These GCLs contain bentonite clay, which, when hydrated, offers only as much shear strength as the clay itself. Examples of unreinforced GCLs include Claymax 200R (CETCO, Arlington Heights, Illinois) and Gundseal (GSE, Houston, Texas). It should be noted that these products differ significantly. Claymax is made with a layer of bentonite laminated between two encapsulating geotextiles. Gundseal consists of a layer of bentonite adhered to a geomembrane. Unreinforced GCLs are used in applications where significant shear forces are not expected. Gundseal is occasionally used on slopes, however, if the bentonite layer is permanently protected from hydration.
- **Reinforced**—These GCLs consist of bentonite clay sandwiched between two geotextiles that are needle-punched or stitched together to reinforce the bentonite layer and to give it additional shear strength. Reinforced GCLs are used in applications where the liner system must be able to withstand shear loads. Examples of reinforced GCLs include Bentomat (CETCO); Bentofix (N AUE GmbH & Co.,

Lübbecke, Germany); and NaBento (HUESKER Synthetic GmbH, Gescher, Germany).

Designing with GCLs

GCLs are intended to replace CCLs. Many GCL design issues involve the comparison of GCL performance to that of CCLs in various situations. These equivalency issues can be categorized as hydraulic, geotechnical (slope stability), and chemical (compatibility with liquid contaminants).

Hydraulic Performance

The hydraulic performance requirements for CCLs are clearly regulated in terms of liner thickness and permeability. From these parameters, a designer can use Darcy's law to determine whether the steady-state flow rate from a GCL can be considered equivalent to that of a CCL under the same confining pressure and head pressure conditions. To perform this analysis, it is necessary to understand that GCL permeability varies considerably with confining stress (Figure 9), and so it is necessary to ensure that relevant confining stress conditions are used in the calculation. GCL manufacturers can also provide flux data to allow a direct comparison of GCLs and CCLs under similar conditions.

Based on several years of test data and successful field usage, GCLs are now generally considered to be fundamentally equal, if not superior to, CCLs in terms of baseline hydraulic performance, most notably for landfill bottom liner applications where high confining stresses result in low permeability and flux values. Data collected from landfills in the United States (Bonaparte, Daniel, and Koerner 2002) indicate that liner systems containing a GCL leak less than those containing a CCL (Figure 10). These data do not independently compare GCLs and CCLs because the liner systems also contain a geomembrane component. Nevertheless, it is clear that a GCL-based liner system outperforms other liner systems at each life cycle stage of the landfill.

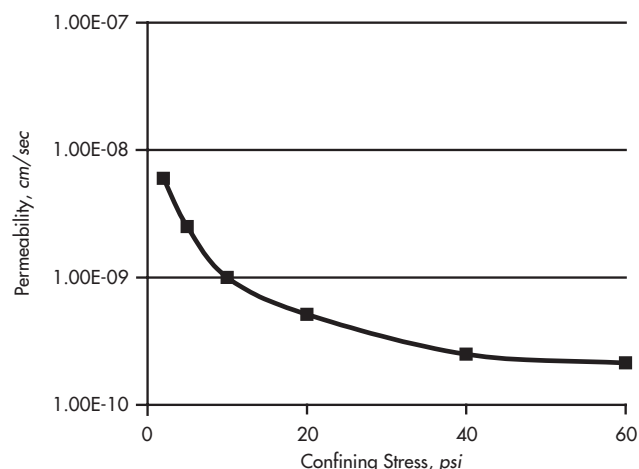
Seam Flow

In any geosynthetic liner system, the potential for a leakage problem is greatest at the longitudinal and lateral seams where adjacent liner panels are connected. With GCLs, there is no mechanical attachment of the panels; they are merely overlapped. Some GCLs require additional granular bentonite along the overlap to ensure that self-seaming occurs. Properly installed, GCLs have been proven to be self-seaming such that the hydraulic performance of the seam is almost the same as unseamed material (Estornell and Daniel 1992). Achieving this result requires some confining pressure, approximately 7 kPa. Cover soil layers typically provide this confinement, with the additional benefit of physical protection of the liner system from equipment, animals, and erosion.

Slope Stability

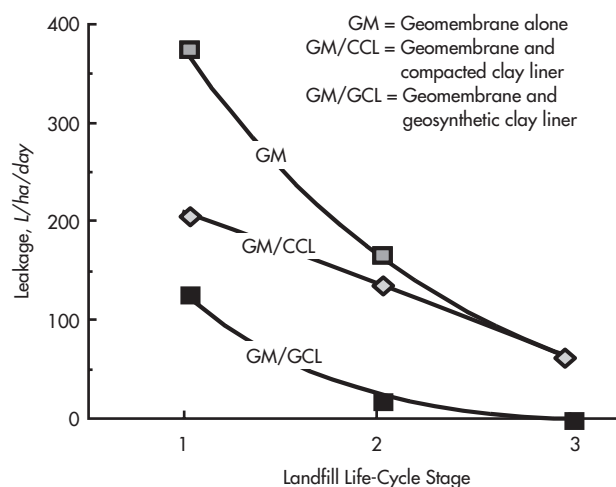
GCLs demand special attention with respect to slope stability. The designer must be aware of the internal strength of the GCL and the strength of its two external interfaces. Project-specific direct shear testing is needed to understand these properties. When project-specific materials are evaluated at a competent geotechnical laboratory, the resulting data can be entered into a mathematical model to assess the stability of the planned design.

Many useful mathematical stability modeling techniques have been developed (Giroud and Beech 1989; Wilson-Fahmy and Koerner 1993; and Soong and Koerner 1996, to name only a few) that expertly address this paramount design concern. Using one of these models, in combination with previous project experience,



Courtesy of CETCO.

Figure 9. GCL permeability decreases as confining stress increases



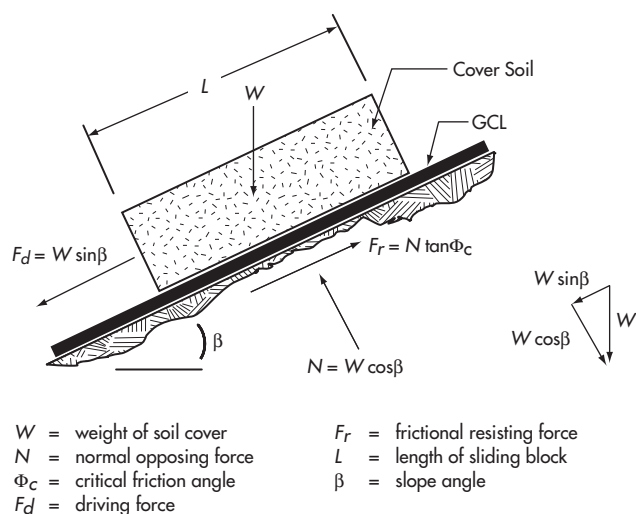
Adapted from Bonaparte, Daniel, and Koerner 2002.

Figure 10. Average leakage rates for different types of landfill liners

large-scale laboratory shear test data, and conservative engineering assumptions, it is possible to design a stable slope even when multiple soil and geosynthetic layers are placed adjacent to one another.

The designer must also assess global slope stability, which is related to the stability of the soil beneath the liner. Global stability considerations can be evaluated using several textbook methods. Koerner (1994) gives a good summary of these considerations.

Interface Shear Strength. A thorough stability analysis requires evaluating every interface in the liner system. Ideally, each interface should be capable of generating enough friction to transfer the driving force into the subgrade. The amount of friction for a given combination of soil and/or geosynthetic layers can be expressed as an angle when the shear strength is measured at several normal stresses. For example, the interface friction provided by a soil cover layer can be tested by measuring the shear strength at normal stresses of 100, 300, and 500 psf (5, 14, and 24 kPa). The angle described by the line connecting these shear values is the friction



Courtesy of CETCO.

Figure 11. Sample slope stability diagram for a soil layer resting on a GCL, which in turn rests on a compacted clay liner

angle between the top of the liner and the cover soil. In a simple sliding block analysis, the slope is stable if the friction angle is greater than the slope angle (Figure 11).

Internal Shear Strength. The first bentonite liners on the market in the mid-1980s were unreinforced, meaning that the internal shear strength of the GCL was no greater than the low shear strength of the hydrated bentonite layer (around 8°). The resulting design process was, therefore, relatively straightforward, although quite limiting because of bentonite's low shear strength. When needlepunched products such as Bentomat were introduced in the early 1990s, peak internal shear strength properties increased significantly. These products can safely be placed on much steeper slopes.

Internal shear strength must be demonstrated both in the short term and the long term, and ideally for the life of the lined facility. Laboratory research (Trauger, Swan, and Yuan 1996) indicates that needlepunch-reinforced GCLs can sustain long-term shear loads. Field-scale testing (Koerner 1996) and actual project experience have yielded similar conclusions relating to the high internal shear strength of GCLs in commonly encountered liner configurations. From the data and experience gained to date, it is reasonable to assume that GCLs will maintain significant internal strength in the long term.

Chemical Compatibility

Any liner must have the ability to resist chemical attack when used in containment applications where contaminants may be present. Although chemical compatibility is actually a subtopic of hydraulic performance, this issue is worthy of a separate discussion.

Sodium bentonite is an effective barrier primarily because it can absorb large quantities of water (i.e., swell). When the bentonite component of the liner hydrates, it becomes a dense, uniform layer with exceptionally low permeability. Water absorption occurs primarily because of the presence of sodium ions situated in the interlayer region between clay platelets (Figure 12).

Contaminant Effects. Sodium bentonite that is hydrated and permeated with relatively clean water will be an effective barrier indefinitely. The interlayer sodium ions, however, can be

exchanged with other cations that may be present in the water during the hydration or permeation process. This type of exchange reaction reduces the amount of water that can be held in the interlayer, resulting in decreased swell. Anions will also reduce swell. The loss of swell usually causes increased porosity and decreased performance as a hydraulic barrier; this is the primary mechanism for the chemical contamination of bentonite. Other chemicals such as organic molecules are far less likely to affect bentonite and are seldom encountered in concentrations needed to affect its performance. Table 4 lists potential bentonite contaminants that are commonly found in liquids requiring containment.

Experience has shown that calcium is the most common source of compatibility problems for bentonite-based liners. Other cations (magnesium, ammonium, potassium) can also contribute to compatibility problems, but they generally are not as prevalent or as concentrated as calcium (Altherr et al. 1985). Such cations may already be present in the water to be contained or may leach into the water from cover soils on the liner.

It is not possible to specify the maximum concentration at which a certain chemical becomes a compatibility problem because of the many variables involved in assessing performance. These variables include exposure time, confining stress, hydraulic pressure, hydration liquid, temperature, and chemical interactions between different contaminants. In lieu of blanket recommendations, routine compatibility tests (ASTM D6141 and D6766) should be performed to determine if the chemical or leachate can affect the liner. The liner may also be sensitive to the chemical composition of soil placed over it, such that limestone and other calcium-rich cover soils should be avoided.

Construction

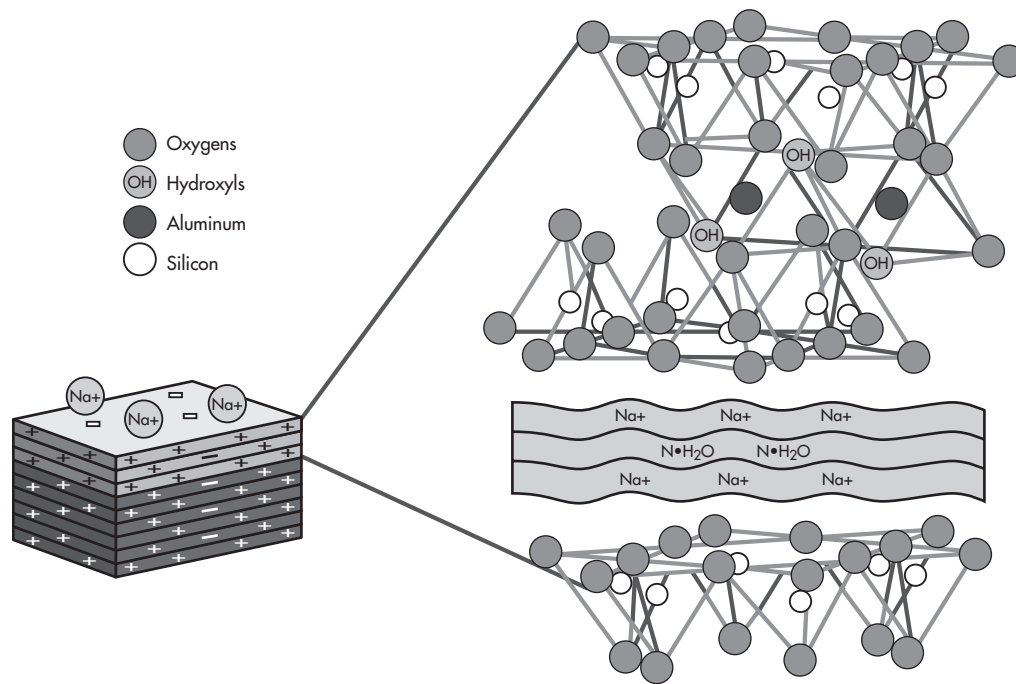
A primary advantage of GCLs over CCLs is their relative ease of construction. Supplied in rolls, GCLs are installed by unrolling the material along the intended path of deployment (Figure 13). A spreader bar and core pipe suspend the roll freely from the moving equipment. Installation rates of 1 ha/day (2.5 acres/day) are not uncommon on large projects, which is a significantly faster deployment rate than for CCLs. Deployment should begin only when the subgrade surface has been made smooth, stable, and free of protrusions.

At the top of a slope, the end of the GCL roll is typically placed in an anchor trench to prevent downslope movement or to promote slope stability (Figure 14). The GCL can be cut with a utility knife to the necessary length and can be installed around foundations and appurtenances by cutting and sealing with dry bentonite or a bentonite paste (Figure 15). GCL manufacturers provide detailed installation guidelines covering other common installation situations such as perimeter wall connections, repairs, pipe penetrations, and corners.

One of the most important steps in the GCL installation process is covering. If covered with another geosynthetic layer (such as a geomembrane), the GCL is not as susceptible to damage by subsequent site activities. If the GCL is covered with soil, however, as is common in landfill cap applications, the GCL can be damaged. Designers should specify the minimum soil thickness that should be maintained between the GCL and covering equipment, and covering activities should be carefully monitored to ensure that the equipment does not come in direct contact with the GCL.

Quality Control

GCLs are factory-made liners and many undergo quality tests in accordance with ASTM D5889. The raw materials (bentonite clay, geotextiles, and geomembranes) undergo testing, as does the



Courtesy of CETCO.

Figure 12. Molecular structure of montmorillonite (bentonite), showing absorbed sodium ions nested within the interlayer water

Table 4. Contaminants that can affect bentonite performance

Cations	Anions
Calcium (Ca ⁺²)	Chloride Cl ⁻ (
Magnesium (Mg ⁺²)	Sulfate SO ₄ ⁻³ (
Potassium (K ⁺)	Nitrate NO ₃ ⁻ (
Ammonium (NH ₄ ⁺)	Carbonate (CO ₃ ⁻)
Sodium (Na ⁺)	Hydroxide (OH ⁻)
Iron (Fe ⁺²)	
Aluminum (Al ⁺³)	

NOTE: Other contaminants may exist; these are the ones most commonly encountered.



Courtesy of CETCO.

Figure 13. Typical GCL installation method



Courtesy of CETCO.

Figure 14. Placement of a GCL into an anchor trench



Courtesy of CETCO.

Figure 15. Sealing a GCL around a structure

finished GCL product. The engineer receives QC information upon delivery to ensure that quality criteria have been achieved. The factory-oriented QC process for GCLs means that there is little field QC required, which results in time and cost advantages over CCLs.

Engineers often require additional quality data such as permeability or direct shear test data before granting final approval of the GCL materials. The scope and frequency of these tests are quite dependent on the nature of the project. In general, GCLs exhibit consistent hydraulic and mechanical properties, tending to reduce the need for frequent (and costly) tests.

Economics and Market Trends

The GCL market is fairly stable in North America but is rapidly evolving in other parts of the world. The two major GCL manufacturers in North America share a market estimated to be 15 million sq m in 2004. Europe, with a 2004 estimated market of 12 million sq m, has approximately six GCL manufacturers, creating a more fragmented and regionalized marketplace that caters to the unique regulatory, cultural, and economic status of European countries.

Asia has approximately four credible GCL producers, with up to 15 other companies (many in China) claiming to provide GCLs. The largest Asian GCL market is China, whose rapidly expanding economy requires secure waste containment facilities. Hong Kong, Korea, and Japan have used GCLs for a longer period of time, since approximately 1993, but they are not perceived as growth markets. The total Asian market is approximately 3 million sq m.

GCL pricing has decreased dramatically since its introduction in the early 1990s. North American unit pricing at that time was approximately \$5.50/sq m but has since dropped to an average of \$3.00/sq m for standard products (on a medium-sized project of 10,000 sq m). The price decrease represents the evolution of GCL technology from low-volume specialty product to high-volume commodity product. Pricing levels in North America have been relatively stable since 1999, with occasional price increases offsetting increased raw materials costs. In Europe and Asia, pricing over the past 5 years has fallen more quickly, although these markets are also showing signs of stabilization. Another factor affecting prices has been consolidation within the geosynthetics industry, where various mergers and acquisitions are creating a stabilizing force in the GCL market.

GCLs are heavy, and freight costs are often significant. In North America, freight costs range from \$0.10/sq m to \$0.70/sq m,

with an average of \$0.40/sq m. Exporting GCLs from Europe or North America adds ocean freight costs and increases the typical freight charge to \$0.60–\$1.00/sq m.

A nominal estimate of the installation cost of GCLs in North America is \$1.50/sq m. This cost includes only the materials handling and deployment processes and does not include appurtenant activities such as subgrade preparation or covering. In consideration of labor wages worldwide, deployment costs in Asia are expected to be somewhat lower than this amount, whereas in Europe (especially Western Europe) deployment costs would be higher. In total, then, the installed cost of a GCL in North America can be reasonably estimated as \$4.90/sq m (\$3.00 + \$0.40 + \$1.50).

CUTOFF WALLS

Cutoff walls are a unique category of clay barriers. In consideration of the vast amount of horizontal clay barriers used worldwide for water and waste containment, the usage of cutoff walls is small and the discussion contained herein is limited. Detailed design and construction methods are available in works by Spooner et al. (1985), Xanthakos (1985), and Noyes (1975). In addition, two ASTM publications (Alther et al. 1985; Millet, Perez, and Davidson 1992) also offer relevant information from previous technical symposia on slurry walls. Cutoff walls still represent an important technology, however, for controlling groundwater flow and for mitigating the damage created by ineffective horizontal barriers built in decades past.

Design

Cutoff wall applications involve building a subsurface vertical barrier to control groundwater or contaminant flow. Therefore, the first step in the design of a subsurface barrier is to evaluate the site conditions and overall feasibility (Spooner et al. 1985). In certain cases, limited access because of existing infrastructure may not allow the area of concern to be encircled to the extent necessary to control groundwater movement. Additionally, the depth to groundwater must be evaluated to ensure that it is close enough to grade to allow trenching. Most cutoff walls are not feasible or cost-effective if the depth is greater than 30 m, although successful cutoff walls have been installed as deep as 125 m. Finally, the geology of the site must be examined to determine whether trenching is possible. Sites with shallow bedrock are seldom acceptable for cutoff wall techniques and sites without an accessible aquiclude may not be feasible for cutoff wall construction.

Assuming that there are no insurmountable site and feasibility restrictions, the next phase of design involves selecting the type of wall to install. There are many types of cutoff walls, each with their own set of advantages and limitations. Walls containing clay as the principal hydraulic barrier are SB walls, CB walls, and SCB walls. The designer selects the appropriate wall type based on the nature of the subsoils, the hydraulic performance requirements for the cutoff wall, chemical compatibility issues (Day 1994), structural considerations, and cost. With information pertaining to site constraints and performance requirements, it is possible to select a wall type most suitable for the project. Table 5 lists some of the major points of comparison between SB and CB walls. SCB walls would fall in the middle of these ranges.

The next step in the design is to create a specification for the installing contractor. The specification should include all relevant performance properties of the construction materials and the finished wall, including final permeability, compressive strength, and thickness. Darcy's law can be used to determine the wall thickness required for adequate containment at a certain *in situ* permeability. It is also possible to provide a performance specification in which

Table 5. General comparison between SB and CB cutoff walls

Design Parameter	SB	CB
Permeability	Lower (10^{-8} – 10^{-9} m/sec)	Higher (10^{-7} – 10^{-8} m/sec)
Strength	Low	Higher
Constructability	Harder	Easier
Chemical compatibility	Varies	Varies
Cost	Lower	Higher

methods and materials are left to the discretion of the contractor (Spooner et al. 1985).

Construction

Cutoff wall construction typically involves four concurrent steps: *slurry mixing*, *trench excavation*, *backfill mixing*, and *backfill placement*. Slurry mixing involves using an aqueous bentonite mixture that is pumped into the trench to prevent collapse during excavation. With a density greater than that of water, the slurry displaces groundwater, coats the interior of the trench walls, and stabilizes potentially unconsolidated soils that may be prone to collapsing the trench. The slurry is mixed in dedicated tanks equipped with high-shear impellers for completely dispersing the bentonite. The concentration of the bentonite slurry is usually in the range of 4%–7%, although it is more typical to specify the viscosity of the slurry rather than its bentonite concentration. Throughout the slurry mixing and trenching process, the quality of the fluid must be continually checked to ensure it does not become contaminated with soil particles.

Trench excavation is accomplished with a backhoe or, for deeper walls, a cable-suspended clamshell. Many purpose-built attachments and enhancements to this equipment have been developed to facilitate efficient excavation in wide-ranging subsoil conditions such as sands, stiff clays, and rock (Millet, Perez, and Davidson 1992). The most critical aspect of the excavation process is preventing trench collapse. This requires a well-developed plan for integrating the activities of the slurry and the excavation equipment. Another important excavation parameter is the verticality (plumbness) of the trench; it is always to be desired, especially if the finished wall must meet certain strength requirements.

Backfill mixing refers to the ingredients constituting the barrier component of the trench. These ingredients will consist of native soil, bentonite, cement, or some combination of the three. Attapulgit is sometimes used as an alternative to bentonite. The primary objective in mixing the backfill is to achieve uniformity of the mixture to prevent the development of preferential flow zones. It is also necessary to ensure that the mixture is sufficiently wet to flow evenly into the trench. To accomplish these objectives, the designer may specify particle-size requirements for the bentonite and the soil backfill. In most cases, the bentonite content of the backfill mixture will be approximately 2%–4% by weight and the water content will be 25%–35% (Millet, Perez, and Davidson 1992).

Backfill placement is accomplished either by injecting the mixture through a tremie pipe to the bottom of the trench or by pushing with a bulldozer and allowing it to fall by gravity along a sloped surface at the end of the excavation. Backfill is placed in this manner until it daylight at the top of the trench, by which time the bentonite slurry has been displaced in the area by (ideally) a contiguous layer of low-permeability, reasonably well consolidated backfill. If a CB wall is being built, there is no backfilling process; the CB slurry used to stabilize the trench is simply allowed to harden in place.

The cost of an SB or CB wall is, as would be expected, highly variable, but in soft or medium-soft soils, \$540–\$750/sq m is expected (EPA 1994). CB walls would trend to the higher end of this range.

Quality Control

A comprehensive QC program is required for the cutoff wall to function as designed. Quality testing is performed throughout the construction process to ensure adequate trench depth, excavation into the aquiclude, trench alignment, and trench width (wall thickness). The bentonite or CB slurry should be checked for viscosity, pH, and sand content. The CB or SB backfill should be regularly checked for slump, density, fines content, and hydraulic conductivity. Samples of the backfill should be taken both at the source and in situ. The slope of the backfill trench must also be monitored to ensure that the backfill is deposited properly (Khoury, Fayad, and Ladd 1992).

PERFORMANCE OF CLAY BARRIERS

There is little doubt that early attempts at constructing horizontal and vertical clay barriers were not as successful as they are today. Considerable advances in geotechnical engineering, expanded academic and field research on clay barriers, the development of better test equipment and methods, and tremendous improvements in construction equipment and QC practices have helped greatly improve the success rate of modern clay barriers.

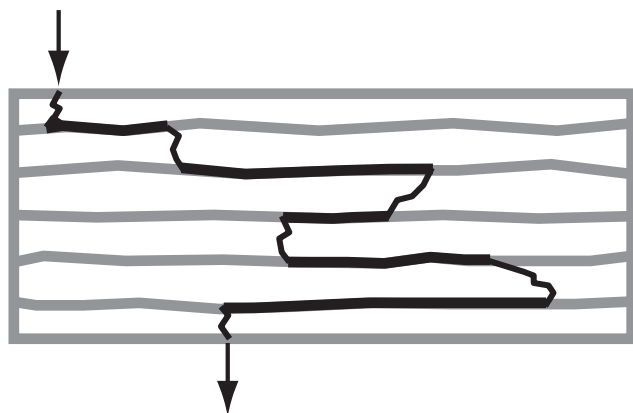
Field Monitoring Data

Indirect evidence of the failure of some clay barriers is present in the number of old landfills that have caused serious environmental contamination. Hundreds of Superfund sites are landfills, a reminder that clay barrier technology was not effective in the past. To be fair, most of the Superfund landfill sites never contained a liner of any type, but many contain a clay liner that was unable to provide suitable containment.

As the incidents of contamination increased, and as general public and scientific awareness of environmental problems also increased, federal research monies were made available to study clay barriers more intently. Research performed by Haxo et al. (1984) showed that chemicals could degrade clays. Elsbury et al. (1990) and Rogowski (1990) showed that there was a dramatic difference between laboratory permeability and actual field performance, where “actual” field permeabilities were several orders of magnitude greater than the designed design value. Additional research (Bo ward and Vallejo 1996; Omidi, Thomas, and Brown 1996; Albrecht and Benson 2001; Chapuis 2002) has shown how desiccation cracks can increase the permeability of clay barriers. And several researchers have documented that freeze/thaw cycling can also cause increased CCL permeability by up to two orders of magnitude (Chamberlain, Iskander, and Hunsiker 1990; LaPlante and Zimmie 1992; Othman and Benson 1992).

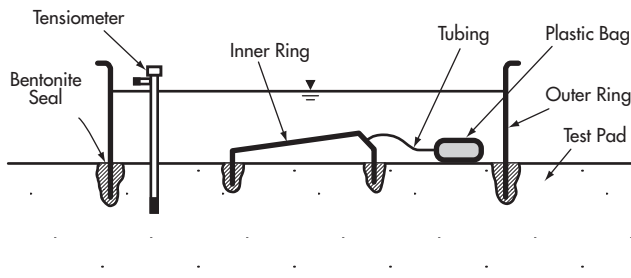
As research accumulated demonstrating that clay liners were often underperforming in the field relative to laboratory tests, a different understanding of clay liners emerged. They were not monolithic barriers with a fixed permeability in which flow strictly obeyed Darcy’s law. Instead, flow through a clay liner was governed by the presence of large-scale defects such as cracks, clods, rocks, and poor interlift bonds. A “short circuit” effect (Figure 16) caused leakage to propagate around and through these defects, resulting in much higher leakage rates than small-scale laboratory permeability tests would reveal.

The sealed double-ring infiltrometer (SDRI) shown in Figure 17 is an important tool for measuring field performance of CCLs



Adapted from Daniel and Benson 1991.

Figure 16. CCL and SBL leakage pathways may result in an actual flow rate far higher than that allowable



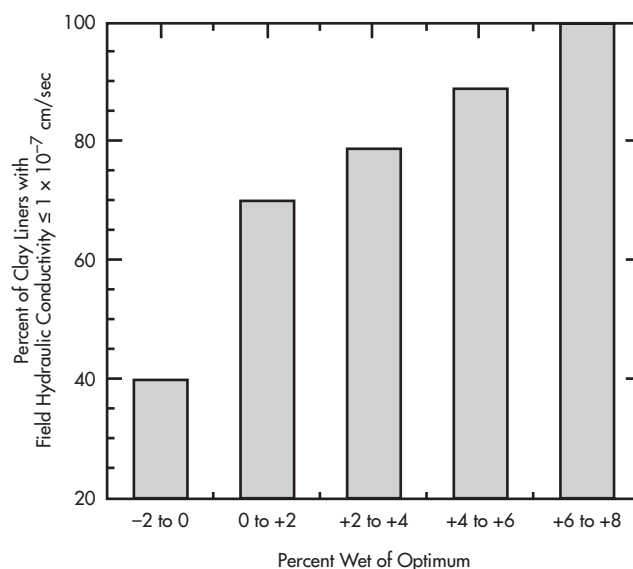
Adapted from ASTM D5093.

Figure 17. An SDRI (shown in cross section) is used to measure the in situ permeability of a clay liner

and SBLs. It offers two advantages over conventional laboratory permeameters. First, the SDRI is installed in an in situ liner so there are no sampling-induced errors that often occur when small-scale permeability samples are extracted. Second, the SDRI is a large-diameter device (>1 m) and can capture macroscale defects such as cracks and interlift flow pathways that might otherwise escape detection. SDRI data, if properly obtained, give a good indication of the field permeability of a clay liner. The relative time and expense of this test, however, make it impractical to perform with the same frequency as small-scale permeability tests.

In the late 1980s and early 1990s, more effort was applied to develop enhanced standards for clay materials screening and to improve the methods of clay barrier construction. With tightened materials and construction controls in place, it is possible to construct clay liners that meet or exceed the required performance criteria. Bonaparte, Daniel, and Koerner (2002) compiled a database of the field performance (mostly SDRI data) of 89 CCLs and found that 75% of the in situ permeability test results were less than 1×10^{-9} m/sec. Of the 22 test pads that did not meet this value, 18 of them measured less than 3×10^{-9} m/sec.

Evaluation of field QC data revealed that the dominant cause for the “failing” permeability test results in these 22 sites was that the soils were compacted at insufficient moisture content (Figure 18). Best results are achieved when the moisture content during compaction is as wet of optimum as feasible. There is a trade-off



Source: Bonaparte, Daniel, and Koerner 2002.

Figure 18. Relationship between CCL permeability and compaction moisture content

between shear strength and permeability, but the data suggest strongly that the soil should be as wet of optimum as possible to maximize the potential for achieving low permeability.

GCLs as a Replacement for CCLs

The development and commercialization of GCL technology have been largely coincident with the development of CCL performance data. As it became apparent that CCLs needed far more engineering analyses, installation expertise, and CQC to perform successfully, GCLs were naturally viewed as an easy solution to the problems of CCLs. GCLs were widely embraced by engineers in the early 1990s (in North America, and somewhat later in other parts of the world), although regulatory acceptance was slow because of the institutional inertia of CCLs and the fundamental thickness difference between the two technologies (there is a perceived risk in replacing a thick liner with a thin one, regardless of the equivalency argument).

GCL manufacturers were quick to identify the technical and practical advantages of their products in light of the growing realization that CCLs often underperform. In time, GCL use in both waste containment and other applications increased to the extent that some generalizations about their field performance could be made in comparison to CCLs. In this regard, many of the performance advantages claimed by GCL proponents were verified (see Hydraulic Performance section), although at the same time, significant engineering limitations of GCLs were also being discovered. These limitations relate mostly to slope stability and chemical compatibility. With a large database of direct shear test results available (Chiu 2002; McCartney, Zornberg, and Swan 2002), the engineering community has a much better understanding of how GCLs perform in many different sloped applications. Additional research (Ruhl and Daniel 1997; Egloffstein 2000; Jo et al. 2001) has set the practical parameters for determining the potential effects of chemical contaminants. There is now enough field experience and laboratory data on GCLs to allow designers and regulators to understand and predict the performance of a GCL in a specific application.

State of Practice of Clay Barriers

Clay barriers have improved considerably since they were first used in waste containment applications in the 1970s. With a better understanding of the engineering properties of CCLs and GCLs and with the advent of rigorous materials and CQC programs, the performance of clay barriers has improved appreciably. These performance improvements have a direct beneficial effect on the protection of human health and the environment.

Although the quality of clay barriers has increased, it is also necessary to briefly discuss the development of geomembrane technology. Maximum containment is achieved only when geomembranes and clay barriers are used together. A clay barrier, regardless of how well it is constructed, is always permeable. A geomembrane, however, is fundamentally impermeable (to liquids) and offers close to 100 % containment. But geomembranes are prone to leakage caused by puncture or improperly welded field seams. With a clay layer present beneath the geomembrane, the amount of leakage is greatly reduced. Indeed, a synergistic effect between the geomembrane and the clay barrier (GCL or CCL) has been modeled by Bonaparte, Giroud, and Gross (1989) and Giroud (1997). These researchers have determined that if the geomembrane and clay barrier are in "intimate hydraulic contact" with one another, the resulting leakage through a geomembrane defect is almost inconsequentialy small.

Therefore, the current state of the practice in modern liner design is to include both a geomembrane and a clay barrier, a system that has proven to give the highest level of containment achievable at reasonable cost. Even better performance is possible if the liner system is subjected to a leak location survey before being put into service. Such surveys can identify the location of geomembrane and GCL defects that might otherwise have contributed to increased flow. The final result of this evolutionary process of liner design and construction is a nearly leak-free liner system. Although it is never possible to guarantee "perfect" leak-free performance, it is possible to approach it.

This does not mean that liner system design practice is at a standstill. The previously described performance improvements apply only to advective flow. As progress is made in eliminating advective flow, diffusive flow—especially of organic contaminants—will begin to challenge the next generation of designers and researchers. Thick clay barriers may once again play an important role in the development of strategies to minimize diffusive flow.

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Flue Gas Desulfurization

David C. Hoffman and Robert C. Freas

Beginning in the 1970s, people throughout the world, especially in Western Europe, Japan, and the United States, have taken more interest in the environment, the sources and causes of pollution, and pollution abatement. In the United States, air quality continues to be an area of primary emphasis. In 1970, for instance, the U.S. Congress passed the Clean Air Act and subsequently revised and strengthened it in 1977 with the issuance of the New Source Performance Standards (effective August 7, 1980). The act was toughened further with the passage of the 1990 Clean Air Act Amendments (CAAA) that created the current Acid Rain Program to address sulfur dioxide (SO_2) and oxides of nitrogen (NO_x) emissions. Additionally, this update included a list of 189 hazardous air pollutants (HAPs) that continues to be evaluated and refined. Most significantly, the 1990 CAAA established a phased program for implementation via a novel cap-and-trade method for attaining allowable emissions.

Because this chapter focuses on SO_2 removal, it should be pointed out that an unwanted by-product of certain NO_x removal technologies has emerged—an increase in sulfur trioxide (SO_3) emissions. The major source of the increased SO_3 , a significantly more toxic and visible substance than SO_2 , is primarily from selective catalytic reduction (SCR) systems employing vanadium-based catalysts.

By far the largest single source of emissions addressed in the Clean Air Act from the 1970s through the 1990 CAAA was from large coal-based electric power generating stations. Consequently, a substantial portion of flue gas desulfurization (FGD) research, development, and equipment installation has been geared to this large utility sector. Several competing FGD technologies were touted during the 1970s, employing various equipment configurations and different reagents to react with and reduce the gaseous SO_2 emissions. At the beginning of the 1990 CAAA's Phase I, the most viable FGD processes were generally equipment configurations employing either limestone or lime as the reagent, and they have continued to be the reagents of choice into the 21st century.

In 2004, a second area of emphasis for FGD has been coal-based industrial boilers. Although individually they are much smaller than any electric utility generating station, they represent a significant source of sulfur emissions. Because of the size of industrial boilers and their location within industrial, commercial, and educational complexes, however, the well-accepted wet scrubber technology employed by electric utilities is not universally appropriate for these applications. Therefore, other types of FGD

equipment and reagents have been developed that meet emission-reduction requirements and are cost-effective for the user.

One particular type of process employed is fluidized bed combustion (FBC) technology. Briefly, FBC suspends the fuel and ground limestone with combustion air, and the ground limestone is the SO_2 removal reagent via in situ calcination to calcium oxide (lime). Since the installation of the first full-scale test unit at Georgetown University (Washington, D.C.) in 1979, several equipment vendors have come forward with an increasing array of more sophisticated FBC units. Currently, FBC technology has reached a technical and economic plateau, in the 250- to 300-MW range, and some are in operation across the United States.

Currently, this large pool of industrial boilers is being analyzed, and emission regulations are being proposed to address the interstate transport of SO_2 and other air pollutants, such as fine particulates and ozone. The most current U.S. Environmental Protection Agency (EPA) proposal on the interstate transport of SO_2 was published in the *Federal Register* on January 30, 2004. This initial proposal is subject to public comment, and, if it stays intact, will affect 29 eastern states and the District of Columbia. SO_2 emissions within this region would drop to 3.6 million st in 2010 (approximately 40% of 2002 levels) and another 2 million st by 2015 (approximately 70% of 2002 levels). NO_x regional emissions will be cut by 1.5 million st in 2010 and another 1.8 million st in 2015—a reduction of approximately 65% from 2002 baseline levels. Quite significantly, emissions will be capped at these levels, with any increases handled by “trading.” The 1990 CAAA, then, created an “ SO_2 emissions allowance per ton of SO_2 emitted” that is equivalent to a corporate stock certificate, and these “allowances” are also publicly traded.

Mercury is now being seriously addressed as a result of the 1990 CAAA's requirement for the EPA to study public health effects of airborne toxic emissions from utilities burning fossil fuels. Again, the utility sector is the largest source of mercury emissions. On December 15, 2003, the EPA proposed two alternatives: (1) installing “maximum achievable control technologies” (MACT) with a planned mercury reduction of 14 st, or 2.9%, by the end of 2007, or (2) establishing “standards of performance” limiting emissions from new and existing utilities in two phases. The first phase of the latter alternative would take advantage of “co-benefit” controls reducing mercury emission via SO_2 and NO_x emissions by 2010 and full implementation by 2018 with reductions amounting to 33 st, or 69%. Mercury reductions are a hotly contested

technology—scientifically as well as economically—and on March 15, 2005, the EPA issued the first rules on mercury emissions.

1990 CLEAN AIR ACT AMENDMENTS

As passed, the 1990 CAAA empowered the EPA with extensive regulatory powers. The amendments are composed of 11 parts, or titles, that impact most major industries in the United States, including the mining industry. Title IV, Acid Rain Control, however, has the greatest impact on FGD requirements for utilities and other industrial coal-based sources of sulfur emissions. A much overlooked section of the CAAA, Title III, Hazardous Air Pollutants, addresses 189 airborne toxic substances that are required by law to be controlled by a MACT. With a combination of theoretical research and, most importantly, actual operating technologies, emission reductions of each airborne toxin will be mandated and implemented using MACT guidelines. This is a new approach using the best operating systems to establish the baseline emission regulation. Thus far into the 21st century, these HAP controls have proved to be the real challenge.

Title IV was implemented in two phases. Phase I ran from 1995 to 2000 and was applied primarily to the largest coal-based sources from 1995 to 1999. In fact, 110 electric generating stations in 22 states were listed (*Congressional Quarterly* 1990; Bureau of National Affairs 1991). The basic sulfur emission allowance is calculated at a rate of 1.1 kg (2.5 lb) of SO₂ per million Btu of heat input multiplied by the amount of fuel burned in that particular unit. During this Phase I period, about 89,000 MW of generating capacity were equipped with FGD systems.

Phase II, which began in 2000, further tightens the restrictions of Phase I and also triggers NO_x emission controls for these units. The Phase II calculation is based on 0.5 kg (1.2 lb) of SO₂ emissions per million Btu and also includes restrictions on NO_x emissions, which have been clearly identified with the decline in air quality and are part of the Acid Rain Program. Further NO_x emission reductions have been implemented at state levels to address regional air pollution concerns caused by haze and smog. Thus, the federal government prompted the installation of several types of NO_x reduction systems and processes on major power plants through state implementation plans. The timetable for full compliance is now clearer as more units become operational, and a May 1, 2007, deadline seems more achievable.

ACID RAIN CONTROL RESULTS

At the end of 2002, the 1990 CAAA achieved the following results:

- Electric generating sources (3,208 units) reduced annual SO₂ emissions in 2002 by 41% from 1980 levels, or about 7.1 million st. (Banked SO₂ allowances have steadily decreased from 2000 to 2002.)
- Total NO_x reductions in the Acid Rain Program achieved a goal of 2 million st below projected emissions without Title IV enforcement in 2000. Actual results of 3 million st below projections were achieved by adding state controls, primarily in the Northeast.

Although results exceeded most expectations, there is continuing pressure to reduce these pollutants further and to continue to protect public health and welfare for future generations.

FLUE GAS DESULFURIZATION TECHNOLOGIES

Overview

Several technologies are available to both utility and industrial boiler operations for reducing SO₂ emissions. These include wet lime or limestone scrubbing, semidry scrubbing, dry scrubbing, and

Table 1. Existing FGD systems

Reagent Type	Megawatts Scrubbed	Percentage
Lime-Based		
Magnesium-enhanced	14,100	14.4
Semidry	9,200	9.4
Wet lime	5,100	5.2
Lime-F/A*	4,300	4.4
Other	200	0.2
Total Lime-Based	32,900	33.6
Wet Limestone	55,800	57.2
Other	8,900	9.1
Totals	97,600	100.0

* F/A = fly ash.

FBC technology, as well as several less well-known and essentially unproven systems. The selection of a particular process is typically an economic one, but other considerations are the sulfur and Btu contents of the coal, the cost of SO₂ sorbent, the disposal of solid waste generated by sulfur removal, and local socioeconomic factors. In addition, alternatives such as the implementation of coal-cleaning or gasification technologies, solvent-refined coals, and firing with coal-water mixtures or other coal blends also impact the selection of a sulfur-removal system. The Electric Power Research Institute has sponsored research on all the primary FGD methodologies as well as investigations of the availability and effectiveness of a variety of sorbents (EPRI 1991).

At the end of 2002, the total U.S. electrical generating industry (utilities and nonutilities) consisted of the following:

- Net summertime generating capacity of approximately 905,000 MW, including
 - Electric utilities' capacity of approximately 561,000 MW, or about 62% of U.S. generation
- Net summertime coal-based generating capacity of approximately 315,000 MW, or about 35% of U.S. generation, including
 - Electric utilities' capacity of approximately 244,000 MW, or about 77% of generation and about 27% of total U.S. generating capacity
 - 100,000 MW of scrubbed coal-based units, or 32% of U.S. coal-based capacity and 11% of total U.S. generating capacity

In summary, the United States has come a long way since 1970 in improving the air quality with respect to SO₂ removal, but 67% of coal-based capacity still needs attention to reduce SO₂ emissions.

Wet Scrubbing

About 90% (based on megawatts scrubbed) of the existing electric utility generating units with commercial FGD systems employ lime-limestone processes based on wet calcium. Table 1 breaks these FGD systems down further.

Although the wet lime and limestone reagents are uniquely different, the basic process chemistry is similar. The details for a wet lime or limestone system are fairly complex and include both the liquid phase chemistry of SO₂ absorption, the liquid-solid chemistry of lime-limestone dissolution, and the liquid phase precipitation of calcium sulfite-sulfate salts. Calcium reagent materials, either lime or limestone, provide alkalinity for SO₂ removal in the wet scrubber. This generates sulfite and sulfate salts as calcium-based by-products

from the removal of the SO_2 from the flue gas stream. These by-products may be in slurry form or a high solids filter cake, but in either case they require an environmentally safe disposal or reuse. Because this chapter is not intended as an in-depth discussion on scrubber systems, the reader is referred to a report written by Srivastava (2000).

Since the mid-1990s, the preferred method of disposal for scrubber by-products has been the conversion-oxidation of these salts into calcium sulfate (or gypsum) for, primarily, wallboard construction. This synthetic gypsum is technically competitive with natural products but is economically dependent on the location of the FGD source materials and major construction markets.

Another factor in deciding between wet lime and wet limestone systems is the solubility and dissolution rates of these calcium-based reagent materials and how they will affect the total alkalinity per gallon of reagent slurry recirculated within the scrubber. In very general terms, wet lime systems require less hardware and less tonnage of calcium-based reagents than a wet limestone system to remove sulfur from flue gas. Today, it is not uncommon to achieve SO_2 removal efficiencies in ranges of 98%+ from either lime- or limestone-based FGD systems. These wet systems usually are applied to coal-fired flue gases that are in excess of 1.5% sulfur. Both reagents (lime and limestone) require buffering agents. When using lime, magnesium oxide is added to quicklime, or magnesium-dolomitic lime is used. In limestone systems, the addition of weak organic acids helps to obtain these high SO_2 removal efficiencies on a consistent basis. Such buffers as adipic acid, dibasic acid (DBA, the most common), and formic acid can enhance limestone removal and utilization, especially to achieve continuous 95%+ SO_2 removal efficiency.

In deciding between lime or limestone reagents, the following are major evaluation parameters:

- Availability and cost of required land area
- Capital installation costs
- Reagent costs (including delivery) and slurring costs:
 - Lime: slaking systems
 - Limestone: fine grinding systems with >90%+ passing 44 μm
- Reliability of reagent supplier(s)
- Technical support from reagent suppliers
- Parasitic electrical demand for complete FGD system evaluated at current electrical market replacement costs
- Ability to remove additional pollutants (e.g., SO_3 and mercury currently addressed by MACT)
- Cost of disposal or resale of by-products (primarily gypsum and fly ash)
- Water treatment requirements for effluent water discharges in terms of quality and volume

The most common equipment FGD design is an open spray tower that can handle the flue gases from 800 to 900 MW per tower. Reagent utilization varies and is generally in the range of 1.02 to 1.10 moles of reagent applied per mole of SO_2 removed.

Semidry Scrubbing

Semidry scrubbing involves reacting a sulfur-containing flue gas with an alkaline reagent slurry resulting in a dry by-product being generated and captured for disposal or reuse. These systems use spray atomizers or dual fluid injection systems prior to baghouse filters or electrostatic precipitators to remove reaction by-products. Today, the most common atomizer is the rotary disc type that spins at several thousand revolutions per minute, producing a fine mist that contains the slurried reagent. These units have been used successfully in industrial boilers, municipal waste incinerators, and utility plants.

Limestone cannot be used in these systems because they rely on the SO_2 and lime reaction plus the evaporation of the slurry water to occur in a matter of seconds. The preferred reagent is lime; however, some systems use sodium carbonate or bicarbonate reagents. Sodium is generally more costly than lime, and sodium-based by-products can be deleterious to the environment because of sodium's high solubility and mobility.

In a very simplified form, the spray dryer incorporates a milk-of-lime slurry, which is atomized to a fine particle size, typically 50 to 75 μm in diameter. The slurry is sprayed into the reaction chamber at a low moisture level allowing the SO_2 -CaO (calcium oxide) reaction to take place and for the slurried water to evaporate. A fabric filter or electrostatic precipitator immediately follows the reaction chamber and removes reaction by-products and coal fly-ash particulates. This design is optimized when a fabric filter is employed, as it removes an additional 25% to 35% SO_2 across the bags. As a result, sulfur is removed from the flue gas as a dry waste product. Because of the physicochemical kinetics of the SO_2 reaction, each reaction module usually is limited to about 250 to 350 MW of the flue gas volume. To achieve up to 94% SO_2 removal, the sulfur content of the coal is restricted generally to less than 1.5% sulfur.

SO_2 removal and fuel sulfur levels reduce the suitability of semidry scrubbing systems. Additionally, reagent utilization is lower than in wet, open spray towers; however, by-product reuse helps reduce the overall reagent consumption. Reagent utilizations vary and are, by convention, described as moles of lime applied per mole of inlet SO_2 . Typical utilizations range from 1.25 to 1.5 with a fabric filter and by-product reuse or recirculation.

Major advantages of semidry scrubbing over wet systems are lower capital costs per applied megawatt; small land area requirements; minimal use of water; no water treatment system needed for wastewater effluent; SO_3 removal and possible mercury removal; nearly invisible stack emission; and an immediate, dry by-product for disposal. Because of its fine powder consistency and potential market outlets, the resulting economics limit its reuse applications. Today, most of these systems are used for western low-sulfur coals. The added benefits of SO_3 removal, and possible mercury capture, however, are causing many eastern utilities to rethink its suitability. Although the semidry scrubbers do not have the complex liquid-phase chemistry of wet scrubbing, they still have process limitations. These include inlet SO_2 concentrations and temperature drops across the spray dryer (i.e., approach to saturation, composition of slaking water, and lime activity). Some lime suppliers are able to assist in fine-tuning these considerations to achieve an optimal semidry FGD operation.

Dry Scrubbing or Dry Alkali Injection

The previously discussed systems involve the use of a water-based alkaline slurry that remove SO_2 and create by-products that are handled easily for disposal or for reuse or sale. In dry scrubbing, a dry, finely divided reagent is injected directly into the boiler or flue gas ducts for gas-solid reactions. Typical reagents are hydrated lime, finely ground limestone, and powdered sodium carbonate or bicarbonate material (usually the natural products called trona and nahcolite, respectively). The first initial dry scrubbing systems incorporated lime as the sorbent, but the subsequent development of dry alkali injection technology also employed trona as a reagent. Public Service Company of Colorado announced the first commercial application of a trona-based dry injection system for a 500-MW unit that began operating in the late 1990s. As previously stated, sodium-based scrubbing causes problems for handling and disposing of by-products because of sodium's high solubility, and mobility and leachability.

With the injection of these reagent(s) into the upper regions of the boiler, flue gas temperature becomes an important reaction parameter for optimizing the sulfur reactions. Of further concern is sodium's ability to corrode steel boiler tubes. The disadvantages of lime and limestone injection into the boiler are physical fouling of the boiler tubes and low SO_2 removals. With any of these reagents, removals generally are limited to less than 40% in the boiler and from 50% to 70% in the ducts when moisture is added. Duct fouling becomes a major concern when moisture is added. Reagent utilizations are typically in the 3.0 to 7.0 mole range for the calcium-based systems (based on moles of calcium applied to inlet SO_2 moles). Overall success of dry reagent applications has been quite minimal in the United States; however, limestone and lime boiler injection has had some success in Europe where lower removals are sometimes acceptable.

In duct injection, lime has been used successfully outside the high-temperature boiler regions because of its customization with respect to surface area, internal pore volume, and particle size. As HAPs and their respective MACTs gain more attention, use of special lime hydrates that have higher surface areas and pore volumes can remove certain acid gases such as hydrochloric acid (HCl) and hydrofluoric acid (HF) plus select volatile organics. With the use of these special limes, duct injection has been successful in Europe and may be employed in the United States to address various HAPs as listed in the 1990 CAAA.

In addition to these applications, dry injection with reasonable reagent utilizations in the 1.0 to 3.0 mole range for reduced removals of SO_2 (ranging from 50% to 70%) is being discussed more openly at present. In 2004, the Institute of Clean Air Companies proposed this approach to the EPA in addressing SO_2 removals from smaller and older industrial and utility boilers not covered by the 1990 CAAA. Under certain circumstances, the introduction of lime slurry or water mist into the duct subsequent to the boiler will improve the removal or increase the reagent utilization.

SO₃ Removal

SO_3 is produced from the combustion of sulfur-bearing fuels when some SO_2 —estimated at 1% to 3%—is oxidized to SO_3 . The combustion of heavy fuel oil results in the most prolific SO_3 emissions, because the vanadium contaminant of the oil catalyzes the conversion to SO_3 . In 1980, about 10% of U.S. utility generation was from heavy fuel oil. In 1999 this generation was about 2%, and today, the percentage is most likely less. SO_3 emissions regained the spotlight with the addition of SCR systems that employ vanadium-based catalysts for NO_x control. After wet SO_2 scrubbing, stations employing SCR systems might see SO_3 emissions nearly double, in addition to emitting a very visible bluish plume from stacks. This issue came to light in 2001–2002 with problems associated with an electric power plant at Gallipolis, Ohio.

SO_3 is produced as a very tiny aerosol particle readily passing through the wet scrubber and is converted into sulfuric acid smog that can settle quickly to ground level, causing severe health issues and property damage. This also occurred at the plant at Gallipolis. The solution is to inject an alkali reagent before or immediately after the SCR system. Alkalies such as magnesium hydroxide, sodium bisulfite, and calcium hydroxide have been used with limited success. The problems associated with the use of these alkalies are

- Buildup of unused reagent and reaction by-products in the ducts
- High reagent utilizations in the range from 2.0 to 10.0; typically from 2.0 to 6.0 (moles of calcium per mole of inlet SO_3)

- Consistent SO_3 removals over the range of boiler generation loads
- The lack of demonstrated SO_3 monitoring methods and continuous emission instrumentation

The most proven reagent is sodium bisulfite, but recent advances using calcium hydroxide, dry or in slurry form, appear to be the most cost-effective method. The ultimate goal of all these approaches is

- To remove SO_3 to safe levels without any visible plume—typically less than 5 ppm
- If possible, to improve boiler efficiency by lowering the air preheater outlet temperatures below the previously limiting acid dewpoint, thus greatly improving boiler energy conversion efficiency and economics

As previously mentioned, this appears to be an “eastern problem” in the United States because of the relatively higher concentration of SCRs on high-sulfur eastern coals; smog and haze concerns in national parks and scenic areas; and the use of wet FGD systems. In the American West, semidry systems are more prevalent, but even when wet FGD systems are used, coal sulfurs are usually less than 1.5%, and population densities are less. Nevertheless, the West also has scenic areas that suffer from smog and haze (e.g., the Grand Canyon).

Other FGD Systems

External fluidized bed systems for flue gas treatment using calcium hydroxide as the fluidized medium have received more attention worldwide as larger systems come online in China. They appear to present several advantages, such as lower installed capital costs and lower parasitic operating electrical demand, reportedly less than 1% parasitic load. The claim of high SO_2 removal (>98%) is unsubstantiated in the United States, and the potential for reducing SO_3 and other pollutant reductions are under investigation, but generally these FBC claims are believed feasible. Currently, a major concern is their reported module size limitation with current maximums of 500 to 600 MW per module versus wet FGD maximums of 800 to 900 MW. As a result of China's installation of these larger units, operating information is starting to become available for a more systematic evaluation of their actual online performance.

Although the aforementioned technologies are the predominant systems currently applied commercially, other systems are being investigated and tried. For more information on these other technologies, the reader is referred to references published on the U.S. Department of Energy (DOE) and EPA Web sites (www.doe.gov and www.epa.gov, respectively).

Fluidized Bed Combustion

This technology involves directly mixing limestone with coal in the boiler during combustion. The bed of coal and limestone is fluidized by injection of air through the bed. The upward force of air equalizes the downward force of gravity so that the entire bed takes on the appearance of slowly boiling water (Bubenick, Hall, and Dirgo 1981; Roeck 1982; Remick 1985). Limestone is calcined within this combustion environment. The calcined lime that is produced absorbs SO_2 , which is released from coal in the fluidized bed, producing calcium sulfite–sulfate.

Although FBC technology has proven reliable over the last three decades, the process has undergone a technical evolution that has increased both efficiency and the choice of fuels that may be employed. FBC units currently operating around the world use a variety of fuels ranging from high-quality, low-sulfur coal to municipal sludge, sawdust, and coal slag. Normally, utility a nd

industrial boilers use higher-quality fuels, whereas cogeneration facilities, which may have multiple operating objectives, more commonly use alternate fuels.

FBC technology is divided into two primary methodologies: atmospheric and pressurized. The atmospheric FBC units can be subdivided further into bubbling fluidized bed (BFB) and circulating fluidized bed (CFB); the former is the older, more basic technology. BFBs are characterized by low air velocity, relatively thin fuel or reagent bed thickness, and proportionately higher plan area. This technology generally has been restricted to boilers with a steam-generating capacity of less than 100 stpy. Conversely, CFBs operate through the bed at air velocities that are three to four times higher than conventional BFB units. This has the positive effect of decreasing the plan area of the bed; however, at higher velocities, combustion and reagent particles are transported out of the bed with the combustion gases (Kindy 1982; Goldstein, Brown, and Kenney 2003). To utilize these particles and maintain the efficiency of the system, combustion gases pass through an air classifier that removes particles by recycling them back to the combustion bed; hence the name "circulating fluid bed."

FBC technology began its first commercial use in the late 1960s and early 1970s when one of the earliest BFB units was installed at Georgetown University. The technology has gradually grown to the point where several hundred FBC units are now in use in the United States. Figure 1 shows the location of many of these units and provides an indication of the distribution pattern for this technology's application. Although early FBC systems initially were restricted to smaller industrial boilers, advances in CFB technology now allow this system to be used on power generating plants with capacities in excess of 250 MW (Kettunen et al. 2003). Larger units have been permitted in the United States but are not yet operational.

Large generating station designs that utilize FBC systems are turning to pressurized fluid bed combustors (PFBCs). PFBC technology is less well advanced than the atmospheric systems and not as commercialized. Nevertheless, the technology is being employed on a 360-MW unit, the Karita power plant, operated by Kyushu Electric Power Co. in Japan (Koike et al. 2003). In a PFBC unit, the combustion bed thickness is much greater than in an atmospheric system, and the plan area is proportionately less. The increased bed thickness, up to about 4.9 m (16 ft), allows for the same intimate contact between coal and limestone but also may require gradation control on both coal and limestone (DOE 1989b). In the Karita PFBC unit, coal is crushed to about 0.64 cm (0.25 in.) and fines are virtually eliminated. Gas turbine compressors, rather than large forced-air draft fans, provide the combustion air, which is forced into the pressure vessel where combustion actually takes place.

Finally, one of the major advantages of FBC systems is their ability to burn a variety of fuels. For example, 15 medium-sized CFB units in Pennsylvania utilize low-grade reject coal stored in waste piles from decades of high-grade coal production. These stockpiles leak mercury and sulfur into nearby streams and rivers. Unpublished EPA studies recently concluded that CFB units burning coal refuse produce fly ash that captures both mercury and sulfur compounds. Goldstein et al. (2003) discuss the use of coal waste in FBC units, and Jukola et al. (2003) consider new technology designed to increase efficiency when using coal waste. FBC is more than just a means of sulfur capture in combustion gas streams; it also represents an alternate technology in waste-stream recycling and reduction.

RAW MATERIAL REQUIREMENTS

The United States has approximately 97,600 MW of electric generating capacity fitted with FGD scrubbing equipment. It is estimated that these systems utilize approximately 3.6 million stpy of lime

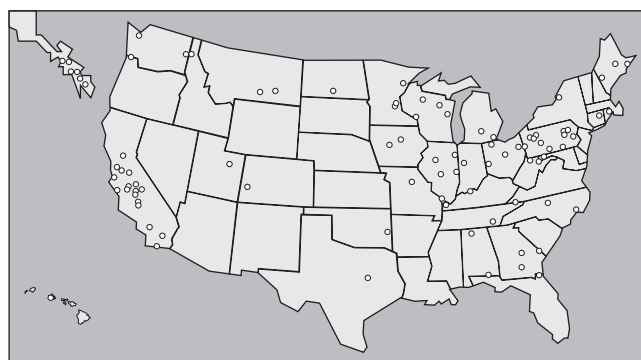


Figure 1. FBC boilers in the United States

and another 8.3 million stpy of limestone. These are estimates of the existing lime–limestone reagent requirements imposed by previous FGD regulations starting in the 1970s and culminating in the 1990 CAAA. This demand for calcium-based reagents was created by reducing 1980 SO₂ emissions of 17.2 million stpy to 10.2 million stpy in 2002, a drop of 41%.

Many forms of air emission legislation are currently being discussed. To put the current situation into perspective, if the Clear Skies initiative of February 2002 moves forward, a 73% further reduction in SO₂ to a 3 million stpy cap by 2018 is envisioned with an intermediate cap of 4.5 million stpy by 2010. Thus, another 7.2 million stpy SO₂ reduction may be in the offing. This does not include any future emission reductions needed for growth in electrical demand over the same time period.

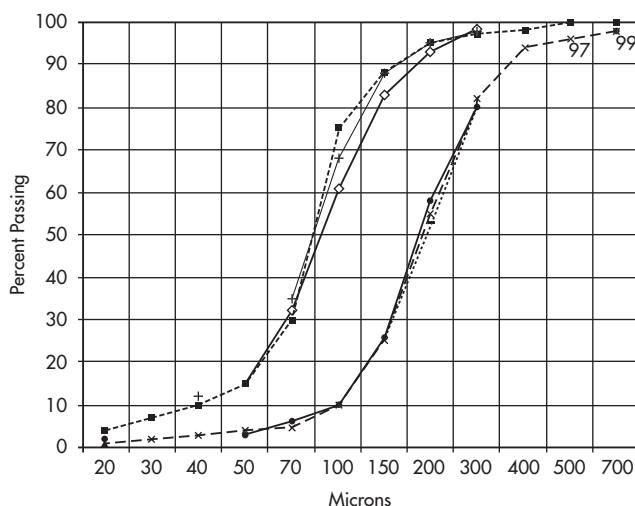
If one assumes the "status quo" on the lime–limestone reagent demand, this 70% additional SO₂ removal translates into an estimated total lime–limestone market of about 6 million stpy lime and 15 million stpy limestone, adjusted for reagent impurities. Timing for this market is largely unknown, but it should occur near the end of the next decade (by 2020).

One of the most basic decisions that the electric utility generating industry must weigh is the cost of transporting coal from the western states to eastern locations versus the cost of additional scrubber requirements imposed by utilizing eastern high-sulfur coal. This is further complicated by the fact that low-sulfur eastern coals could command a premium price. As a result, the utilities must determine the optimum coal sulfur level they can afford to purchase versus the capital cost associated with appropriate scrubber installation and operation. With transportation costs affected by rapidly fluctuating fuel costs, this increases the risk factor in deciding between the choice of coal and corresponding FGD costs.

Not only are technical and commercial issues at play, but the biggest issue may be the politics involved. Deregulation is one major political issue, and when and how this may occur will vary from region to region. A positive outcome could be that power producers will farm out various FGD unit processes to specialists outside the utility industry while retaining close control of the basic "gas path" systems. Thus, the electrical generator owner may realize a more competitive cost picture by subcontracting noncore operations.

FGD Lime and Limestone Reagent Guidelines

The guidelines for lime in FGD are particularly concerned with chemical purity, reactivity, and percentage of insoluble material, about the same as in most other lime applications. The basic chemical requirement for lime is that it must possess the highest possible



NOTE: The lines within the figure represent the upper and lower control limits of limestone used in an FBC unit as specified by three different users.

Figure 2. Representative FBC limestone size distributions

available lime index. Both quicklime and hydrated lime have American Society for Testing and Materials (ASTM) standards to which the FGD system owner or operator can reference when purchasing the lime-based reagent. The measure of available lime also applies to lime systems employing magnesium-enhanced scrubbing. Physical sizing requirements of lime are strictly a material handling and storage issue and should not be linked directly to its chemical parameters. It should be noted that quicklime, or calcium oxide, is a reactive chemical and requires special handling and storage requirements. Additionally, quicklime's affinity for water must be determined for each type of slaking system used to convert calcium oxide into calcium hydroxide, which is the form used in most FGD applications. Lime reactivity together with the slaking equipment choice will affect the particle sizing of the resultant hydroxide particles produced. In general, the smallest particle-size distribution provides the highest surface area, which is usually a big positive for increased reactivity. For more information on lime, the reader is referred to the Lime chapter in this book and to the Web site of the National Lime Association in Arlington, Virginia (www.lime.org).

The chemical requirements for limestone are usually 95% + CaCO_3 , less than 3% MgCO_3 , and minimal inert (SiO₂, Fe₂O₃, Al₂O₃). The "as received" physical sizing specification is mostly a handling issue but also is related to the type of grinding equipment needed to reduce the as-received limestone to a 325 mesh (44 μm) or finer for slurring and increased chemical reactivity. If one is doing the grinding onsite or involved in the grinding decision, another physical or chemical parameter to determine is the Bond Work Index—the power requirement per short ton of raw limestone to grind to 95% –325 mesh (44 μm) or some other defined size. Typically, this value is 10 or less and helps in selecting the type of grinding equipment. The trace flue gas chemical, fluoride, can cause "blinding" of ground limestone in the scrubber's reagent slurry, resulting in higher than normal limestone utilization and lower SO₂ removals.

Physical specifications for FBC are generally much more rigorous, with a narrower range of acceptable particle-size distribution. The reactivity of the limestone may also be a factor in sorbent selection, and the user may also consider limestone porosity. As a result, competitive bids from vendors may be subject to performance quali-

fication on pilot-scale units. The specialized physical specifications for FBC limestone classification generally do not match standard highway specifications for crushed limestone and may result in a higher price for the FBC limestone. FBC units may also have magnesium limitations, generally a maximum of 2% to 3% MgCO_3 .

A typical atmospheric FBC reagent specification normally calls for a high-purity limestone, >95% CaCO_3 , and a very narrow particle-size distribution range such as 30 mesh \times 200 mesh. Figure 2 shows the particle-size distribution curves with upper and lower limits for three CFB units. The CFB manufacturers also specify high-reactivity limestone while at the same time requiring low thermal and mechanical decrepitation during combustion and calcination (Rozelle, Pisupati, and Scaroni 2003). The narrow particle-size distribution has caused some FBC operators to utilize a blended product that may be slightly out of specification at one end of the distribution curve.

The narrow specifications for FBC provide a challenge for reagent suppliers. The narrow size distribution results in a low product yield and a high percentage of fines. These fines are waste unless the limestone producer has an outlet for the –200-mesh material produced. If the supplier produces a limestone product that is significantly outside the specification curve, reagent efficiency will drop precipitously as coarser material falls into the bottom ash and finer particles are blown out with combustion gases.

By-product Materials

By-product materials may be classified into two categories: disposable (throwaway) products and regenerated products.

The waste products from most FGD systems built prior to the 1990 CAAA were disposable. Up until Phase II of the 1990 CAAA, utilities disposed of the vast majority of by-product materials in landfills operated solely for that purpose or in permanent slurry impoundments permitted for that purpose. These surface disposal facilities may include FGD waste products and captured fly ash and bottom ash material. In order to dispose of scrubber by-products in a landfill, the by-products must be rendered stable for an extended period of time. This may be done using materials (lime-based) that induce a pozzolanic (cementitious) reaction. Stabilization is necessary because nonoxidized wet scrubber systems generate by-products that may exhibit thixotropic properties. In any case, the by-product is purely a waste with no commercial value.

Regenerative processes, on the other hand, are designed so that by-product materials can be marketed, thereby reducing overall operating costs of the FGD system. To date, the predominant regenerative system in the United States produces synthetic gypsum used for wallboard manufacturing. To generate an acceptable gypsum product, the scrubber system is designed for forced oxidation that yields a calcium sulfate (gypsum) by-product material. The utility, therefore, must commit itself to producing high-purity gypsum as well as electricity. Although most experience in producing synthetic gypsum through forced oxidation comes from limestone-based FGD systems, wet magnesium-enhanced systems also are able to make commercial synthetic products along with other magnesium-based products.

Not all FGD synthetic gypsum producers are able to sell their by-products because location and economic conditions dictate the commercial feasibility of building a wallboard plant at the site of production. Nevertheless, synthetic gypsum production may offer a better way to "store" or landfill FGD by-products because of its ease in dewatering, improved handling ability, and limited solubility.

Gypsum production is most cost-effective in wet FGD applications. The semidry and dry systems produce a by-product with limited reuse that is ultimately destined for landfill disposal. Some of the potential uses for this dry by-product are associated with

geotechnical engineering or synthetic aggregate production. These semidry and dry FGD by-products may have significant reuse applications, but new research and development needs to be explored to find more economic ways to use these by-products.

CONCLUSION

The 1990 Clean Air Act Amendments have had a significant impact on permissible emissions from new and existing coal-fired boilers in both the utility and industrial markets. This, in turn, has had a major impact on the mining industry.

First and foremost is the impact on the coal industry. The breadth of this is yet to be determined, but some degree of source switching is anticipated. This is expected to have a negative impact on Illinois, Indiana, and Ohio coal producers while having a positive effect on low-sulfur Appalachian and western coal producers. This shift in sourcing and demand is expected to result in pricing changes that, depending on the sulfur content of the coal, may result in either premiums or discounts.

Flue gas desulfurization represents a very real and growing potential market for lime, limestone, dolomite, and other industrial minerals. The size of the market remains somewhat unknown along with its timing. The demand for reagent materials, including the demand from existing scrubbers and those likely to come online between 2005 and 2020, is expected to reach 19 to 20 million stpy by 2020. Even though this is a large market, it is somewhat restricted geographically because of transportation costs and availability of supply. As always, transportation of industrial minerals is a major cost factor and will be no less a consideration in supplying the utility industry with lime and limestone or other products for FGD applications.

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Water and Sewage Treatment

Starr Curtis and Ayman El-Midany

INTRODUCTION

There is no doubt that water is the most important fluid to life. It is vital for life on Earth because of its unique properties, which change drastically in the presence of waste materials (e.g., organic, inorganic, heavy metals, dissolved or suspended solids; see Table 1) (Henze et al. 2001). Many minerals and chemicals, some of which are mineral-derived, are used to treat both potable water and domestic sewage wastewater and solids, as discussed throughout this chapter.

The waste materials affect water quality by changing the water's physical, chemical, and biological characteristics (see Table 2). Most of the changes in these properties make the water objectionable to use, especially as drinking water, in addition to their effect from an aesthetic and a health perspective. Moreover, the presence of chemical compounds affects the survival of aquatic life and may corrode or rust metal pipelines conveying water or other materials under water streams.

SOURCES OF WASTEWATER

Contamination comes from different sources, including waste disposal and accidental spills. Common sources of wastes are industrial wastes, sewage disposal systems, municipal landfills, mining and petroleum production, agriculture, urban areas, and saltwater intrusion.

The problem of treating wastewater is increasing daily. Different industries generate large amounts of wastewater; Table 3 lists U.S. wastewater production by industry (Nathanson 2003).

Wastewater is problematic not only because of its quantity but also because of concentrations of harmful constituents in the sewages. Table 4 gives an example of the typical composition of untreated wastewater in the United States.

CONTAMINANTS AND THEIR LIMITATIONS

Table 5 gives the maximum contaminant levels (MCLs) of inorganic chemicals, as determined by the U.S. Environmental Protection Agency (EPA), that can be discarded to free-flowing outlets of a public water system.

In this regard, the American Water Works Association (AWWA) has also set water quality goals. Table 5 shows the EPA MCLs and Table 6 presents the AWWA MCL goals. Achieving the limits of concentrations for each component listed in Table 6 requires treatment. The origin and source of the contaminants in the

Table 1. Wastewater components and their environmental impacts

Component	Environmental Impact
Metals (Hg, Pb, Cd, Cr, Cu, Ni)	Toxicity, bioaccumulation
Other inorganic materials (acids, bases, etc.)	Corrosion and toxicity
Biodegradable organics	Aquatic life change
Other organic materials	Toxicity, bioaccumulation, aesthetic inconveniences
Microorganisms	Health problems
Taste and odor	Toxicity, aesthetic inconveniences
Temperature	Changing life conditions
Radioactivity	Toxicity, accumulation

Table 2. Water parameters and related impurities

Parameter	Impurity
Physical	Solids
	Temperature
	Color
	Odor
Chemical, organic	Proteins
	Carbohydrates
	Fats and oils
	Grease
	Surfactants
Chemical, inorganic	pH
	Chlorides
	Alkalinity
	Nitrogen
	Phosphorus
Chemical, gaseous	Carbon dioxide
	Oxygen
	Hydrogen sulfide
	Methane
Biological	Bacteria
	Viruses

Table 3. Average U.S. industrial wastewater production by industry

Industry	Average Wastewater Production, m ³
Car repair/wash facilities	800
Textile mills	175
Galvanic industries	110
Tanneries	50
Laundries	40
Print shops	35
Slaughterhouses	7.5
Canneries	6
Breweries	5
Dairies	1.35
Electrical circuitry	1.0
Photography laboratories	1.0

Table 4. Typical composition of untreated wastewater (upper limits)

Constituent	Concentration*
Alkalinity	200
Biological oxygen demand (BOD)	300
Chlorides	100
Chemical oxygen demand (COD)	1,000
Suspended solids	350
Settleable solids, mL/L 20	
Total dissolved solids (TDS)	1,000
Total nitrogen	80
Total organic carbon	300
Total phosphorus	20

* All values in milligrams per liter unless otherwise noted.

Table 5. Maximum contaminant level (MCL) of inorganic chemicals (EPA standards)

Contaminant	MCL, mg/L
Arsenic	0.05
Barium	1.0
Cadmium	0.01
Chromium	0.05
Lead	0.05
Mercury	0.002
Nitrate (as N)	10.0
Selenium	0.01
Silver	0.05

wastewater determine the sophistication of the required treatment process.

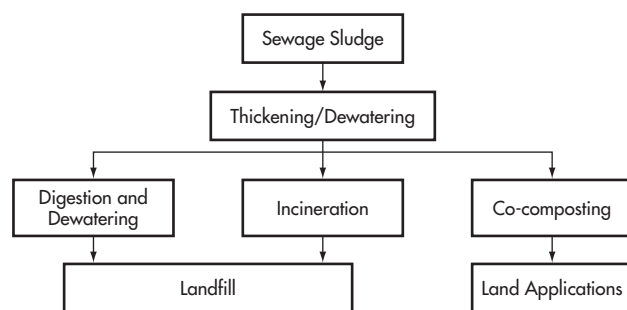
WATER TREATMENT PROCESSES

The primary treatment for wastewater is a separation process that separates the impurities and harmful constituents from the water to allow its reuse. The several types of separation processes used in wastewater treatment can be classified as physical, chemical, or biological treatments. In reality, a combination might be used, but each treatment is described by the predominant removal process—physical, chemical, physicochemical, or biological.

The treatment processes to remove sludge, heavy metals, and radioactive materials are presented in the following paragraphs.

Table 6. AWWA water quality goals

Component	Maximum Contaminant Level Goal, mg/L
Turbidity	<0.1 ntu
Color	<3 color units
Odor	None
Taste	None objectionable
Aluminum	<0.05
Copper	<0.2
Iron	<0.05
Manganese	<0.01
TDS	200.0
Zinc	<1.0
Hardness	80

**Figure 1. Sludge treatment alternatives**

Sludge Treatment

Suspended solids from the settling tank or clarifiers in wastewater treatment plants are the main source of sludge. Sludge characteristics differ from one sludge to another. In fact, no two sludges are the same in all aspects, in addition to changes in characteristics with time due to variations in pH, temperature, and so forth.

Sludge has both physical and chemical characteristics. The solid concentrations, volatile solids, and rheological characteristics are physical. The solid concentration determines the behavior of the sludge, its volume, and how it will be handled. Volatile solids are important for the sludge disposal because of gases and odors from the sludge in addition to the concentrations of pathogens. On the other hand, the rheological parameters determine the behavior of sludge under applied forces and are mainly used for scale-up processes.

The chemical composition of sludge is important for using it as fertilizer (which depends on the availability of nitrogen, phosphorus, or potassium). The presence of heavy metal, which comes primarily from industrial waste, determines the toxicity of sludge and consequently controls its usage.

Sludge treatment involves two processes: sludge stabilization and dewatering. The first process reduces or removes the aesthetic problems and noxious odors associated with sludge. The sludge can be stabilized by lime or aerobic or anaerobic digestion. The second process, however, increases the solids content of the sludge and decreases its total volume. Sand beds, filtration, centrifugation, coagulation/flocculation, and sedimentation are among the processes used for sludge dewatering. Several schemes can be used for sludge treatment, and Figure 1 gives treatment alternatives.

MUNICIPAL SOLID WASTE

Municipal solid waste (MSW) consists of all discarded solids and semisolids. Neither hazardous nor radioactive solid materials are

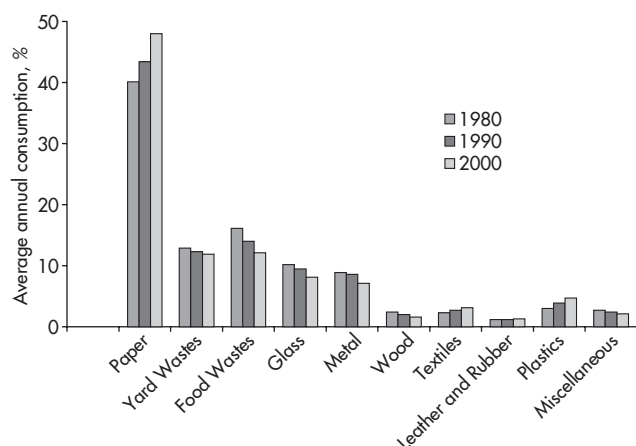


Figure 2. Annual average consumption of U.S. solid wastes (on dry mass basis) for 1980, 1990, and 2000

Table 7. Proximate and ultimate chemical analysis of MSW

Component	Proximate Analysis, %
Moisture	15–35
Volatile matter	50–60
Fixed carbon	3–9
Noncombustible matter	15–25
Heat value	3,000–6,000 Btu/lb
Component	Ultimate Analysis, %
Moisture	15–35
Carbon	15–30
Hydrogen	2–5
Oxygen	12–24
Nitrogen	0.2–1.0
Sulfur	0.02–0.10

included in the annual average of MSW in the United States shown in Figure 2. The main characteristics of MSW are gross composition, moisture content, particle size, chemical composition, and density. Table 7 gives the proximate and ultimate chemical analyses of MSW.

The MSW is removed by either landfilling or incineration, which converts the waste to other forms no longer detrimental to the environment. The incinerated MSW may also be processed further to yield proven beneficial components (e.g., combustors that can convert water into steam to power heating systems or generate electricity).

Source reduction, reuse, recycling, and composting can divert large portions of municipal solid waste from disposal. Some MSW, however, must still be placed in landfills. Desirable landfill operating practices consist of compacting and covering waste frequently with several inches of soil to reduce odor; to control litter, insects, and rodents; and to protect public health. Many modern landfills are well-engineered facilities that are properly designed, located, operated, monitored, closed, cared for after closure (including remediation when necessary), and financed to ensure compliance with federal regulations.

In the incineration process, shown in Figure 3, combustion converts hazardous waste to less bulky, less toxic material. Carbon

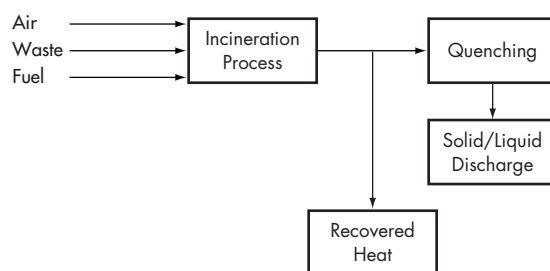


Figure 3. Schematic diagram for waste incineration system

Table 8. Mineral-derived chemicals used in the treatment of drinking water*

Chemical Name	Formula	CAS Registry No. [†]
Alumina	Al ₂ O ₃	1344-28-1
Bentonite	Variable (clay rock)	1302-78-9
Calcium carbonate	CaCO ₃	471-34-1
Calcium carbonate (limestone)	CaCO ₃	1317-65-3
Calcium fluoride	CaF ₂	7789-75-5
Calcium hydroxide	Ca(OH) ₂	1305-62-0
Calcium oxide	CaO	1305-78-8
Dolomite	CaCO ₃ •MgCO ₃	16389-88-1
Dolomitic quicklime	CaO•MgO	1305-78-8/ 1309-48-4/ 16389-88-1
Hectorite	Na _{0.3} (Mg,Li) ₃ Si ₄ O ₁₀ (F,OH) ₂	12173-47-6
Iodine	I ₂	7553-56-2
Magnesium carbonate hydroxide	3.2MgCO ₃ •Mg(OH) ₂ •3.2H ₂ O	7760-50-1
Magnesium hydroxide	Mg(OH) ₂	1309-42-8
Magnesium oxide	MgO	1309-48-4
Phosphoric acid	H ₃ PO ₄	7664-38-2
Polyphosphoric acid	H ₃ PO ₄ + n P ₂ O ₅	8017-16-1
Potassium chloride	KCl	7447-40-7
Silica dioxide	SiO ₂	14808-60-7
Sodium carbonate (soda ash)	Na ₂ CO ₃	497-18-8
Titanium dioxide	TiO ₂	13463-67-7
Tricalcium phosphate (hydroxyapatite)	Ca ₅ (PO ₄) ₃ OH	12167-47

* List derived from ANSI/NSF (1988).

[†] The Chemical Abstract Service (CAS), a subsidiary of the American Chemical Society, assigns a unique number to chemical compounds. This CAS Registry Number is widely used for identification on material safety data sheets (MSDSs) and chemical databases.

dioxide, water, and ash are the principal incineration products. If incineration products contain undesirable components, secondary treatment is required (i.e., afterburning, scrubbing, or filtration).

The advantages of incineration as a disposal method are that it is a controlled process; that it is a broadly applicable, well-known process for mixed wastes; and that no large land space is needed. It has some disadvantages, however—the equipment is expensive, complete disposal is not always achieved, and air pollution control technology is required.

Table 9. Chemicals used in potable water processing and their function

Product Function	Chemical Name	Product Function	Chemical Name
Adsorption	Activated carbon	Disinfection and oxidation (continued)	Sodium chlorite
	Alumina		Sodium hydroxide
	Manganese dioxide		Sodium hypochlorite
Algicide	Calcium hypochlorite		Sodium percarbonate
	Copper sulfate		Sodium permanganate
	Sodium percarbonate		Sulfur dioxide
Coagulation and flocculation	Aluminum chloride	Filtration and adsorption	Activated carbon, coal-based
Corrosion and scale control	Aluminum sulfate, alum		Anthracite (coal)
	Bentonite		Diatomaceous earth
	Calcium carbonate		Ferric oxide
	Calcium hydroxide		Ferric oxide/hydroxide
	Calcium oxide		Garnet
	Ferric chloride		Gravel
	Ferric sulfate		Greensand
	Ferrous chloride		Lapis sand
	Hectorite		Perlite
	Kaolinite		Silica sand
	Magnesium carbonate		Zeolite
	Polyaluminum chloride		Zeolite—clinoptilolite
	Polyaluminum silicate sulfate	Fluoride adjustment	Fluosilicic acid
	Silica		Hydrofluosilicic acid
	Sodium aluminate		Sodium fluoride
	Dolomitic quicklime		Sodium fluorosilicate
	Ferrous sulfate		Sodium silicofluoride, sodium fluosilicate
	Calcium carbonate	pH adjustment	Calcium carbonate
	Calcium hydroxide		Calcium hydroxide
	Dipotassium orthophosphate		Calcium oxide
	Disodium orthophosphate		Hydrochloric acid
	Magnesium carbonate		Magnesium hydroxide
	Magnesium hydroxide		Magnesium oxide
	Monosodium orthophosphate		Monosodium orthophosphate
	Phosphoric acid		Potassium carbonate
	Polyphosphoric acid		Potassium hydroxide
	Potassium carbonate		Sodium bicarbonate
	Potassium hydroxide		Sodium carbonate
	Potassium triphosphate		Sodium hydroxide
	Sodium bicarbonate		Sulfuric acid
	Sodium bisulfite	Precipitation	Calcium carbonate
	Sodium carbonate (soda ash)		Magnesium hydroxide
	Sodium hexametaphosphate		Sodium hydroxide
	Sodium hydroxide (caustic soda)	Sequestering	Calcium carbonate
	Sodium polyphosphates, glassy		Magnesium carbonate hydroxide
	Sodium sesquicarbonate		Monosodium orthophosphate
	Sodium silicate		Polyphosphoric acid
	Sodium triphosphate		Potassium triphosphate
	Sodium zinc polyphosphate		Sodium hydroxide
	Sodium zinc potassium polyphosphate		Sodium polyphosphates, glassy
	Sulfuric acid		Sodium silicate
	Tetrasodium pyrophosphate		Sodium triphosphate
	Titanium dioxide		Tetrapotassium pyrophosphate
	Tripotassium orthophosphate		Tetrasodium pyrophosphate
	Trisodium orthophosphate, dodecahydrate		Trisodium phosphate anhydrous
	Zinc chloride	Softening	Calcium carbonate
	Zinc orthophosphate		Calcium chloride
	Zinc sulfate monohydrate		Calcium hydroxide
Dechlorination	Activated carbon		Calcium oxide
	Calcium thiosulfate		Carbon dioxide
	Ferrous sulfate		Potassium chloride
	Sodium metabisulfite		Sodium carbonate (soda ash)
	Sodium bisulfate		Sodium chloride
	Sodium bisulfite		Sodium hydroxide (caustic soda)
	Sodium sulfite	Taste and odor control	Activated carbon
	Sulfur dioxide		Bentonite
Disinfection and oxidation	Calcium hypochlorite		Calcium carbonate
	Chlorine		Calcium hydroxide
	Chlorine dioxide		Copper sulfate
	Hypochlorous acid		Dolomite
	Oxygen, ozone		Potassium permanganate
	Potassium permanganate		

Table 10. Access to improved water supply and sanitation facilities by world region*

Region	Access to an Improved Water Source, %		Access to Improved Sanitation, %	
	1990	2000	1990	2000
World	76.6	82.3	50.7	60.6
Asia (excluding Middle East)	71.6	80.5	24.0	43.2
Central America and Caribbean	78.0	85.9	67.9	75.6
Europe†	~100.0	~100.0	~100.0	~100.0
Middle East and North Africa	na‡	83.0	na	82.0
North America	100.0	100.0	100.0	100.0
Oceania	89.1	86.7	96.7	93.5
South America	84.3	86.7	74.1	78.1
Sub-Saharan Africa	53.5	58.2	54.6	53.8

Adapted from UNICEF 2001.

* Data were originally collected under the UNICEF–World Health Organization (WHO) Joint Monitoring Program.

† Estimated.

‡ na = not available.

Table 11. Water and sanitation progress and goals

Progress between 1990 and 2000	Unfinished Business (as of 2000)	UNICEF Millennium Development Goals (September 2000)
Water: Universal access to safe drinking water		
816 million additional people obtained access to improved water supplies.	<ul style="list-style-type: none"> Some 1.1 billion people still lack access. Global coverage increased by only 3%, to 82%. Water quality problems have grown more severe in a number of countries during the decade. Coverage in low-income areas remains low, especially in informal settlements. 	By 2015, reduce by half the proportion of people without sustainable access to safe drinking water—free from microbiological and chemically hazardous constituents.
Sanitation: Universal access to sanitary means of excreta disposal		
747 million additional people had access to improved sanitation facilities.	<ul style="list-style-type: none"> 2.4 billion people, including half of all Asians, lack access. Global coverage increased by only 5%, to 60%. 80% of those lacking sanitation live in rural areas. 	By 2015, reduce by half the proportion of people who do not have access to basic sanitation.

Adapted from UNICEF 2001.

Potable Water and Sewage Treatment

As mentioned earlier, many minerals and chemicals, some of which are mineral derived (Table 8), are used to treat potable water and domestic sewage wastewater and solids. Table 9 lists the principal processes used in water treatment and the chemicals used in each process. Because lime (as calcium oxide, calcium hydroxide, and dolomitic lime) is the largest chemical (by tonnage) used in water treatment, this chapter deals primarily with this product. Recently, many factors—public health incidents, water shortages, greater “green” awareness, and more numerous or more widely publicized pollution potential for water supplies—have focused scrutiny on water treatment. National and local legislative and regulatory bodies have enacted regulations aimed at conserving and ensuring water quality and at improving and protecting public health. A greater number and variety of treatment processes have increased chemical usage. In recent years, national and international bodies have published specifications for chemicals used in water treatment. Several organizations conduct inspection and testing programs to independently confirm the quality of chemicals offered commercially.

DRIVING FORCES FOR POTABLE WATER AND SANITATION

The availability of safe water and improved sanitation is an indicator of quality of life. Safe drinking water must be free of microbiological and chemical hazards to human health and substantially free of objectionable odors, tastes, and appearance. Improved sanitation

involves disposing of human excreta by means of a facility or method that isolates or destroys disease organisms. Access to safe drinking water and improved sanitation treatment varies widely around the world (Table 10).

Although there has been progress in providing safe drinking water and improved sanitation around the world, the UNICEF assessment and goals for improvement show how far there is to go (Table 11).

POTABLE WATER TREATMENT

Regulatory Framework

The goal of potable water treatment is to reliably convert available raw water to an affordable, consistent, stable, palatable water supply that is free of infectious agents, toxic impurities, and objectionable tastes, odors, and turbidity. Legally enforceable drinking water standards limit the maximum allowable levels of specific impurities in public water supplies. These are generally based on WHO's *Guidelines for Drinking-Water Quality* (WHO 2004), reflecting scientific knowledge available and the principle that water intended for human consumption can be consumed safely on a life-long basis.

In the United States, the EPA regulates 87 parameters in the Primary Drinking Water Standards (EPA 2003) under the authority of the Safe Drinking Water Act (SDWA), which was passed in 1974 and amended in 1986 and 1996.

The European Union regulates 48 parameters in standards promulgated as Council Directive 98/83/EC (EUROPA 2003) on

Table 12. Potable water treatment

Treatment Step	Function
Screening	Removes coarse particulate matter
Coagulation and rapid mixing	Adds treatment chemicals that attract and bind fine particulate matter
Flocculation	Promotes the growth of the particles binding the fine impurities
Sedimentation	Allows the flocculated particles to precipitate or settle out of the treated water
Filtration	Removes the fine particles remaining after the sedimentation process and yields turbidity-free water
Disinfection	Kills any organisms that remain in the water or treatment system and maintains, if appropriate, a residual disinfection capacity for the distribution system
Storage and distribution	Stores and distributes the treated and disinfected water to users in a manner that preserves its purity and safety

Table 13. Summary statistics of softening plants in the United States by process

Softening Process	Number of Plants	Average Daily Production, mgd	Total Daily Production, mgd
Softening	353	0.85	299
Coagulation-softening	265	8.50	2,246
Softening-iron removal	366	0.95	348
Coagulation-softening-iron removal	45	3.60	162

the quality of water intended for human consumption, which has updated and replaced the Drinking Water Directive of 1980.

Treatment Processes

Treatment processes have been developed to remove or inactivate raw water components that may be hazardous to human health. The principal steps of most water treatment processes (Table 12) may use several chemicals (Table 9). Some water suppliers (principally those whose source is groundwater or low-turbidity surface water) omit the sedimentation step, and so their treatments are called direct filtration processes.

Newer membrane processes are increasingly important in potable water treatment, particularly in desalination of brackish or seawater. Synthetic membrane filters exclude particles down to the size of ions while passing water molecules by means of pressure. Treatment chemicals can be used in pre- or posttreatment steps to increase the efficiency and economy of the process and to extend the life of the membranes.

Drinking Water Treatment Chemicals

Many chemicals find use in processes to convert a raw water resource to a potable water supply that meets the prevailing water quality standards. The purity of chemicals used in potable water treatment is subject to governmental regulations. In the United States, drinking water treatment additives must comply with the ANSI/NSF Standard 60, *Drinking Water Treatment Chemicals*, which “establish(es) minimum requirements for the control of potential adverse human health effects from products added to water for its treatment” (ANSI/NSF 1988, p. v.). “This standard covers products intended to be added to water in the production of drinking water for such purposes as: disinfection, oxidation, filtration, scale control, corrosion control, pH adjustment, softening, precipitation, sequestering, fluoridation, coagulation, flocculation,

or miscellaneous treatments, including water well products” (ANSI/NSF 1988, p. 1). The purity criteria for water treatment chemicals are determined by the amounts of impurities contributed to the product water from the maximum treatment dosage of the treatment chemical. The impurity limits of the drinking water standards, the maximum treatment chemical dosage, and a safety factor determine the maximum allowable contribution of impurities from the treatment chemicals.

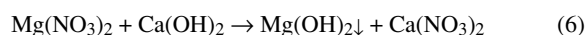
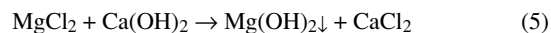
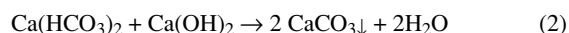
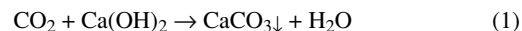
Water Softening

Lime use in water treatment primarily involves water softening, where it reduces carbonate hardness caused by dissolved bicarbonate and carbonate compounds. Currently there are more than 1,000 domestic water softening plants (Table 13) in most sections of the country, but particularly in the midwestern states, in Florida, and in Texas, where limestone bed rock abounds (ASCE/AWWA 1990). Among the other uses for lime in water treatment are coagulation, disinfection, and removal of heavy metals due to high pH softening; removal of certain radioactive and organic compounds and fluorides; neutralization of acidic water; removal of silica, particularly with dolomitic lime; and removal of color. Most of the above advantages accompany water softening, although at some plants lime is used specifically for one purpose, such as silica removal with dolomitic lime, minimizing pipeline corrosion by addition of lime to correct aggressive water, and others.

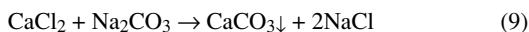
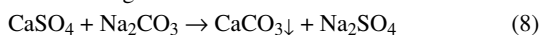
Hardness in water comprises two types—carbonate hardness, caused by dissolved calcium and magnesium carbonates and bicarbonates; and noncarbonate hardness, caused by dissolved noncarbonate salts, particularly calcium sulfate, calcium chloride, magnesium sulfate, and magnesium chloride. Total hardness is the sum of the carbonate hardness and noncarbonate hardness. Waters are classified as soft (0 to 75 mg/L as CaCO₃), moderate (75 to 150 mg/L), hard (150 to 300 mg/L), and very hard (above 300 mg/L). Most water plants strive to reduce total hardness to about 100 mg/L, although in recent years the tendency in some cities has been to allow a little higher value to reduce both chemical costs and the amount of water softening sludge produced.

There are four basic types of softening plants: lime softening, primarily to reduce carbonate hardness; lime-soda softening, for reduction of both types of hardness (in some plants caustic soda is used in place of soda ash, but it is more costly); split lime-zeolite, where a base exchange mineral is employed in place of soda ash (this system also requires sodium chloride to regenerate the zeolite mineral); and finally, zeolite softening, which is generally used in small systems for private residences and small municipalities. The principal disadvantages of the last system are its relatively high cost and the salt requirement, which introduces considerable quantities of soluble salts into the wastewater discharge system.

Lime neutralizes carbon dioxide, forming calcium carbonate, a precipitate, to convert soluble bicarbonate to calcium carbonate, and also to precipitate magnesium hydroxide. The following reactions occur in lime softening:



Reactions involving soda ash are as follows:



The principal by-product formed is calcium carbonate, a filterable insoluble precipitant referred to as water softening sludge. The quantity is large, as indicated by the fact that in precipitating the calcium ion, Equation (2), two moles of calcium carbonate are formed for every mole of calcium ion removed from the water. In large plants, the sludge is voluminous and often presents a disposal problem. Generally, the sludge is placed in a lagoon, or it may be dewatered with vacuum filters, belt and filter presses, or centrifuges, and then disposed of on farm fields as an agricultural liming material. Its high calcium carbonate content and fineness enhance its value as a liming material. Another use is as a neutralizing chemical in industrial and sewage treatment plants. A few large municipal plants have successfully recycled the sludge by dewatering and then calcining the material in rotary or fluidized kilns to produce quicklime for reuse at the softening facility.

After lime softening, the pH and alkalinity of the treated water must be adjusted to a level suitable for human consumption. Often a small stream of raw water is mixed with the treated water to achieve the desired alkalinity level, requiring further sterilization.

The finished water must be nonaggressive (noncorrosive) to the distribution system and also must not scale. To achieve this balance, the pH and alkalinity must be adjusted. Tools such as the Langelier index can determine the aggressive nature of the water. Recarbonating the treated water with CO_2 gas can often achieve the desired pH and alkalinity.

Formation of some protective scale is often desirable, but care must be taken to ensure that excessive scale and decreased flow levels are not induced. A thin calcium carbonate scale will protect the water from the dissolved salts of heavy metals, iron deposits (red water), and objectionable taste. Several specialty chemicals such as glassy polyphosphates are used to ensure a protective coating without excessive scaling.

Coagulation

Because many water supplies, particularly river water, contain suspended solids, it is usually necessary to add coagulants to remove turbidity. The principal coagulants are aluminum sulfate (alum), ferric chloride, ferric sulfate, polyaluminum salts, and lime. Lime is also used for pH control with the other coagulants. The optimum pH for alum is 5.5 to 7.5 (typically 7.0) and for the ferric salts, 5.0 to 8.5 (typically 7.5). Because many waters are acidic in nature, lime is nearly always used to raise the pH to attain the optimum coagulation efficiency; small plants often use liquid caustic soda instead of lime.

In recent years, various polyelectrolytes have been developed for use as coagulants, either alone or with the above metal ion coagulants. In many cases, lime is also used with certain polyelectrolytes. In the coagulation step, the lime is generally added with the coagulant chemical, although it often may be advantageous to add the lime ahead of the coagulant. Besides providing the proper pH, lime also acts as a filter aid, particularly with gelatinous-like sludges formed with certain water and coagulant combinations that are difficult to filter.

Purification

Research as far back as 1913 (Riehl 1962) indicated that treatment with excess lime (to pH 11+, with holding times of 24 to 48 hr) destroys *Escherichia coli*. More recent research confirmed these earlier findings, and work has also been extended to other bacteria,

Table 14. EPA's hazardous waste groups

Hazard Classification	Type	Category	Examples
Source	Specific	F	Halogenated and nonhalogenated solvents, electroplating sludge
	Nonspecific	K	Oven residue, brine modification muds
Level	Acute	P	Arsenic oxide, potassium silver cyanide, and toxaphene
	Regular	U	Carbon tetrachloride, DDT, and xylene
Others			Exhibits ignitability, corrosivity, reactivity, or toxicity

viruses, parasites, and parasite eggs. Sterilization is attributed to physical absorption of the pathogens on the flocs that settle out following the lime softening-coagulation reaction and the destruction of pathogens by the high pH. According to Boynton (1980), a serious epidemic of infectious hepatitis in Bombay, India, which was traced to the potable water supply, was stopped using excess lime treatment to a pH of 11+. Despite encouraging experience with lime sterilization, however, it can never fully replace chlorine as a disinfectant because the latter's residual content protects against later contamination in the water distribution system.

Removal of Heavy Metals and Radionuclides

Radioactive wastes can be a product of fuel cycles in nuclear power plants, nuclear weapons and their manufacturing, radiopharmaceutical manufacture and use, biomedical research and application, and a number of other industrial uses. The common and important radionuclides are krypton-85; strontium-90; iodine-131; cesium-137; tritium; cobalt-60; carbon-14; uranium-235 and 238; and plutonium-239. The treatment of the radioactive wastes is still a challenge because of the long decay times and the required disposal site specifications.

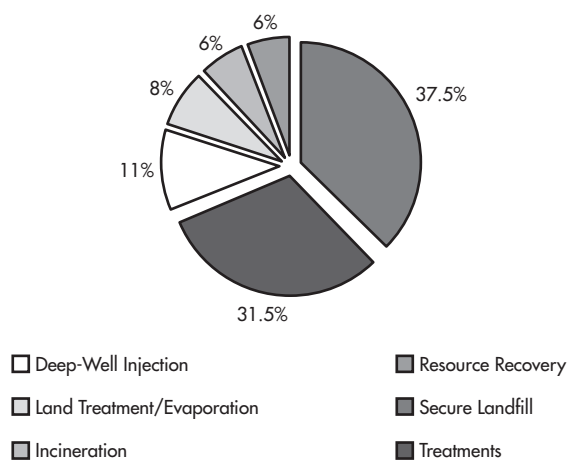
In the United States, nuclear power plants supply 20% of electricity (Weiner and Matthews 2003). In the late 1990s, shutting down the U.S. nuclear industry was seriously considered. But the electricity shortage in California in 2000–2001 may play an important role in the acceptability of nuclear energy because no large-scale alternative energy sources have been established (i.e., wind power, solar power, etc.).

On the other hand, hazardous wastes are harmful for the environment and for life, and they cannot be handled or disposed of without special precautions. The EPA has grouped hazardous waste into five categories, which are listed in Table 14. Table 15 lists the maximum allowable concentrations of hazardous waste (40CFR261.24), and Figure 4 shows the commercial disposal technologies used.

Table 16, based on EPA data summarized from various research studies involving laboratory or pilot-scale experiments, indicates that a variety of heavy metals, including arsenic, barium, cadmium, chromium, fluoride, lead, mercury, silver, and others, can be removed from potable water by raising the pH from 6 to 11, depending on the metal involved (ASCE/AWWA 1990). These data are based on conventional treatment involving coagulation with alum or iron salts, followed by lime or lime-soda softening. Treatment steps include mixing, flocculation, sedimentation, and filtration. The elevation in pH precipitates the metals out of solution for ready removal. As noted, the pH elevation occurs during lime or lime-soda softening or coagulation with alum or ferric salts abetted by lime addition. The mechanism of removal for inorganic contaminants may be precipitation of insoluble metal hydroxides, carbonation, coprecipitation with iron or aluminum hydroxides, or adsorption with natural turbidity or on floc particles formed during the reaction.

Table 15. RCRA hazardous waste limits by toxicity characteristic (TCLP)

Contaminant	Chemical	Maximum Concentration, mg/L
Arsenic	As	5.0
Barium	Ba	100.0
Cadmium	Cd	1.0
Chromium	Cr	5.0
Lead	Pb	5.0
Mercury	Hg	0.2
Selenium	Se	1.0
Silver	Ag	5.0
Endrin	1,2,3,4,10,10-hexachloro-1,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-endo, endo-5,8-dimethano naphthalene	0.02
Lindane	1,2,3,4,5,6-hexachlorocyclohexane, gamma isomer	0.4
Methoxychlor	1,1,1-trichloro-2, 2-bis[p-methoxyphenyl] ethane	10.0
Toxaphene	C ₁₀ H ₁₀ Cl ₈ , technical chlorinated camphene, 67–69% chlorine	0.5
2,4-D	2,4-dichlorophenoxyacetic acid	10.0
2,4,5-TP Silvex	2,4,5-trichlorophenoxypropionic acid	1.0



NOTE: Treatments include physical, chemical, and biological.

Figure 4. Commercial disposal technologies for hazardous material**Table 16. Summary of treatment processes for inorganic contaminants**

Contaminant	Process	pH Range	Comments
Arsenic +5	Ferric sulfate coagulation	6–8	NA*
	Alum coagulation	6–7	NA
	Lime softening	>10.5	NA
Arsenic +3	Ferric sulfate coagulation	6–8	Oxidation to As ⁵⁺ by chlorination required prior to coagulation
	Alum coagulation	6–7	
	Lime softening	>10.5	
Barium	Lime softening	10–11	NA
	Ion exchange	NA	Normal cationic exchange resins effective
			Effective over full lime-softening range
Cadmium	Ferric sulfate coagulation	7–8	
	Lime softening	NA	
Copper	Stabilization and corrosion control	Site-specific	NA
Chromium +3	Ferric sulfate coagulation	6–9	NA
	Alum coagulation	7–9	NA
	Lime softening	>10.5	NA
Chromium +6	Ferric sulfate coagulation	7–9.5	NA
Fluoride	Ion exchange	Neutral pH recommended	Ion-exchange media: activated alumina or bone char
	Lime softening	>11	Fluoride coprecipitates with magnesium hydroxide, high magnesium required
Lead	Ferric sulfate coagulation	6–9	NA
	Alum coagulation	6–9	NA
	Lime softening	NA	Effective over full lime-softening range
Inorganic mercury	Stabilization and corrosion control/ferric sulfate coagulation	Site-specific, 7–8	NA
Organic mercury	Activated carbon	NA	Powdered and granular carbon effective
Nitrate	Ion exchange	NA	Ion-exchange media: strong base resin
Radium	Lime softening	NA	Effective throughout entire softening range
	Ion exchange	NA	Normal cationic exchange media effective
	Reverse osmosis	NA	NA
Selenium +4	Ferric sulfate coagulation	6–7	NA
	Ion exchange	NA	Ion-exchange media: strong base resin or activated alumina
Selenium +6	Reverse osmosis	NA	Alumina
	Reverse osmosis	NA	NA
Silver	Ferric sulfate coagulation	7–9	NA
	Alum coagulation	6–8	NA
	Lime softening	NA	Effective over full lime-softening range
Zinc	Stabilization and corrosion control	Site-specific	NA

* NA = not applicable.

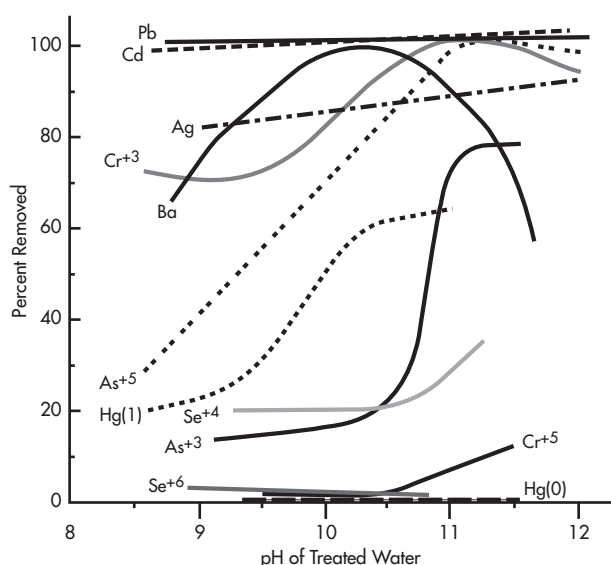


Figure 5. Removal of inorganic contaminants by lime softening

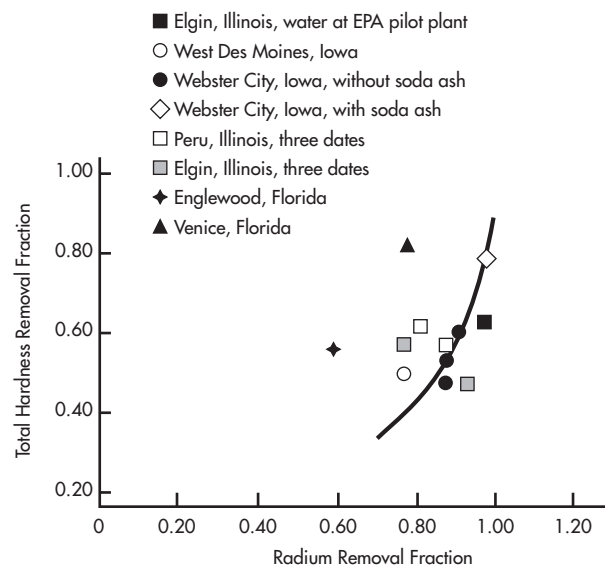


Figure 6. Lime-soda process: total hardness removal fraction versus radium removal fraction

Table 17. Efficiency of dissolved solids removal treatments

Removal Process	Dissolved Solids					
	Suspended Solids	Oxygen Demand		Nitrogen Compounds		
		BOD ₅	COD	Ammonia (NH ₃)	Organic Nitrogen (N)	Phosphate (PO ₄)
Activated carbon adsorption	80–90	70–90	60–75	—	50–90	—
Ion exchange	—	40–60	30–50	85–98	80–85	85–98
Electrodialysis —	—	—	—	30–50	—	30–50
Reverse osmosis	95–98	95–99	90–95	95–99	95–99	95–99

Figure 5 shows the extent of removal of various inorganic contaminants by lime softening, based on a pH of 8 to 12 (ASCE/AWWA 1990). Note in particular that lead and cadmium are completely removed at pH 8, arsenic+5 and chromium+3 at pH 11, and barium at pH 10. Other metals show substantial removal at elevated pH.

Radium, an alkaline earth material chemically similar to calcium and barium, is removed during lime softening and generally not during coagulation. Removals of 70% to 95% have been reported, with greater removals occurring with greater hardness removals (Figure 6) (ASCE/AWWA 1990). Generally, the higher the pH during softening, the greater the radium removal.

Neutralization of Acid Water

The growing concern about the presence of lead in drinking water has increased the use of lime for neutralizing slightly acid water. Raising pH to >7 prevents the dissolution of solder lead in pipe fittings. Further, lime corrects corrosive waters with excess CO₂ by absorption of the gas, forming a thin calcium carbonate deposit on the inside of the pipes.

Silica Removal

Waters containing silica are especially harmful in high-pressure boilers and turbines because of the formation of troublesome scale on the pipes and turbine blades. When dolomitic lime is used in the softening process, much of the silica is removed by its reaction with magnesium oxide and hydroxide.

Removal of Other Impurities

Lime is also used to help remove various other impurities, especially manganese, fluorides, iron, and organic tannin, which cause undesirable colors. Generally, lime softening will remove 80% to 90% of the color, and activated carbon removes the balance.

SEWAGE WASTEWATER TREATMENT

The goal of wastewater treatment is to safely collect, treat, and dispose of human excreta in a manner to prevent spread of disease and return the treatment processes to productive use. The principal methods of sewage treatment involve a number of steps:

1. Collection of the waste
2. Conveyance in a confined manner to a treatment facility
3. Separation of the solid wastes from the liquids
4. Treatment of liquids
 - a. Reduce the pathogen content and nutrient content. Biological growth media are commonly used to promote a non-pathogenic biological community which cannibalizes the pathogens.
 - b. Remove the biological component by clarifiers and filters. The biological sludge is usually treated with the solid waste stream.
 - c. Disinfect the treated water for safe discharge or reuse.

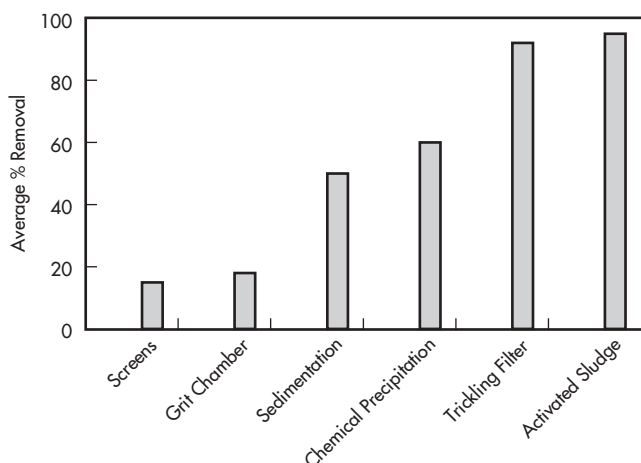


Figure 7. Treatment efficiencies for removal/destruction of bacteria in wastewater

5. Treatment of solids

- a. Reduce the volume and pathogen levels of the solids wastes. Incineration, drying (natural or artificial), and aerobic and anaerobic digesters are commonly used in large installations.
- b. Isolate, dispose of, or reuse the disinfected residual solids in a safe manner.

Table 17 describes the removal efficiency of several treatments to remove dissolved solids, and Figure 7 charts the efficiency of treatments to remove or destroy bacteria.

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Fertilizers

William C. Herz and Harry L. Vroomen

INTRODUCTION

Plants obtain nutrients from both air and soil, and nutrient balance is vital to soil fertility and crop production. Plants absorb carbon dioxide (CO_2) mainly from the air, although some CO_2 may be dissolved in soil water that is absorbed by plant roots. CO_2 , a gaseous form of carbon and oxygen, supplies the carbon that usually makes up 50% or more of plant structure. It is important to recognize that many factors control soil productivity and fertilizer use is only one of them. Fertilizers are most effective when overall attention is paid to the nutrient balance of the soil and all required nutrients are present in correct ratios.

Growing plants use water more than any other biological substance. Plant nutrients dissolve in soil water and enter the plant via root absorption. Water is then given off into the air as the plant breathes or transpires. Water also supplies hydrogen and oxygen to plants. Plant roots absorb nutrient cations or anions by contact exchange with soil clay particles. In terms of fertilizer/water interaction, appropriate fertilization can help prevent stresses resulting from low-water years. In fact, appropriate fertilization will increase yields in wet or dry weather (water use efficiency).

Inorganic or mineral nutrients essential to plants are supplied through the soil. The inorganic or mineral composition of plants is usually less than 5% of their weight. In most crop-growing areas, much of this nutrition is inadequately supplied from soil reserves and must be provided by fertilizers. The role of the fertilizer industry is to supply economical, efficient, good-quality fertilizers to improve or maintain soil productivity for optimum crop production.

Other than carbon, hydrogen, and oxygen, the essential plant nutrients that must often be added to soils or plants are categorized as primary nutrients (nitrogen [N], phosphorus [P], and potassium [K]); secondary nutrients (calcium, magnesium, and sulfur); and micronutrients (boron, chlorine, copper, iron, manganese, molybdenum, and zinc). These classifications, which are based on the quantity of nutrients utilized by plants, do not imply their function or degree of necessity.

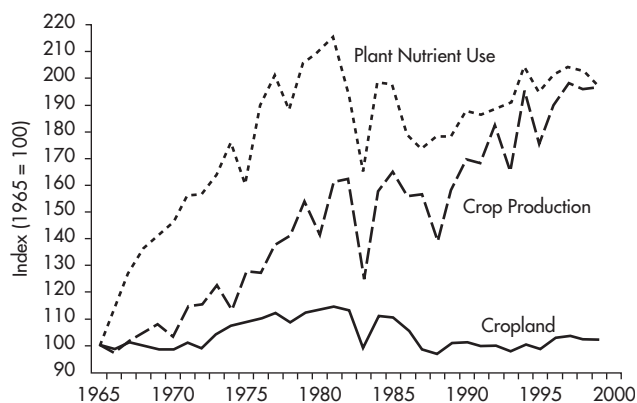
Much attention has been paid recently to the environmental impact of fertilizers and nutrients in the environment in general. In response, the science of fertilizer application and management practices in general are evolving to integrate a sophisticated suite of practices called best management practices (BMPs). These practices may include the use of advanced fertilizer products such as slow- or controlled-release fertilizers; soil testing; precision agriculture; and

the use of crop rotation, buffer strips, or other site-specific practices as needed to prevent unintended release of nutrients to the environment.

AGRICULTURAL PRODUCTION AND PLANT NUTRIENT USE

Until about 1900, demands for higher crop yields were met simply by bringing new agricultural lands into cultivation. Since that time, great progress has been made in increasing yields through fertilization and improved crop varieties and cultural practices. At the same time, land under cultivation throughout the world has remained relatively constant or, as in the United States in recent years, has been taken out of production. Figure 1 illustrates the relationship of agricultural production to crop acreage and consumption of the primary plant nutrients in the United States since 1965. This figure demonstrates the great increases in productivity accomplished with declining levels of cropland over the past several decades.

In the past 40 years, particularly during the 1980s and 1990s, the growth of the U.S. fertilizer industry has been relatively stable. In 1962, U.S. farmers used 24.1 Mt of fertilizer materials at a total expenditure of \$1.5 billion. In 1990, total fertilizer consumption exceeded 43.2 Mt, valued at more than \$7 billion. Table 1 indicates farm expenditures and plant nutrient consumption in the United



Adapted from AAPFCO and The Fertilizer Institute 2003 and earlier issues; Economic Research Service, USDA 2004.

Figure 1. Nutrient use, cropland, and crop production indices

Table 1. Estimated farm expenditures in billions of dollars for fertilizers, and plant nutrient consumption in the United States*

Year†	Total Fertilizer Expenditure	Primary Plant Nutrients, thousand t			
		Nitrogen	Phosphate	Potash	Total
1960	NA‡	2,738	2,572	2,153	7,463
1965	1.921	4,639	3,512	2,835	10,986
1970	2.224	7,459	4,574	4,036	16,069
1975	6.447	8,601	4,507	4,453	17,561
1980	8.269	11,407	5,432	6,245	23,084
1985	8.114	11,493	4,658	5,553	21,704
1990	7.036	11,076	4,345	5,203	20,624
1995	9.347	11,719	4,425	5,128	21,272
2000	10.021	12,334	4,314	4,972	21,620

* All consumption figures updated from the U.S. Department of Agriculture, Association of American Plant Food Control Officials.

† Fertilizer year ending June 30.

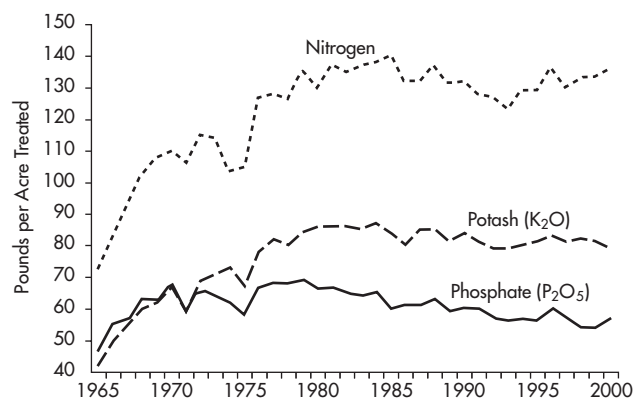
‡ NA = not available.

States from 1960 to 2000. Phosphate and potash are expressed as P_2O_5 and K_2O , respectively. To convert phosphate to phosphorus, multiply P_2O_5 by 0.44 and multiply K_2O by 0.83 to convert to potassium.

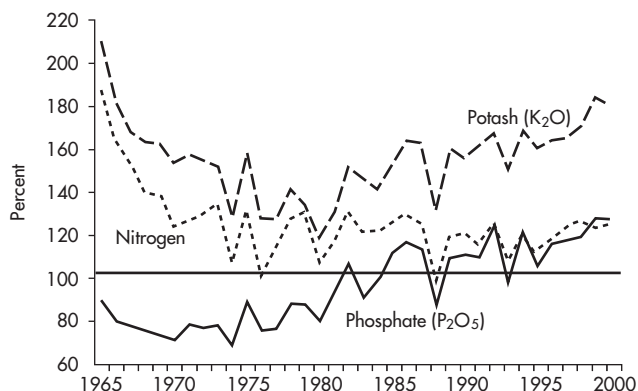
Food demand for a growing world population stimulated crop production in the United States during the 1960s and 1970s. Farmers rapidly expanded plant nutrient application rates in an attempt to increase crop production and farm income. Then, as farm commodity prices fell in the face of overproduction, farmers began to reduce application rates. Crop yields have continued to set new records, however, as farmers have increased the efficiency of fertilizer use through improved soil fertility and management practices. Figure 2 illustrates the pattern of U.S. plant nutrient application rates for corn over the past four decades. This figure also shows that nutrient consumption in the United States was remarkably stable during the period from 1980 to 2000.

As application rates of phosphorus and potassium have declined in recent years, crop removal of these nutrients is depleting the nutrient supply in some soils. With the current emphasis on sustainability in agriculture, nutrient removal will become a critical factor in future crop production. Figure 3 illustrates the change in nutrient removal ratios for the United States from 1965 through 2000. A value greater than 100% indicates that more nutrient is being removed from the soil than is being added. The figure clearly demonstrates that macronutrient withdrawal is significantly exceeding input, especially for potash, a situation that will ultimately result in deficits over time.

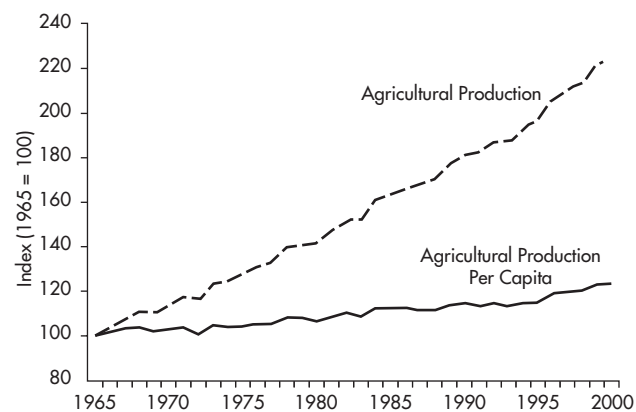
In March 2004, the world population was greater than 6.35 billion people. The widespread forecasts of food shortages and famine that were predicted in earlier years have not come to pass. Although population estimates for 2050 range from approximately 9 billion to almost 12 billion, world per capita food production has kept pace with population growth and diets have steadily improved (see Figure 4). There may always be pockets of limited food supplies, but with the proper use of fertilizers and other agricultural inputs, the success of world agriculture will continue. Fertilizer has been and will remain the keystone to adequate food and fiber production in the coming years.



Adapted from Vroomen 1989; Economic Research Service, USDA 1994; USDA National Agricultural Statistics Service 2001 and earlier issues.

Figure 2. Nutrient application rates for corn

Source: Johnston and Usherwood 2002.

Figure 3. Nutrient removal rates

Adapted from Food and Agriculture Organization of the United Nations 2004.

Figure 4. Agricultural production and agricultural production per capita

PRIMARY PLANT NUTRIENTS IN FERTILIZERS

Primary nutrients (nitrogen, phosphorus, and potassium) are designated as such because of the amounts required and their significance to plant growth. Practically all soils are deficient in nitrogen. Most soils are also deficient to varying degrees in available phosphorus and potassium. Consequently, these nutrients comprise the vast majority of fertilizers applied to soils.

Nitrogen

Nitrogen is part of every living cell and is essential for plant growth. Plants require large amounts of nitrogen for normal growth. Adequate nitrogen is also important for water use efficiency. The use of nitrification inhibitors or slow-release formulations of nitrogen can improve the efficiency of nitrogen use. Nitrogen fixation must occur before nitrogen can be used by plants, and most forms of nitrogen will increase soil acidity.

The world needs a tremendous amount of protein, and sound agronomic practices including the use of nitrogen fertilizers can help fulfill the protein requirement of higher yielding, more protein-rich crops. Using an assumption of 40 g (1.4 oz) of protein per person per day for the entire world population, daily consumption would be approximately 545 million lb and annual consumption would be greater than 100 Mtpy.

Nitrogen accounts for about half of the total nutrients applied as fertilizers in the United States. Table 2 shows consumption of nitrogen fertilizer in North America and other world markets in recent years, and Table 3 lists the International Fertilizer Industry Association's (IFA) statistical classifications for regions and countries. North America and Western Europe have decreased in importance in the world market as fertilizer use has increased dramatically in eastern Europe and Asia in the past decade. In 2000, Asia accounted for 43% of world nitrogen use, followed by North America at 12%.

The manufacturing process for nitrogen fertilizers involves the fixation of atmospheric nitrogen through a chemical process called the Haber-Bosch equation. Commercially available sources of nitrogen include both organic and inorganic forms. Nitrogen is mainly

absorbed from the soil by plants as nitrate (NO_3^-), but may also be taken up as ammonium (NH_4^+) ions, and all nitrogen must be converted to these forms before it can be absorbed by the plant. After entering the plant, nitrogen is converted into complex compounds and ultimately into proteins.

In the past, virtually all nitrogen was applied to soil in the form of animal manures. Certain soils in Europe have a synthetic surface layer more than 0.9 m thick resulting from centuries of manure application. One of the earliest commercial sources of nitrogen was guano (excreta and remains of sea fowl found in deposits on certain arid islands). This material can contain as much as 13% nitrogen and about 9% phosphorus. Neither manure nor guano is an important commercial source of fertilizer today, although environmental regulation of large animal operations will likely increase the importance of manure utilization. In fact, several state-of-the-art pilot plants that convert poultry litter to commercial fertilizer have been built. Animal manures are applied to soils primarily because of the need for disposal, but manures may supply significant amounts of nitrogen to fields near their source of origin. It is important to note that organic nitrogen comprises 97%–98% of the nitrogen found in soil. This form of nitrogen cannot be used by plants but is gradually transformed by soil microorganisms to ammonium. Ammonium is not leached to groundwater to a great extent. Because ammonium is a positively charged ion (cation), it is attracted to and held by the negatively charged soil clay, making it available to plants.

Commercially important inorganic sources of nitrogen include ammonium nitrate (NH_4NO_3), available in both solid (33%–34% N) and liquid (19%–21% N) forms; ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$, 21% N]; calcium nitrate [$\text{Ca}(\text{NO}_3)_2$, 15% N]; potassium nitrate [KNO_3 , 13%–15% N]; urea (NH_2CONH_2 , 45%–46% N); anhydrous ammonia (NH_3 , 82% N); and nitrogen solutions (28%–32% N), a combination of ammonium nitrate and urea solutions. Figure 5 shows the relative importance of these products in the United States. Worldwide, urea has become the leading nitrogen fertilizer because of its high nutrient content and applicability to most crop management practices.

Table 2. World nitrogen fertilizer consumption by region, Mt

Year	Western Europe	Central Europe	Eastern Europe & Central Asia	North America	Latin America	Oceania	Africa	WANA* (former Middle East)	South Asia	Northeast and Southeast Asia	East Asia (former Socialist Asia)	World	Developed Economies†	Developing Economies‡
1960	3.35	0.76	0.77	2.82	0.42	0.03	0.14	0.26	0.31	1.20	0.77	10.83	8.55	2.28
1970	7.08	2.74	4.61	7.69	1.34	0.14	0.52	0.75	1.91	1.62	3.36	31.75	23.13	8.61
1975	8.42	3.88	7.34	10.00	1.89	0.19	0.83	1.24	2.81	2.06	5.24	43.90	30.79	13.11
1980	10.20	4.18	8.26	11.77	2.83	0.28	1.21	1.92	4.93	2.73	12.47	60.78	35.79	24.90
1985	11.10	4.55	10.95	10.77	3.40	0.38	1.24	2.59	7.34	3.47	14.57	70.37	38.86	31.51
1990	10.38	3.35	8.58	11.40	3.73	0.50	1.29	3.24	10.26	4.35	20.32	77.56	35.39	42.16
1995	9.80	2.00	2.55	12.74	3.91	0.83	1.11	3.40	12.94	4.72	24.06	78.07	28.88	49.18
2000	9.33	2.29	2.56	12.06	4.98	1.23	1.36	4.05	14.39	4.87	24.07	81.19	29.07	52.12

Source: International Fertilizer Industry Association (IFA) 2004.

* WANA = West Asia and Northeast Africa.

† Developed economies include Western Europe, Central Europe, Eastern Europe, Central Asia, North America, Northeast Asia, Australia, New Zealand, Israel, and South Africa.

‡ Developing economies include Central America, South America, Africa (except South Africa), West Asia (except Israel), Northeast Africa, South Asia, East Asia, Oceania (except Australia and New Zealand).

Table 3. IFA regions and countries statistical classification

West Europe	Central Europe	Eastern Europe and Central Asia (former Soviet Union)	North America
Austria	Albania	Estonia	Canada
Belgium/Luxemburg	Bulgaria	Latvia	United States
Denmark	Czech Republic	Lithuania	
Finland	Slovak Republic	Belarus	
France	Hungary	Russian Federation	
Germany	Poland	Ukraine	
Greece	Romania	Armenia	
Iceland	Bosnia and Herzegovina	Azerbaijan	
Ireland	Croatia	Georgia	
Italy	Macedonia	Kazakhstan	
Netherlands	Slovenia	Kyrgyzstan	
Norway	Yugoslavia	Moldova	
Portugal		Tadjikistan	
Spain		Turkmenistan	
Sweden		Others	
Switzerland			
United Kingdom			
Central America and the Caribbean	South America	Africa	West Asia and Northeast Africa (former Middle East)
Costa Rica	Argentina	Algeria	Cyprus
Cuba	Brazil	Morocco	Iran
Dominican Republic	Chile	Tunisia	Iraq
El Salvador	Colombia	Cameroon	Israel
Guatemala	Ecuador	Côte d'Ivoire	Jordan
Mexico	Peru	Ethiopia	Lebanon
Nicaragua	Uruguay	Kenya	Saudi Arabia
Trinidad	Venezuela	Mauritius	Syria
Others	Others	Nigeria	Turkey
		Senegal	Egypt
		South Africa	Libya
		Sudan	Others
		Tanzania	
		Zambia	
		Zimbabwe	
		Others	
South Asia	Northeast Asia	East Asia (former Socialist Asia)	Southeast Asia
Afghanistan	Japan	China	Indonesia
Bangladesh	Korea Republic	Korea P.D.R.	Malaysia
India	Taiwan/China	Vietnam	Myanmar
Nepal			Philippines
Pakistan			Thailand
Sri Lanka			Others
Others			
Oceania	<p>The designation employed and the presentation of material in this information product do not imply the expression of any opinion whatsoever on the part of the International Fertilizer Industry Association (IFA) concerning the legal status of any country, territory, city or area or its authorities, or concerning the delimitation of its frontiers or boundaries.</p>		
Australia			
New Zealand			
Others			

NOTES:

Developed Economies: West Europe, Central Europe, Eastern Europe and Central Asia, North America, Northeast Asia, Australia, New Zealand, Israel, and South Africa.

Developing Economies: Central America, South America, Africa (except South Africa), West Asia and Northeast Africa (except Israel), South Asia, Southeast Asia, East Asia, Oceania (except Australia and New Zealand).

Source: International Fertilizer Industry Association (IFA) 2004

Nitrogen is applied to soils either before planting, at planting, or after planting as a side dress application. All inorganic sources of nitrogen convert to the usable nitrate form rather rapidly in warm, moist soils, but nitrates may leach rapidly under certain conditions. The crop, soil, and weather conditions dictate which materials and application methods are best, but some general principles are applicable. Soil conditions that have the greatest influence on nitrification or denitrification include soil pH, moisture content, temperature, aeration, and amount of plant residues in the soil. Leaching can contribute to ground water and surface water pollution. Loss of nitrates by leaching is undesirable from all standpoints. The loss is minimized and crop use maximized by the following proper management practices:

- Split the applications of nitrogen on sandy or shallow soils where leaching or erosion hazards are greatest and when heavy rates of nitrogen are required.
- Apply nitrogen during the growing season on soil subject to leaching and erosion.
- Apply the proper amount of nitrogen and other plant nutrients for vigorous crop growth; base this amount on a soil test.
- Use good soil conservation techniques to minimize erosion losses of topsoil.

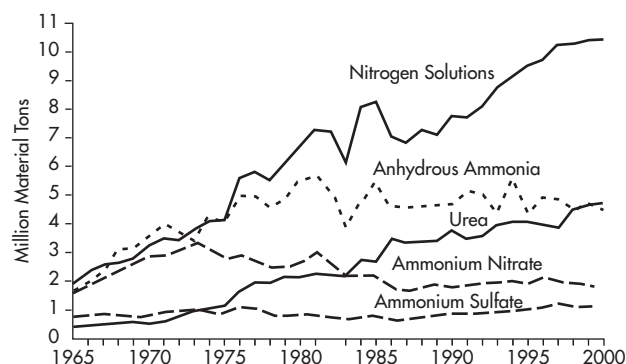
Phosphorus

Phosphorus is essential for normal growth and maturity. It plays a role in photosynthesis, respiration, energy storage and transfer, cell division, cell enlargement, and several other processes in plants. Adequate phosphate also has many other beneficial properties, including helping roots and seedlings develop more rapidly, improving winter hardiness, increasing water use efficiency, contributing to disease resistance in certain plants, and hastening maturity—all important to harvest and crop quality. Of the three primary nutrients in fertilizers, phosphate is required by plants in quantities about one tenth as high as those of nitrogen and potassium. In 2000, total phosphate used in the United States was approximately 4.5 Mt. World consumption of phosphate has been level over the last 25 years; from 32.03 Mt in 1980 to 32.48 Mt in 2000 (Table 4).

Phosphorus is absorbed from soils by plants principally as the orthophosphate (H_2PO_4^-) ion. Once inside the plant, it enters into the composition of phospholipids and nucleic acids. A major metabolic role of phosphorus in the cells of both plants and animals is the provision of energy that results from the high-energy phosphate bonds. In the growing plant, phosphorus is most abundant in growing tissues where it is utilized in the synthesis of nucleoproteins. As the plant matures, phosphorus accumulates in the seed and fruit.

Fertilizer phosphorus is highly reactive with clays and organic constituents in soils and forms relatively insoluble compounds. As a result, it does not move downward with percolating groundwaters but tends to accumulate in the surface layer of soil. Thus, after several years of high phosphorus fertilization, farmers are able to reduce their phosphorus fertilization rates without loss in crop yields. High crop yields, however, usually require a maintenance application of phosphate fertilizer.

The development of the modern phosphate fertilizer industry dates back to 1840 when Justus van Liebig, a German scientist, demonstrated that the fertilizer value of bones was significantly increased by treatment with sulfuric acid. Two years later, the process by which phosphate rock (apatite) was treated with sulfuric acid to produce ordinary superphosphate (20% P_2O_5) was patented in England by John Bennett Lawes. Commercial production began in the United States in 1852.



Source: AAPFCO and The Fertilizer Institute 2003 and earlier issues.

Figure 5. Consumption of selected nitrogen materials

In today's fertilizer phosphate industry, nearly all products originate from phosphate rock. It is still acidulated with sulfuric acid using essentially the same principle employed in England more than 100 years ago. Ordinary superphosphate dominated the phosphate market until recent years when new materials began to replace it, primarily because of their higher phosphate content and lower transportation costs. The three products currently dominating the world phosphate market include normal superphosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$], concentrated superphosphate [$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$], and complex fertilizers including monoammonium phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$); di ammonium phosphate [$(\text{NH}_4)_2\text{HPO}_4$]; and nitric phosphates of varying analyses. Figures 6 and 7 illustrate how the production of ammonium phosphates has grown since its introduction in the U.S. fertilizer market in the 1950s.

Nearly all commercially available sources of phosphorus are highly water soluble. However, when the calcium phosphates, such as normal superphosphate, are ammoniated to make other complex fertilizer products, the high pH of the manufacturing process often causes further reaction of calcium with the phosphorus, resulting in precipitation of insoluble calcium phosphate compounds. These products are more effective on acid soils than on alkaline soils.

Most crops recover only 10%–30% of mineral phosphorus during the first year following application. Overall recovery can vary widely, depending on phosphorus source and a number of other variables, but much of the residual phosphorus will be available to succeeding crops. Other important considerations in phosphorus application to soil and its utilization by plants is soil pH. The soil pH range for optimum phosphorus availability is 6.0 to 7.2. In more acid soils, phosphorus can be complexed by iron and aluminum compounds. At alkaline pH levels, phosphorus reacts with calcium, forming insoluble calcium phosphates. These problems are partially overcome by liming acid soils and applying only highly water-soluble phosphate sources on alkaline soils.

Because of its relative immobility in soils, phosphorus must be incorporated into the soil for optimum effectiveness. Broadcasting phosphate fertilizers with subsequent incorporation is an effective method of application. Recovery of applied phosphorus is usually higher, however, when it is placed in a band beside the seed row, particularly when a available soil phosphorus levels are quite low. At low rates, some phosphate fertilizers have been effectively applied in direct contact with the seed. Broadcasting still dominates phosphorus fertilizer application in the United States, but band application at seeding continues to grow in importance, especially with the use of liquid phosphate materials.

Table 4. World phosphate fertilizer consumption by region, Mt

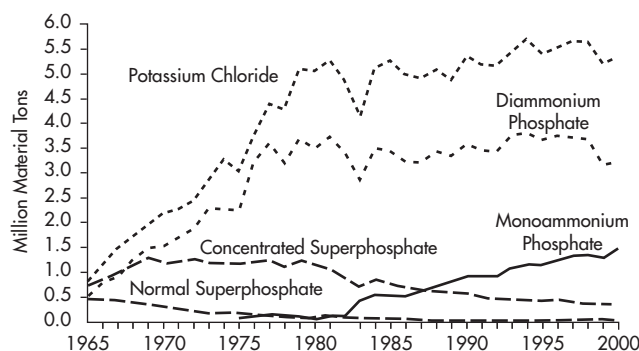
Year	Western Europe	Central Europe	Eastern Europe & Central Asia	North America	Latin America	Oceania	Africa	WANA* (former Middle East)	South Asia	Northeast and Southeast Asia	East Asia (former Socialist Asia)	World	Developed Economies [†]	Developing Economies [‡]
1960	3.87	0.64	1.09	2.56	0.33	0.80	0.28	0.11	0.09	0.69	0.23	10.73	9.64	1.09
1970	5.89	1.86	3.13	4.67	0.93	1.08	0.50	0.31	0.63	1.03	1.07	21.11	17.59	3.52
1975	5.38	2.57	4.74	5.24	1.68	0.90	0.73	0.65	0.65	1.27	1.97	25.78	19.83	5.95
1980	5.89	2.76	5.59	5.56	2.77	1.20	0.97	1.03	1.60	1.57	3.10	32.03	22.16	9.87
1985	5.26	2.79	7.62	4.50	2.33	0.99	0.96	1.47	2.55	1.80	3.18	33.47	22.27	11.20
1990	4.49	1.50	7.81	4.39	2.67	0.80	0.83	1.87	3.89	2.18	6.03	36.07	19.97	16.10
1995	3.62	0.65	0.80	4.77	2.50	1.37	0.74	1.52	3.61	2.16	9.20	30.94	12.10	18.84
2000	3.09	0.59	0.58	4.50	3.84	1.61	0.75	1.58	5.17	1.68	9.09	32.48	11.29	21.19

Source: International Fertilizer Industry Association (IFA) 2004.

* WANA = West Asia and Northeast Africa.

† Developed economies include Western Europe, Central Europe, Eastern Europe, Central Asia, North America, Northeast Asia, Australia, New Zealand, Israel, and South Africa.

‡ Developing economies include Central America, South America, Africa (except South Africa), West Asia (except Israel), Northeast Africa, South Asia, East Asia, Oceania (except Australia and New Zealand).



Source: AAPFCO and The Fertilizer Institute 2003 and earlier issues.

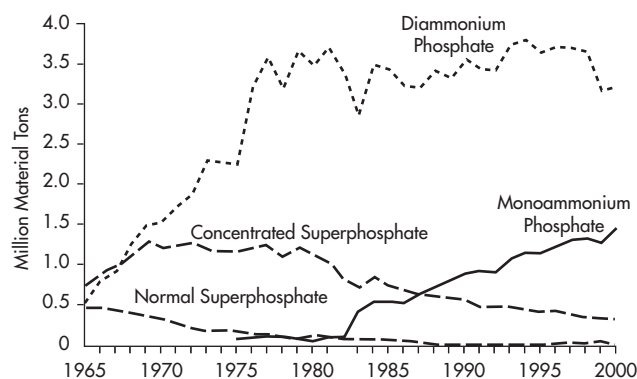
Figure 6. Consumption of selected phosphate and potash materials

Potassium

Potassium is one of the vital three primary nutrients, along with nitrogen and phosphorus. Primary minerals generally considered to be the original sources of potassium include orthoclase and microcline feldspars, muscovite, and biotite. Many high-yield crops have potassium contents that exceed their nitrogen content. Potassium is vital to photosynthesis, and when deficient, photosynthesis declines and the plant's respiration increases. The deficiency symptoms lower the plant's carbohydrate supply. The potassium content of fertilizers is expressed as K_2O equivalent, or potash, even though no K_2O exists as such in fertilizer materials. To convert from K to K_2O , multiply by 0.83.

From 1960 to 2000, world potash consumption increased by more than 250%. Table 5 shows that it increased from 8.48 to 21.86 Mt during this period. From 1980 to 2000, however, world consumption changed little. Muriate of potash (potassium chloride, or KCl) is the dominant source of fertilizer potassium throughout the world. Other important, but much less significant, sources are sulfate of potash (K_2SO_4), potassium magnesium sulfate ($K_2SO_4 \cdot MgSO_4$), and potassium hydroxide (KOH).

Growing plants absorb potassium as the K^+ ion. Potassium is unlike the other mineral constituents in that its exact metabolic role



Source: AAPFCO and The Fertilizer Institute 2003 and earlier issues.

Figure 7. Consumption of selected phosphate materials

in the plant is unknown. It occurs in the ionic state and not as a component of compounds within the plant, but potassium is indispensable for plant growth and most plants require it in large quantities. Some known functions of potassium include the following:

- It is essential to protein synthesis.
- It breaks down carbohydrates, a process that provides energy for plant growth.
- It helps to control ionic balance and provides turgor; potassium-deficient plants wilt more easily.
- It helps the plant overcome the effects of disease and improves winter hardiness.
- It activates more than 80 enzyme systems that regulate the rates of major plant growth reactions.

Potassium and phosphorus application methods are very similar. Most potassium is broadcast, with a lesser amount band-applied near the seed row at planting time. Muriate of potash is usually mixed with phosphorus fertilizers and the two nutrients are applied simultaneously to soils. Almost two thirds of the potassium used in the United States is applied to soils of the Corn Belt in the Midwest.

Table 5. World potash fertilizer consumption by region, Mt

Year	Western Europe	Central Europe	Eastern Europe & Central Asia	North America	Latin America	Oceania	Africa	WANA* (former Middle East)	South Asia	Northeast and Southeast Asia	East Asia (former Socialist Asia)	World	Developed Economies [†]	Developing Economies [‡]
1960	3.74	0.66	0.77	2.06	0.24	0.09	0.10	0.01	0.07	0.69	0.05	8.48	7.96	0.52
1970	5.35	1.99	2.57	4.01	0.64	0.21	0.23	0.04	0.28	0.89	0.08	16.29	14.85	1.44
1975	5.19	3.15	5.18	4.95	0.93	0.20	0.32	0.05	0.32	0.97	0.16	21.42	19.32	2.09
1980	5.63	2.70	4.90	6.10	1.83	0.22	0.37	0.08	0.71	1.23	0.62	24.39	20.22	4.17
1985	5.71	2.72	6.82	4.98	1.70	0.23	0.42	0.14	0.93	1.49	0.47	25.63	21.23	4.40
1990	5.09	1.50	5.16	4.87	2.00	0.24	0.44	0.19	1.50	1.90	1.81	24.61	17.47	7.14
1995	4.33	0.57	0.94	5.08	2.33	0.38	0.40	0.18	1.34	2.17	2.84	20.55	11.95	8.60
2000	3.56	0.64	0.74	4.79	3.41	0.38	0.43	0.34	1.80	1.94	3.83	21.86	10.91	10.95

Source: International Fertilizer Industry Association (IFA) 2004.

* WANA = West Asia and Northeast Africa.

† Developed economies include Western Europe, Central Europe, Eastern Europe, Central Asia, North America, Northeast Asia, Australia, New Zealand, Israel, and South Africa.

‡ Developing economies include Central America, South America, Africa (except South Africa), West Asia (except Israel), Northeast Africa, South Asia, East Asia, Oceania (except Australia and New Zealand).

SECONDARY PLANT NUTRIENTS IN FERTILIZERS

Although plants require calcium, magnesium, and sulfur—the secondary micronutrients—in smaller amounts than the primary nutrients, their role in plant nutrition is easily as important as that of the primary nutrients. Many crops contain as much sulfur (S) as phosphorus, sometimes more. Increasing crop yields, sandy soils, and leaching caused by high rainfall or irrigation are factors that influence the use of magnesium and sulfur in fertilizers. The use of fertilizer calcium strictly as a nutrient is limited and dictated by special crop needs and unusual soil conditions. Common fertilizer materials containing these secondary nutrients are potassium sulfate, sulfate of potash-magnesia, gypsum, normal superphosphate, magnesium sulfate, elemental sulfur, and calcium nitrate.

Calcium

Calcium is important not only as a plant nutrient, but also as a factor responsible for maintaining desired physical and biological conditions in the soil. Of the exchangeable bases found in soil (potassium, magnesium, calcium, and sodium), calcium is dominant, normally accounting for 50% to 80% of the total. Calcium is absorbed by plants as the Ca^{2+} ion. Inside the plant, calcium forms structural compounds that are part of cell walls, stimulates root and leaf development, helps activate several plant enzyme systems, and helps balance organic acids in the plant. Calcium is also important in the reduction of nitrates during the formation of plant proteins. Deficiencies in calcium manifest in abnormal development of growing points (terminal buds) and poor root growth.

Most soils contain sufficient calcium for plant growth. Many soils are too acid for optimum plant growth, however, before calcium application. Soil pH can be increased to a desirable level most economically with broadcast applications of finely ground agricultural liming materials. Lime supplies are virtually unlimited and commercial deposits have been found in most agricultural areas. Common lime materials are derived from calcite (CaCO_3), dolomite ($\text{CaCO}_3 \cdot \text{MgCO}_3$), and to a lesser extent, basic slag, which is a calcium silicate material that contains some phosphorus and magnesium. These materials are sometimes used as fillers in mixed fertilizers, although more than 95% of agricultural lime is applied

Table 6. Use of agricultural liming materials in the United States

Year*	Liming Materials, Mt
1910	3.20
1920	3.30
1930	3.10
1940	4.40
1950	6.80
1960	11.70
1970	18.00
1980	17.60
1990	15.70
2000	19.60

* Fertilizer year ending June 30.

directly to soils. Table 6 shows agricultural lime consumption in the United States.

Soils of the humid regions east of the Mississippi River generally require higher rates and more frequent applications of lime. Soil calcium and magnesium may be leached from those soils by relatively high rainfall, resulting in a decrease in the soil pH. In addition, application of nitrogen fertilizers indirectly increases soil acidity. As a general rule, 3 kg/ha of calcite are required to neutralize the soil acidity resulting from every kilogram per hectare of nitrogen applied to soils. Typical amounts of calcium in the soil range from less than 0.1% to as much as 25%, with arid, calcareous soils containing the highest levels.

In addition to creating a desirable soil pH level for optimum plant growth and resulting in a more desirable soil physical condition, a secondary effect of lime is that soil pH influences the availability of other nutrients. Although phosphorus availability is greatest at pH 6.0 to 7.2, the micronutrients copper, iron, manganese, and zinc generally are less available as the soil pH approaches neutrality. These micronutrients must often be applied to the soil or crop as fertilizers.

Crops such as peanuts and tomatoes require a relatively large amount of soluble calcium. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is often used where these crops are grown and is usually applied directly to soil rather than as a component of mixed fertilizers. Sources of much less significance for their calcium content are normal and concentrated superphosphates and calcium nitrate.

Magnesium

Magnesium is absorbed by plants as the Mg^{2+} ion. Its role as the central atom of the chlorophyll molecule is of major significance. Magnesium also aids in phosphate metabolism, plant respiration, and the activation of many enzyme systems. The use of high-calcium lime materials and the natural tendency of many soils to be low in available magnesium have stimulated the practice of including soluble magnesium sources in some premium fertilizer products. These soluble magnesium materials may increase the crop production efficiency of the primary nutrients.

Magnesium sources either added to other fertilizers or applied directly to soil can be classified by their chemical nature or by their degree of water solubility. A source must either be water soluble or convertible to a water-soluble form before the magnesium can be absorbed by the plant. Magnesium sources that are soluble or readily available are hydrated magnesium sulfates and sulfate of potash-magnesia (langbeinite: $\text{K}_2\text{SO}_4 \cdot 2\text{MgSO}_4$). Included in the hydrated magnesium sulfate group are kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) and epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$). Sources that are only slightly water soluble but that become soluble over a period of 2 to 4 years include dolomite, brucite ($\text{MgO} \cdot \text{H}_2\text{O}$), magnesite (MgCO_3), basic slag (which contains various nutrients and usually from 2% to 8% Mg), and periclase (MgO). Although most of the soluble magnesium materials are mixed with other fertilizers, nearly all other magnesium sources are directly applied to soils. Dolomite, by far the most significant source, is applied to soils at rates of 1 to 3 t/ha.

Sulfur

Sulfur has been recognized as an essential plant nutrient for more than 140 years. Further, it has been basic to the fertilizer industry since its inception because of the treatment of phosphate rock with sulfuric acid in the manufacture of superphosphate. In that process, the sulfuric acid reacts with calcium in phosphate rock, resulting in the formation of gypsum. Gypsum is not removed from normal superphosphate so that the product contains 1.2% sulfur. At one time, normal superphosphate was the chief source of sulfur in fertilizers, and nearly all mixed fertilizers contained some normal superphosphate. In recent years, however, increasing importance has been placed on high-analysis phosphates (the industry uses "high analysis" to mean "high nutrient content"). In these products, sulfuric acid is used to treat phosphate rock, but the sulfur is removed with further processing to higher analysis phosphate materials.

Some plants require almost as much sulfur as the yodophorus. Sulfur enters the plants as the sulfate (SO_4^{2-}) ion and becomes a necessary component of protein. It is also a constituent of the mustard oil glycoside, which imparts characteristic odors and flavors to such species as mustard, onions, and garlic.

The major sources of sulfur in today's fertilizers are ammonium sulfate, normal superphosphate, potassium sulfate, langbeinite, and gypsum. In chemically manufactured mixed fertilizers, sulfuric acid is still in wide use for neutralization of the ammonia used in their formulation. In certain areas where response to sulfur is obtained, langbeinite is increasing in importance as a sulfur source. Elemental sulfur also is commonly used, but its oxidation to the available sulfate form requires time and reduces soil pH levels.

Ammonium thiosulfate [$(\text{NH}_4)_2\text{S}_2\text{O}_3$] is a widely used sulfur source in the fluid fertilizer industry. It is made by reacting sulfur dioxide (SO_2) and aqueous ammonia, with further reaction with elemental sulfur. It contains about 26% sulfur, which soon oxidizes in soil to the sulfate form and is completely soluble in liquid N-P-K mixtures. It is important to the fluid fertilizer industry because fluids are normally sulfur-free and are not compatible with most other sulfur sources.

MICRONUTRIENTS IN FERTILIZERS

Micronutrients are essential to plants but are required only in minute quantities. The availability of specific micronutrients is related to soil pH, generally decreasing as soil pH increases from 5 to 7. Micronutrients that must be added to certain soils as fertilizers include boron, copper, iron, manganese, molybdenum, and zinc. Chloride has also been recognized as a micronutrient and has recently been noted to play an important nutritional role in small grains, corn, and sorghum. Micronutrient products may be divided into three primary classes: inorganics, organic complexes, and synthetic chelates.

In certain crops, deficiencies of micronutrients have been increasing in recent years. This can be caused by increased crop production, high yield goals, exclusive use of N-P-K fertilizers without micronutrients, and diminished soil reserves of available micronutrients. These factors have combined to increase the consumption of micronutrient fertilizers, particularly in recent years. Data on U.S. micronutrient consumption was not collected until 1967 when the U.S. Department of Agriculture obtained information from known producers of copper, iron, manganese, molybdenum, and zinc. Use of manganese and zinc is much higher than that of the other micronutrients. This is because manganese and zinc are mainly applied to corn, wheat, soybean, cotton, and rice, crops that are grown over the largest acreage in the United States.

Micronutrient sources vary considerably in physical state, chemical reactivity, cost, and availability to plants. They are classified as inorganic, synthetic chelates, and natural organic complexes. Typically micronutrient application rates are determined by correlating soil tests with levels found in plant materials. Plant analysis can also be used to confirm deficiencies, and amendments must be applied as early as possible, preferably before planting.

Micronutrient fertilizers, like primary nutrients, should be applied on an as-needed basis and are typically applied with multi-nutrient-mixed fertilizers. They may be incorporated in chemically manufactured fertilizers, in blends, or in fluids. In certain cases, micronutrients are applied directly to soils or used as foliar sprays. Micronutrients must be water soluble before they can be absorbed by plants. The solubility or availability of copper, iron, manganese, and zinc to plants decreases with increasing soil pH; that of boron and molybdenum generally increases with increasing soil pH. Ultimately, the choice of micronutrient source is related to the method of application, compatibility with other fertilizers, cost, agronomic effectiveness, and ease of application.

Boron

Boron is added to more fertilizers than any of the other micronutrients. Boron fertilizers usually are required for optimum growth of alfalfa, cotton, and clovers. A large number of plant species will not tolerate more than traces of soluble boron. Conversely, many plant species will not produce seed without adequate boron, and deficiency symptoms include stunting; hollow stems and fruit; discolored, brittle leaves; and poor pollination resulting in loss of flowers and buds. Boron is added to mixed fertilizers, typically as borate

ion (BO_3^-) or boric acid (H_3BO_3). Most plant-available boron is found in the soil or organic matter. Conditions that favor increased mineralization include warm, moist soil and good aeration.

Chloride

The chloride ion is the micronutrient most recently recognized as essential. Recent evidence indicates that chloride has a nutritional role in grains, corn, and grain sorghum. Chloride is very prevalent in soil, commonly occurring as soluble salts such as sodium chloride (NaCl), calcium chloride (CaCl_2), and magnesium chloride (MgCl_2). Chloride acts as the counterpoint during potassium uptake, thus playing a role in ionic balance, electrical charge balance in physiological functions, and the initial reactions of photosynthesis. Chloride deficiency typically presents with leaf tip wilt, with subsequent bronze discoloration followed by necrosis. Smaller kernel size, delayed maturity, and restricted, highly branched root systems may also be symptoms. Forms of fertilizer chloride can include ammonium chloride (NH_4Cl), calcium chloride, magnesium chloride, and potassium chloride. Each of these forms provides the additional benefit of nutrients, with ammonium chloride recently growing in popularity in the Midwest.

Copper

Copper is necessary for carbohydrate and nitrogen metabolism as well for lignin synthesis in cell walls. These structural properties help prevent wilting in growing plants. Copper is known to stimulate seed production and functions as a coenzyme and regulator responsible for photosynthesis and chlorophyll production. Because plants absorb copper readily, its application with mixed fertilizers is one of the important ways of ensuring that this essential nutrient in animal nutrition is in sufficient concentrations in animal feeds. Many soils—especially the leached, sandy, and excessively cropped soils—need copper applications for optimum crop production, and highly organic soils are also often deficient in copper. Copper is usually added to mixed fertilizers as sulfates, oxides, and chelates. Cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), cupric oxide (CuO), copper sulfate monohydrate ($\text{CuSO}_4 \cdot \text{H}_2\text{O}$), and cuprous oxide (Cu_2O) are the some important sources from which copper fertilizers originate.

Iron

Iron is involved in chlorophyll formation and acts as a catalyst in plant growth. Lack of sufficient iron in plants results in a readily identifiable Fe-chlorosis or yellowing of the plant. Iron also functions within enzyme systems associated with energy transfer, nitrogen reduction and fixation, and lignin formation. Although most soils contain sufficient iron, it may not be available to the plant, particularly in calcareous, high-pH soils. Therefore, supplemental iron is applied as a fertilizer or foliar spray. Soil applications of inorganic iron sources generally are not effective in supplying iron for crops growing on high-pH soils. Inorganic sources such as ferrous sulfate (FeSO_4) or ferric sulfate [$\text{Fe}_2(\text{SO}_4)_3$] may be used as foliar sprays, but they are rapidly converted to forms that are not as available to plants when they are applied to soils alone or with other fertilizers. Some iron chelates are more effective for soil application, but their high cost restricts their use to crops with high cash values.

Manganese

Manganese is another essential micronutrient closely associated with iron and has somewhat similar functions in the plant. Manganese will not take the place of iron, but its absence or excess reduces the effectiveness of iron. Manganese, copper, and iron are probably the main oxidation-reduction regulators in plants. A avail-

able manganese is often deficient in agricultural soils, particularly those that have been recently limed. Manganese is supplied in the form of sulfates, oxides, oxysulfates, and chelates. Usually the less-soluble oxides are less effective, although this depends mainly on granule size. The primary forms that supply these manganese materials for fertilizer are manganese sulfate (MnSO_4) and psilomelane (mixed Mn-oxides), but the manganese in these sources must be reduced to the divalent form to be available to plants. By-product manganous oxide (MnO) is also used as a source of manganese.

Molybdenum

Of all the essential elements, molybdenum is required by plants in the lowest amounts. Molybdenum is present within the coenzymes that facilitate nitrogenase, an enzyme associated with the reduction of nitrates in plants. There are some soils on which little plant growth can be sustained without molybdenum applications. Molybdenum very often stimulates the growth of legumes because of its role in nitrogen metabolism. Given its role in pollen development, molybdenum deficiency may impair nitrogen metabolism, protein synthesis, sulfur metabolism, and grain and fruit formation. Notably, excess dietary molybdenum has been found to result in copper deficiency in grazing animals such as ruminants. The mechanism is the formation of thiomolybdates, which contain sulfur and molybdenum and appear to prevent the absorption of copper.

Molybdenum has a narrow “window” from essentiality to toxicity, wherein small excess amounts may cause harm. Molybdenum is incorporated, alone or as part of a general micronutrient mixture, in many mixed fertilizers in very low concentrations. Molybdenum occurs within soil minerals as an anion (MoO_4^{2-}), and is extremely mobile in soil. The main molybdenum sources are sodium molybdate and ammonium molybdate, which are produced from roasting of the mineral molybdenite (MoS_2), as is molybdic acid (Mo_3O_8).

Zinc

Zinc in plant nutrition is closely associated with the role of copper, mainly as a coenzyme. Most zinc-deficient plants are stunted or grow improperly, and maturity is often delayed. Zinc deficiency occurs in wide areas of the United States, but zinc fertilizers are mainly applied to corn and rice. Zinc is usually incorporated in mixed fertilizers as sulfates, oxysulfates, oxides, and chelates. Most of these sources have been prepared from the mineral sphalerite (ZnS) or from by-product oxides and sulfates from zinc-processing operations and other industries. Zinc, like copper, has a significant residual effect after application, lasting 5 years or longer. Soil testing is the most appropriate way to determine zinc levels.

REGULATION

Fertilizers are regulated primarily at the state level. The Association of American Plant Food Control Officials (AAPFCO) is an organization of fertilizer control officials from each state in the United States, Canada, and Puerto Rico who are actively engaged in the administration of fertilizer laws and regulations. Other AAPFCO members are research workers employed by these governments who are engaged in any investigation of mixed fertilizers, fertilizer materials, their effect, and/or their component parts. The organization strives to gain uniformity by consensus among each of these entities without compromising the needs of the consumers, protection of the environment, or fair competition among the industry.

ADVANCED EFFICIENCY FERTILIZER PRODUCTS

Fertilizer consumers today have many more viable nutrient management choices than they did just 10 years ago. Thanks to

advancements in technology, fertilizer consumers now have several options, including slow and controlled-release fertilizers and urease and nitrification inhibitors—which delay nitrogen availability—when deciding how to supply crops with the essential nutrients. Although controlled-release fertilizers have been around for more than 50 years, recent advances in technology have made them a cost-effective and viable alternative for row crops such as corn and wheat. Nutrient management plans to help increase efficiency and minimize unwanted environmental effects are becoming a requisite component of production agriculture. The use of advanced fertilizers can contribute significantly to protecting the environment by reducing nitrogen losses and improving nitrogen efficiency while improving yields.

Simply stated, slow and controlled-release fertilizers are either absorbed, coated, occluded, or reacted. All four types deliver extended, consistent supplies of nitrogen to the crop. Urease and nitrification inhibitors reduce the rate of transformation of nitrogen into a plant-available form.

Slow and Controlled-Release Fertilizer

These types of fertilizers contain a plant nutrient in a form that delays its availability for plant uptake and use after application, or that extends its availability to the plant significantly longer than a reference “rapidly available nutrient fertilizer” (such as ammonium nitrate or urea, ammonium phosphate, or potassium chloride). A variety of mechanisms can bring about such delay of initial availability or extended time of continued availability, including controlled water solubility of the material (by semipermeable coating, occlusion, or by inherent water insolubility of polymers, natural nitrogenous organics, protein materials, or other chemical forms); slow hydrolysis of water-soluble, low-molecular-weight compounds; or other unknown means. For instance, nitrification inhibitors inhibit the biological oxidation of ammoniacal nitrogen to nitrate nitrogen, whereas urease inhibitors inhibit hydrolytic action on urea by the urease enzyme. When applied to soils, the effect of these inhibitors is less nitrogen lost by volatilization. Of course, producers must recognize an economic or environmental benefit for these products to begin to gain widespread acceptance in the marketplace.

How Do These Products Work?

Advanced efficiency products may work in a variety of ways:

- As nitrogen sources with low solubility in wastewater resulting from a complex molecular structure that releases nitrogen through microbial decomposition
- As materials releasing nutrients through a coated surface
- As materials releasing nutrients through a membrane that may or may not itself be soluble (encapsulation)
- As nutrient-releasing materials incorporated into a matrix that itself may be coated
- As materials releasing nutrients in delayed form because of a small surface-to-volume ratio
- As absorbed fertilizers taken into an absorbent material in which availability of nutrients is increased through occlusion

Slow and controlled-release fertilizer and nitrification and urease inhibitors can increase the efficiency of nutrients applied, generally resulting in higher crop yields, while working to reduce nitrogen transport to air and water. Other advantages of these products include

- Improved agronomic efficiency
- Realization of significant savings in labor, time, and energy

- Lowered risk of environmental pollution by reducing the potential loss of nutrients to air and water between applications
- Uptakes by the plants through gradual nutrient release, increased nitrogen efficiencies, reduced emissions of nitrous oxide (N₂O), oxides of nitrogen (NO_x), and ammonia
- Increased mobilization of phosphate in the rizosphere
- Reduction of seedling damage when seed-placed levels of urea/urea-containing fertilizers are too high

In addition to ensuring that the soil is provided with sufficient nutrients to grow an abundant supply of food, the fertilizer industry is committed to the environmentally sound use of its products. Modern farming practices use fertilizer nutrients to build high-yielding, nutritious crops and also make it possible for people to continue to use large areas of land for forests, parks, and wildlife areas. Although available cropland continues to decrease (Figure 1), crop production continues upward.

The development of advanced fertilizer technologies has added an important facet to the fertilizer industry's environmental stewardship program and to the suite of BMPs farmers may utilize to keep nutrients “in the agricultural box.” With the use of these crop nutrients, farmers improve nitrogen efficiency by reducing excess nitrogen release and evaporation losses, thereby contributing to environmental protection. And because advanced fertilizer technology products are typically applied once per growing season, their use also reduces the potential loss of nutrients between applications and increases uptakes by the plants through gradual nutrient release.

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Adhesives, Caulks, and Sealants

Randy Sandrik

INTRODUCTION

Adhesives, caulks, and sealants (ACS) are compounds that bond or fill surfaces. Although they have different functions, these three categories are generally discussed together because they have similar compositions. Many ACS compounds include industrial minerals in their formulation with a loading, by volume, that ranges from 0% to 80% (average of roughly 50%). In practice, several hundred separate ACS compounds are used in thousands of different products.

Functionally, adhesives are chemical compounds that bond two surfaces together; they are used in packaging, construction, product manufacturing, and installation of wood, metal, rubber, plastics, ceramics, and fiberglass materials. Caulks are generally a low-performance sealant, thick and nonpourable with high concentrations of fillers. They are used to fill joints, spaces, or gaps. Higher performance sealants are based on polymers of sulfides, silicones, and urethanes and are used in weatherproofing, filling, sealing, and product manufacturing.

ACS is a global industry, and ACS sales in 2003 were about \$27 billion (Owen 2003). By region, this breaks down to \$10 billion in North America, \$8 billion in Western Europe, \$7 billion in Asia, and \$2 billion in the rest of the world. In the United States, this \$8 billion business employs 22,000 people, producing ACS in almost every state. Most ACS products are made in California, Ohio, and Texas (U.S. Department of Commerce 2004).

USES OF ACS

ACS compounds are used in almost every aspect of daily life, with myriad structural and nonstructural applications. The following is a breakdown of ACS use by industry:

- Construction: New building construction; fire stops; plaza decks; heating, ventilating, and air conditioning; bridge and deck joints; industrial assembly processes; renovation and finishing of homes; industrial assembly processes; ceramics; cladding; concrete; glass; fixed glass curtain walls; flooring; paneling; precast cement; roofing; structural glazing; and tiles.
- Automotive and aircraft sealants: Acoustics, gaskets and seals, joints and fasteners, interior sealants, threshold sealing, and window sealing.
- Equipment components: Aerospace applications, automotive components, glass, fiber-optic assembly, plastics, and surface-mount printed circuit boards.

- Packaging and labeling: Bags, hot and cold seals, wood gluing, and pressure-sensitive adhesives.
- Other industries: Carpeting, footwear, appliances, wire/cable, porosity sealing, glass fiber bonding, rubber, laminating, aerosol adhesives, medical (from bandages to cardiac surgery), marine, backing, and foam.

Table 1 lists some specific ACS products by classification as adhesive, caulk, or sealant.

FORMULATING ACS PRODUCTS

The formulation of an ACS product is based on economics and desired product properties. Industrial minerals, when included in the formula, tend to be used as extenders, fillers, or pigments. Although industrial minerals usually make up about 50% of the weight or volume of a typical ACS product, they represent only about 10% of the finished product costs. The more expensive basic components include the binder that provides the strength and adhesion required (normally organic resins), diluents (for viscosity control), hardeners (also known as curing agents that combine with the binder), catalysts, accelerators, inhibitors and retarders (to improve cure time), modifiers (which include the industrial mineral as a filler, extender, or pigment), thinners, plasticizers, stabilizers, and wetting agents.

Table 1. Specific products by classification

Adhesives		
• Tape	• Furniture	• Fiber optics
• Book binding	• Canvas treatment	• Factory housing
• Gaskets	• Synthetic fiber binding	
Caulks		
• Epoxy sticks	• Tub and tile caulk	• Caulking compound
• Drywall	• Adhesive caulk	• Plastering mud
• Putty tape	• Urethane caulk	
Sealants		
• Joint sealer	• Silicone rubber	• Polyurethane foams
• Room-temperature vulcanizing (RTV) silicone	• Waterproofing	• Bandages
	• Acoustical sealant	• Glazing

There are many ways to produce ACS but generally, four manufacturing systems are employed: (1) water base, (2) hot melt, (3) solvent, and (4) other. In the United States in 2003, the ACS manufacturing systems were water base (56%), hot melt (20%), solvent (14%), and other (10%).

CLASSIFYING ACS PRODUCTS

ACS products are classified in many ways, including by product type, by testing and standards, and by manufacturer type and subtype. Product types can be classified according to each product's method of bonding, bonding temperature, composition of the main components, number of components, form (elastic or rigid; structural or nonstructural), permanence, performance and conductivity, and application (water- or solvent-based).

Products are also described by performance testing that may include tensile strength, compression load, shear strength, peel load, plowing, torsional fatigue, and cleave load. Standards for ACS products include tear resistance, outgassing, durability, printability, mildew resistance, thermal performance, fire rating, acoustics performance, corrosion resistance, and atmospheric effects.

Manufacturers produce ACS according to the following end uses:

- Adhesives based on natural polymers
- Polymer dispersions and emulsions
- Hot-melt adhesives
- Solvent-based adhesive systems
- Adhesives—reactive (polymerizing) systems
- Adhesives based on water-soluble polymers
- Other adhesives
- Construction sealants
- Transportation sealants
- Consumer sealants
- Assembly/other sealants

For adhesives, manufacturer subtypes include assembly, building construction, consumer, footwear, leather, transportation, paper, and woodwork. For caulks and sealants, the subtypes are butyl, latex, modified silicones, oil-based caulks, polyvinyl acetate caulks, polysulfides, silicones, solvent acrylics, and urethane.

Adhesives can also be classified according to distribution channel (direct or via distributor to the end user); technology (hardening/nonhardening, hot/warm melt, solvent, or waterborne); and chemistry (acrylic, bituminous, epoxy, ethyl vinyl acetate [EVA], polyurethane, polysulfide, or rubber).

INDUSTRIAL MINERALS USED IN ACS PRODUCTS

Most ACS products contain industrial minerals, but not all (e.g., several hot-melt and polymer adhesives). Where industrial minerals are used, they are normally added as a single ingredient, but some blends are used as well. Globally, about 250 listed companies, with at least 1,000 operations, produce the following industrial minerals:

- Calcium carbonate as precipitated calcium carbonate (PCC) or ground limestone, marble, or chalk. These minerals are used to lower costs, and in some cases they may adversely affect ACS performance. PCC is also used in viscosity and rheology control and in high-performance adhesives.
- Clay as kaolin, attapulgite, or bentonite. These are used to lower costs and improve performance, with air-floated kaolin improving flow properties and water-washed kaolin raising viscosity to allow for water addition. Calcined kaolin is used in automotive glazing systems. Surface-treated kaolin is also used (alkyl or vinyl silanes) for higher-performance ACS.

- Other industrial minerals, added for very specific reasons, including color, are used in lesser and varying quantities:

- Silica, as precipitated or fumed
- Tripoli
- ATH (aluminum trihydrate)
- Feldspar
- Barite
- Aluminum hydroxide
- Mica
- Talc
- Wollastonite
- Titanium dioxide, TiO₂
- Antimony oxide
- Gypsum
- Pulverized waste

When producing an ultrafine or specialty ACS product, the filler would include the following specialty products, which are also produced globally by many companies.

- Nano-calc and nano-clay
- Fused silica
- Carbon black
- TiO₂

The industrial mineral loadings in ACS typically are adhesives, 0% to 60%; caulks and putty, up to 85%; and sealants, 0% to 40%.

Production and Consumption of ACS

In 2003, 10 Mt of ACS products were produced, at an average cost of \$1.34/lb. This ACS production consumed about 5 Mt of industrial minerals for fillers, extenders, and pigments (Owen 2003). In the same year, global use of 5 Mt included 3.7 Mt of calcium carbonate, 0.7 Mt of kaolin, and about 0.6 Mt of other industrial mineral fillers. Combined, these have a total value of approximately \$300 million.

Because of its low cost and consistent properties, calcium carbonate is the most widely used filler, extender, and pigment in ACS, at about 3.7 Mt in 2003. Coarse, medium, and fine products are used, and prices in the United States in 2003 ranged from \$24/t to \$140/t, averaging \$50/t. In 2003, the global amount of air-floated and water-washed kaolin, the usual forms of kaolin used in ACS was estimated at 0.7 Mt. Kaolin costs are much higher than ground calcium carbonate (GCC) and are generally more than \$85/t. Other mineral fillers, including some grades of PCC and nano-grades, are more than \$250/t.

MARKET OVERVIEW

Market Environment

ACS producers include large national sealant, caulk, and joint compound suppliers and specialty adhesive suppliers. They are regionally supplied, but follow global manufacturing processes.

Industrial minerals suppliers are normally large commodity producers that have the capacity needed to supply large ACS plants. Their processes are geared toward consistency of color and particle-size distribution.

ACS Market Dynamics

Historical market drivers have included new commercial and residential construction and remodeling of homes and commercial properties. Future drivers will include environmental requirements, and growing uses in automotive, electronics, and medical equipment markets.

A few multinational players who have R&D capabilities, brand recognition, and raw material buying power dominate production of ACS. The top 10 producers of ACS in the world in 2003 were Henkel/Locktite, H.B. Fuller, National Starch, Bostik Findley, 3M, Sovereign, F orbo, Rohm and Haas, Berwind (Elmer's), and GE Silicones. In the United States, these producers, as well as USG, Georgia Pacific, National Gypsum, DAP, KCG, Red Devil, and Dow, sell both to "Big Box" retailers who have large buying power and to contractors and distributors, where some brand loyalty still exists.

ACS producers are high-volume/low-price buyers of industrial minerals. Although they look for unique specifications, they also seek to commodify all raw materials. They often bid business out and use multiple suppliers to guarantee supply and keep prices low. They are regional so as to minimize their delivered costs, but their products must meet global specifications. Table 2 lists the attributes and characteristics on which ACS producers and their customers focus.

COST COMPONENTS OF ACS IN THE UNITED STATES

As a reference to relative cost, the following summarizes data from the U.S. Economics and Statistics Administration (U.S. Department of Commerce 2004) on the percentage of cost of raw material components of an average ACS product:

• Other industrial organic chemicals	23%
• Manufacturing parts and supplies	16%
• Resins	14%
• Industrial inorganic chemicals	12%
• Industrial minerals fillers and extenders	10%
• Refined petroleum products	8%
• Synthetic rubber	6%
• Paper and cardboard containers	6%
• Plastic containers	4%
• Starch/dextrin	1%

INDUSTRIAL MINERALS USAGE

The primary industrial mineral used is dry GCC. ACS producers use dry-process GCC for three reasons:

1. Cost reduction (although high GCC loadings adversely affect some performance characteristics). The use of GCC will normally lower binder requirements and allow for increased filler usage.
2. Shrinkage control, improved rheological properties, and water resistance.
3. To provide body and provide optimum adhesion within joints.

MARKET TRENDS

Global demand for ACS was forecasted to increase by 2% to 4% per year from 2002 through 2012. In the United States, the increase was forecasted at 3.5% per year from 2002 to 2012. This forecast included a recovery from the 2001 recessionary base, normal growth, and the introduction of new markets and improved ACS products.

For the same time period, adhesive growth in China is forecast at a 9% annual rate, with many end uses advancing at a double-digit pace. Production of ACS in China has been reported as one of the fastest developing sectors of the country's chemical industry. This is driven by an acceleration of new products, new technologies, and new application areas; some of the growth is from lost production from other countries (as more value-added products are being manufactured in China). Shipments are increasing for both the domestic and the export markets. Problems being addressed in China include decentralized production (more than 1,800 separate plants), lack of

Table 2. Focus of ACS producers and customers

Attribute	Characteristic
Safe	Components of degradation products pose no dangers.
Effective	High loading and adhesion strength.
Usable	Ready to apply; remains manipulative for a short time; solidifies rather quickly.
Affordable	Cost per unit is not prohibitive.
Approvable	No issues with Food and Drug Administration and other agencies

R&D (materials urgently demanded by the market are not being delivered), and insufficient raw and auxiliary materials (primarily resins and solvents that need to be imported) (Yang 2002).

Global ACS growth is driven by increased construction demand (1% to 3%) and increased growth (1% to 3%) from a new demand structure that includes electronics, medical, mechanical fastener replacement, automotive, and solvent-free products. Growth will also continue in higher performance ACS, such as silicones, polyurethanes, and urethane acrylic formulations. The use of PCC, nano-calc, and nano-clays will also influence future product mix. Influential co-products include polyvinyl acetate/acrylic resin and epoxy resin.

Finally, emerging regions of the world (with a combined population of nearly 4 billion and a total gross domestic product of \$7 trillion in 2003) are likely to see the largest growth rate in ACS consumption. By example, their adhesive consumption per capita in 2003 was less than \$2, well below the more than \$20-per-person consumption in the United States. Growth in the emerging economies can be uneven, but in the long term, ACS growth is projected to outpace the overall global economy.

SALES AND DISTRIBUTION DYNAMICS

Logistics drives the use of raw materials for both ACS and the industrial minerals used in ACS. The ACS industry has thousands of small plants, most tied to nearby raw material suppliers and many near population (use) centers. Most ACS plants are small volume and market located. The industrial minerals used by the ACS product formulators tend to be local. Future opportunities include joint efforts, formal or informal, in logistic areas such as reusable pallets, shared plant locations, hauling contracts, and ties into the ordering pattern of downstream ACS users.

Many goods that require ACS, including stand-alone ACS products, rely on distribution systems to get products to diverse and fragmented users. This distribution system has changed significantly over the last 20 years and will continue to evolve. Marketing costs can be up to 30% of sales, and distribution costs can be 15% of sales.

Current considerations include

- Electronic data interchange (EDI) ordering
- Just-in-time-type rapid filling of shipments
- Contractual pricing
- Drop shipments of less-than-truckload quantities to individual stores
- Placement fees, slotting allowances, store detailing, and special terms

PRODUCTS SPECIFICS

Raw Materials

The primary industrial minerals used are calcium carbonate and kaolin.

About 100 large companies and dozens of smaller operations worldwide own calcium carbonate and kaolin raw material supplies. Their mining and processing methods are simple, reserves for expansion exist, entry costs are not prohibitive, permitting is relatively easy because they tend to be seen as “green” compared to other mining, the royalty rates are low, and the operational structure allows for long-term and consistent production.

Dozens of registered companies supply almost all of the other industrial minerals’ content used globally.

Mining and Processing

Surface truck/shovel mines or simple room-and-pillar underground mines produce calcium carbonate for ACS. The mining cost is about one fourth of the total free on board (f.o.b.) raw material cost. Processing, which is about one half of the cost, includes washing or scalping (at some locations), and crushing and grinding. Packaging, which is about one fourth of the cost, is simple, with bulk, semi-bulk, and bagged packaging all easily available. Transportation of finished goods, at about \$0.10/ton-mile in most of the world, can represent 1, 2, or 3 times the actual cost of the industrial mineral f.o.b. purchased price.

Almost all kaolin for ACS is surface mined using conventional dragline or truck/shovel operations. Including reclamation and restoration, the mining cost is also about one fourth of the f.o.b. cost. Processing includes blunging, degritting, and other required application and decontamination steps. With few kaolin operations globally, overall transportation costs are usually high.

PRODUCING ACS

Of the total ACS volume produced, more than 50% is normally made in simple blending/mixing facilities where small batches are mixed, aged, and placed into buckets and boxes that are filled and shipped in case lots. Although the manufacture of adhesives and sealants involves relatively simple processes, extensive knowledge and experience with the raw materials and their formulation and compounding are essential. Few companies perform R&D in these areas. A few of the larger adhesive and sealant manufacturers are vertically integrated, producing resins for captive consumption. Other firms in the industry are highly dependent on raw material suppliers for introducing new technologies. The adhesive and sealant companies then assume responsibility for formulating these new raw materials into products that offer improved performance. This aspect of formulation is where most adhesive and sealant companies derive their competitive advantage—by designing and producing products to satisfy a particular market demand.

MARKET SPECIFICS

Finished Product Specifications

There are thousands of ACS products; therefore, this chapter cannot address individual specifications. The trend for ACS producers will include a base load of commodity grades made at as low a cost as possible, and a continued shift in product mix to higher performance sealants and caulks such as silicones, polyurethanes, and urethane acrylic formulations. High levels of consistency in ACS products are also required. ACS producers will increasingly compete on product performance, consistent thickness, short drying times, adhesion, shrinkage, and color.

Customer Demands

ACS producers see value in many of the following key areas:

- Loading levels (e.g., more industrial minerals loading is better, and loadings of up to 85% are reported)

- Cost reduction (e.g., the pressure is on producers to cut costs each year, and they are improving in their understanding of cost drivers and relationships—such as mean particle size and particle-size distribution—to energy cost. Producers are also beginning to practice state-of-the-art supply chain dynamics.)
- Waste minimization (e.g., using an aggressive data collection and management system, evaporating water from aqueous wastes, using just-in-time coloring, and using solvent recovery)
- Product consistency (e.g., most producers prefer consistent tint and brightness to minimize TiO₂ usage and swings in their products’ color)
- Delivery when expected (e.g., most producers practice just-in-time and other cash-cost-reduction techniques)
- Ability to supply (e.g., a large segment of the ACS business is seasonal, and industrial minerals suppliers must be able to seamlessly meet the changing producer’s demand)

GOVERNMENT, ENVIRONMENT, AND HEALTH CONSIDERATIONS

Environmental, health, and safety issues have been the driving force behind many recent technological changes in ACS production and products.

Volatile Organic Compounds

In the late 1980s, several world governments and nongovernmental organizations identified adhesives and sealants as significant sources of volatile organic compounds (VOCs). In combination with nitrogen oxides, VOCs are responsible for the buildup of ground-level ozone in populous regions of the world. This ozone causes respiratory problems, vegetation damage, and material degradation. Government, environmental, and health goals have often necessitated reformulation of ACS products. Shifting to water-based formulations can significantly reduce the use of petroleum solvents. In addition to reducing VOC emissions, water-based formulations offer advantages such as easier cleanup and less odor. One type of low-solvent formulation (the hot-melt products) is designed for application at elevated temperatures. Low-VOC ACS products are now more commonplace and improved than they were 5 years ago, but their use is restricted by higher costs and by contractors not trained in their differing properties.

Asbestos

Asbestos concerns swept through the industrial minerals portion of the ACS industry in the 1980s and 1990s. Of specific concern was locating asbestiform minerals in the fillers. After the amounts of asbestiform were found to be nonexistent to very low, these concerns faded.

Respirable Crystalline Silica

A current concern is respirable crystalline silica levels. Crystalline silica in the form of quartz is a component of many industrial minerals used in ACS. The manufacturers of ACS will be on the lookout for low-crystalline products and silica-conscious industrial minerals producers. Manufacturing facilities, including mixing rooms and dry product storage, may need to meet the same respirable dust requirements of facilities that have been mandated to handle lead, arsenic, and cadmium.

Renewable Materials

The use of renewable materials and renewable energy in the manufacture of ACS products and their constituents is increasingly important. Industrial mineral producers will want to stay abreast of ACS

producers' concerns as they consider formulations that contain lignins, tannins, carbohydrates (such as soybeans), terpenes, and proteins. The longevity and quality of ACS products, and their own use in making "green products" and helping conserve energy and other resources, will also be important marketing considerations.

TRENDS AND OPPORTUNITIES

ACS is a relatively low-cost component in engineered construction and consumer products. Demand for ACS in the United States is forecast to increase 3.5% per year to 2.5 billion pounds in 2006, while European demand will continue to be half that rate. Demand in China and Asia is likely to grow at even higher rates. The global market will benefit from a moderately favorable outlook in the key durable-goods sector; the ability to displace nails, screws, and other fasteners; increased desire for lightweight composites; and technology breakthroughs in product designs that improve heating and air-conditioning efficiency.

Specific Trends and Opportunities

ACS companies will boost R&D spending. They will increasingly partner with global industrial minerals producers, especially those that can offer both a bundle of minerals and global product consistency.

Some specific targeted improvements include new formulations, including using epoxies to improve adhesion qualities to meet or exceed those of nails, screws, rivets, and other fasteners and welding. A selective use of industrial mineral fillers for weight reduction will help lower delivered costs, and additional use of surface chemistry and surface area of industrial minerals will enhance thixotropy.

New combinations of industrial minerals will provide greater ACS stability and less solvent creep. This will be especially important as ACS users evaluate the ease of robotic applications.

Finally, more environmentally friendly products are being demanded, and the industrial minerals components are generally seen as "green." ACS producers seen as winners will be those who use more fillers and less problematic ingredients such as solvents—this will be key to global market share.

Construction Markets

Construction markets will remain dominant. Housing is growing all over the world, and ACS products are used in new construction, renovation, and finishing of homes and commercial buildings. In the motor vehicle market, also an important segment, sealant usage will get a boost from acceleration in passenger car production; design trends featuring more glass, plastic, and rubber per vehicle; weight reduction; and powder clearcoat commercialization. In structural glazing—a construction process in which caulks/sealants hold glass panels in high-rise buildings in place—silicone products can be used without any mechanical means of fastening. This can be clearly defined as an adhesive application since the silicone material is being used to bond the glass and metal surfaces together. On the other hand, it also serves as a caulk/sealant because it prevents the passage of gases, liquids, or solids through the joint.

Accelerated defense spending will provide opportunities for sealants and caulks in the manufacture of military equipment.

Demand for sealants and caulks in the industrial sector will benefit from a stronger capital-spending environment as companies invest more heavily in new plants and equipment. Although durable-goods markets will see the most rapid gains, the construction industry will remain the largest outlet for ACS, accounting for more than half of total demand by 2006. Though a slowdown is expected in new building construction activity, continuing architectural trends

toward more luxurious and energy-efficient homes will partially offset deceleration in the number of new homes built by raising per-unit consumption of sealants.

In addition, non-building-construction markets, which were quite weak for most of the 1990s, will be boosted by the Transportation Equity Act for the 21st Century, which authorized federal spending programs for highways, bridges, and mass transit projects through 2003. This piece of legislation, and similar infrastructure construction and renovation projects worldwide, should provide opportunities for sealants and caulks in the mid-term, primarily in applications such as sealing expansion and horizontal joints in bridges, parking garages, playgrounds, sidewalks, and aircraft terminals, and sealing cracks in pavement and asphalt.

RAW MATERIAL REQUIREMENTS

New Product Volumes Required

Following are estimates of new mineral production required (from 2003 to 2013) by major ACS industrial minerals components:

• Calcium carbonate	1.2 Mtpy
• Clay	0.2 Mtpy
• Pulverized waste	0.1 Mtpy
• Silica, as precipitated or fumed	<0.1 Mtpy
• ATH	<0.1 Mtpy
• Feldspar	<0.1 Mtpy
• Gypsum	<0.1 Mtpy
• All other industrial minerals	<0.1 Mtpy

Specifications

ACS producers historically used existing industrial minerals producers' grades, many times adjusting formulas to meet local production. Increasingly, the ACS producers are settling in on "best" specifications and are demanding that these specifications be met by a supplier, or suppliers, globally.

These specifications are getting more complicated. Described here are those guidelines, with consideration of a carbonate raw material:

- Mineral (calcium carbonate, magnesite, other)
- Mineral processing (coarse, fine, or ultrafine; PCC or nano-GCC; dry or wet ground; etc.)
- Mineral surface (shape, area, surface treatment, and surface chemistry)
- Size (particle-size distribution [coarse, fine, ultrafine, and nano]; also specifics such as top size)
- Color (amount of yellow, green, red)
- Brightness
- Chemistry (amount of calcium, iron, aluminum, other)

Besides specifications, the ACS producers, and their downstream users, are demanding new levels of consistency, and many producers must now also describe their products in terms of how the processes behave (are they in control, are they capable), and they must supply product CPK data.

SUMMARY AND CONCLUSIONS

The ACS industry is an important consumer of many industrial minerals and is dynamic, with a growth rate that is faster than the global economy. ACS producers are focused on cost reduction and product property improvement, and many producers believe that an increase in the percentages of industrial minerals in their products will result in lower costs and improved properties. To this end,

many ACS producers will continue to look for strategic partners and alliances with industrial minerals producers.

WEB SITES, INFORMATION SOURCES, AND MAJOR U.S. ACS COMPANIES

- *Adhesives Age*: <http://www.chemweek.com/aa>
- Adhesive and Sealant Council: <http://www.ascouncil.org>
- *Chemyclopedia* (American Chemical Society): <http://www.mediabrain.com/client/chemyclop/BG1/search.asp>
- *Chemical & Engineering News*: <http://pubs.acs.org/cen>
- *Chemical Marketing Reporter*: <http://chemicalmarketreporter.com/home/Default.asp?type=0&liSectionID=12>
- *chemicalweek*: <http://www.chemweek.com>
- *The Kline Guide to the U.S. Chemical Industry* (Y184C): available for purchase from http://klinegroup.ecnext.com/coms2/summary_0229-13370_ITM
- U.S. International Trade Commission: <http://www.usitc.gov>
- U.S. Department of Commerce: <http://www.commerce.gov>
- U.S. Department of Labor, Bureau of Labor Statistics: <http://www.bls.gov>

Major U.S. companies involved in the adhesive, caulks, sealants business include 3M Company, Ashland Chemical, Berwind (Eimer's) Products, BF Goodrich, Bostik Findley, Courtaulds Aerospace, DAP Inc., Daubert Chemical, DHM Adhesives, Dow Chemical, Dow-Corning, Eastman Chemical, Essex Specialty Products, H.B. Fuller, GE Silicones, Gibson-Homans, Loctite, Macklanburg-Duncan, Mapei, Morton International, Parachem, Pecora Corp., Koch/Protective Treatments (Koch/PTI), Red Devil, Reynolds Adhesives, Rhone-Poulenc, Rohm & Haas, Schne-Morehead, Sealant Technology, Sherwin Williams, Sonoco, Sun Adhesives, Thiem Automotive (National Starch), Tremco, Tyco Adhesives, Uniroyal, Wacker Silicones, and WR Grace.

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Filler and Coating Pigments for Papermakers

Ian Wilson

INTRODUCTION

Historians attribute the Egyptians in the Nile Delta with preparing the first type of paper, from a marsh grass called *Cyperus papyrus*. They cut the plant's stem into thin strips, softened them in the river, and then pounded them into thin sheets that were then left to dry in the sun. The resulting sheets were ideal for writing on, and Egyptians, Greeks, and Romans used them for record keeping, spiritual texts, and works of art. Papyrus is the basis of the word *paper*. The father of papermaking is Ts'ai Lun, who in 105 AD experimented with a wide variety of materials and refined the process of macerating the fiber of plants until each filament was completely separate. He mixed the individual fibers with water in a large vat with a screen that was submerged and then lifted up through the water, catching the fibers on its surface; when dried, this thin layer of intertwined fiber became what we today call paper. The art of papermaking spread to the Middle East and to Egypt, where it replaced papyrus in the 9th century, followed by Morocco and then Spain (about 1150) and France (1190).

Industrial minerals play a major part in the manufacture of modern paper. Originally, because they were less expensive than fiber, minerals such as calcium carbonate (chalk) and kaolin were used as fillers to reduce production costs. Although cost is still an important factor, minerals have become "functional fillers" that impart specific properties to paper, such as improved printability, brightness, opacity, and smoothness. In paper coating, minerals are used as white pigments to conceal the fiber, thereby improving brightness, whiteness, opacity, and smoothness.

PAPER INDUSTRY STRUCTURE

World Production

In 2003, world production of paper and paperboard was 339 Mt compared with 239 Mt in 1990. A split of this production for 2003 (Table 1) indicates similar levels from North America, Europe, and Asia. Between 1990 and 2003, North America's share of the world market fell from 37% to 30%, whereas Asia increased from 25% to 32% as both Western and Eastern Europe decreased from 33.7% to 31%. The world average annual growth in the production of paper and paperboard during the period from 1990 to 2002 was +2.8%, with Asia showing the largest growth of +5.2%. Of the 339 Mt (Table 1), Asia is now the leading producer with 32%, just overtaking North America and Europe with 30% and 31%, respectively. The top ten producing countries in the world now account for 73%

Table 1. Paper and paperboard production by region in 2003

Region	Production, kt	% of World Production (rounded up)
Asia	110,585	32
Europe	104,093	31
North America	100,280	30
Latin America	16,254	5
Australasia	3,871	1
Africa	3,672	1
Total	338,755	100

Adapted from Paperloop 2004.

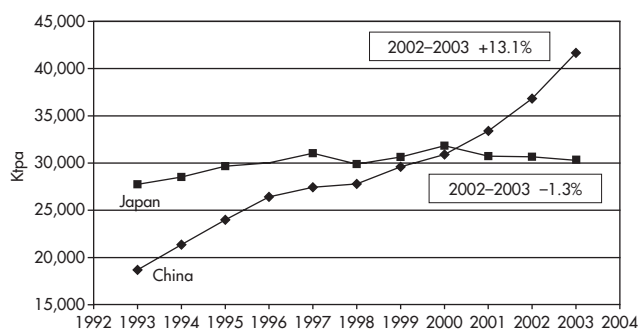
of production (Paperloop 2004), led by the United States (24%), China (12%), Japan (9%), Canada (6%), Germany (6%), Finland (4%), Sweden (3%), South Korea (3%), France (3%), Italy (3%), and all other countries (27%).

The growth of the Chinese market from 1992 to 2003 was dramatic, especially when compared with Japan (Figure 1): the growth rate was 13.1% in China, and the rate decreased by 1.3% in Japan. The Chinese growth was mainly driven by major companies investing in new paper mills in China (including Asia Pulp and Paper Company [APP], UPM-Kymmene, Stora Enso, and Oji Paper) combined with the fast-growing, apparent consumption per capita—in 2003 paper consumption was 36 kg in China, an increase of 24% over 2002. This is still well below the levels of the United States with 301 kg, the United Kingdom with 207 kg, as well as many other countries; and just ahead of Indonesia and India with 23 kg and 6 kg, respectively.

Fibrous Plant Materials Used in Papermaking

Although almost any plant material can be used for papermaking, very few are used because a number of factors determine what makes a good raw material:

- The plant must be abundant, inexpensive, and, if a waste product, of little use to others. It must grow in an accessible place and should grow quickly.
- It must contain a high proportion of cellulose fibers, and its structure must allow the fibers to be isolated from the rest of the plant material with reasonable ease and without undue expenditure of chemicals or heat.



Adapted from Paperloop 2004.

Figure 1. Growth in paper market for China versus Japan, 1993 to 2003

- The fiber itself when isolated should be suitable for paper-making, which means that it should be long and strong, and develop strength on beating. At the same time, it should be capable of being bleached to a good color without undue loss of strength.

Of the many species of plants in the world, the following meet the above requirements and are commonly used in papermaking:

- Seed hairs—cotton
- Bast fibers—flax, hemp, jute, ramie
- Wood fibers—coniferous and deciduous woods
- Leaf fibers—esparto, manila, sisal
- Grasses—bamboo, bagasse

Potential new pulp sources are being developed all the time. Malaysia, for example, announced in March 2003 that the world's first oil-palm-based pulp plant would be set up in Sabah (Borneo) with the capacity to produce 25,000 t of pulp. A new pulping method using empty fruit bunches (EFBs), which are currently a waste product from the palm oil industry, will be developed using

caustic soda technology. If successful, Malaysia has the potential to produce 3 Mtpy of pulp from EFB alone.

Main Paper Grades

Table 2 summarizes the main types of paper grade, their fiber composition, pigment filler and coating loading, and their end uses. Coated paper is coated on one or both sides with a mix of clay and carbonates to create a high quality printing surface. Coated paper can be fine, light weight, medium weight, or machine finished. Uncoated fine paper is used principally for printing and writing. Woodfree, freesheet, or fine paper is paper used by the graphic industry for writing, including office paper such as photocopying and laser printing paper; these may be coated or uncoated.

Leading Producers of Paper and Paperboard

The paper industry continues to consolidate, with the top 10 companies accounting for an increasing proportion of world paper and board capacity. Production by the 10 leading companies in 2003 accounted for 27.9% of global output (Table 3).

In 2001, Finnish-owned Stora Enso increased its capacity to 15.1 Mtpy and International Paper closed down 2.2 Mtpy of its less-efficient capacity; in the same year, UPM-Kymmene acquired Haindl, a leading European producer of publication paper. Publication paper includes newsprint, coated, and uncoated papers (mainly lightweight coated [LWC] and SC). This further consolidation increased UPM-Kymmene's capacity from 8.285 Mtpy to 11.705 Mtpy by 2003. UPM-Kymmene is now the world's largest manufacturer of magazine paper (LWC and SC) with an annual capacity of 5.465 Mt, or about one-quarter of the global market for magazine paper.

MAJOR PIGMENTS USED IN PAPERMAKING

The major pigments used in printing and writing paper (P&W; includes SC, MFC, WFU, and WFC) are calcium carbonate (precipitated calcium carbonate [PCC] and ground calcium carbonate [GCC]), kaolin, and others (talc, TiO₂, and others). Harris (2004) estimated that 30 Mt of these major pigments were used worldwide

Table 2. Paper grades, fiber composition, pigment and coating loading, and end uses

Paper Grade	Fiber Raw Material	Pigments	End Uses
Newsprint	De-inked pulp and/or mechanical pulp	Filler loading up to 12%, originally from de-inked pulp	Newspapers, inserts, flyers (advertising)
Specialty newsprint Books, papers High brightness	De-inked pulp and/or mechanical pulp	Filler loading <10%; specialty pigments can be used as well	Newspaper supplements, newspapers, books, directories, advertising
Supercalendered (SC) papers SC B, A, and A+ grades	Mechanical and chemical pulp	Filler loading up to 35% Filler loading up to 10%; coating 25%–30% of paper weight	Multicolor magazines, catalogs, supplements, inserts, advertising materials; used in gravure and offset printing
Coated mechanical papers (also called machine-finished coated [MFC] paper)	Mechanical and chemical pulp	Filler loading up to 10%; coating typically from 20%–35% of paper weight	Magazines, catalogs, supplements, books, advertising materials
Woodfree uncoated (WFU) papers	Chemical pulp	Filler loading up to 25%	Office papers, writing papers, envelopes, direct mail, magazines, books, advanced materials
Woodfree coated (WFC) paper; also coated fine paper (art printing paper)	Chemical pulp, possible to use some chemi-thermomechanical pulping (CTMP)	Filler loading up to 15% and double/triple coating	Magazines, brochures, direct mail, annual reports, books, advertising materials; higher quality books, reports
Specialty papers	Chemical pulp	Filler load and coating dependent on grade	Label papers, label release papers, food wrapping, packaging
Kraft papers	Chemical pulp	No pigments	Sacks, bags, wrapping and packing, envelopes

Source: Haarla 2002.

in 2002 (Harris 2004), and Figure 2 shows the breakdown of use. Of the 30 Mt of pigment used, 18 Mt was for coating pigments and the split was GCC (53%), kaolin (35%), PCC (9%), and others (3%; this was mainly talc, titanium dioxide, and a few others). The remaining 12 Mt is used as a filler.

ROLE OF PIGMENT PROPERTIES IN PAPERMAKING

For the papermaker, the critical pigment properties are

- Physical properties (also includes optical properties such as brightness, yellowness, and shade; coverage; ink absorption; and others)
 - Particle size and shape
 - Particle-size distribution
 - Aspect ratio (platiness or blockiness—kaolin can be platy and blocky but calcium carbonate is generally rhombohedral [hexagonal] for marble [crystalline limestone])
- Pigment moisture (for pigment handling)
- Pigment hardness—abrasiveness (wear on wire, doctor and slitter wearing)
- Residues, impurities, contamination—origin can be from processing the industrial mineral, from transportation, and from other sources (“runnability”^{*} in paper machine or coating or calendering causes streaks and breaks, which are expensive)

ROLE OF FILLERS IN PAPER

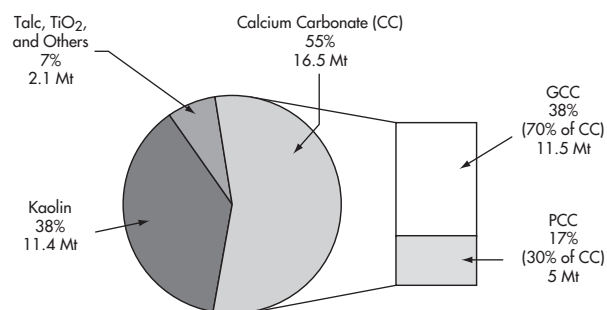
Fillers are highly desirable in printing papers because they increase the opacity, raise the brightness, and generally improve printing properties. The main types of mineral filler for acid papers are talc, hydrous kaolin, calcined kaolin, precipitated silicas and silicates (PSS), and titanium dioxide. For neutral/alkaline papers, talc, hydrous kaolin, calcined kaolin, PSS, titanium dioxide, GCC, and PCC are used. The use of fillers is important when opacity is needed at a low-basis weight, and they are invaluable in packaging grades where low permeability is combined with opacity to protect food from light. There are many fillers: barite, GCC (based on chalk, limestone, and marble), PCC, kaolin, pyrophyllite, mica, gypsum, plastic pigment, satin white, alumina, and titanium dioxide. The properties of the filler derive from the ability of the filler particles to refract and backscatter light through the surface of the sheet. If the filler is not evenly dispersed through the sheet and flocculates in small clumps, then the optical efficiency of the filler will be reduced. If the z-direction distribution of the filler is uneven, then the sheet may appear two-sided. The whiteness of the filler relates to the dominant wavelength of the light. Excluding some uncoated book-publishing grades, papers tend to have a blue whiteness. This requires adding a blue or violet dye to shift the shade of the paper into the desired region of the spectrum.

Because dyes reduce brightness, high-brightness filler must be used or optical brightening agents added for premium grade, such as company stationery and direct mail papers. The importance of avoiding filler flocculation emphasizes the point that fillers are not simply inert optical entities but interact with other additives, not only in terms of their own distribution but also to influence sheet structure such as formation, bulk, pore structure, and surface topography (texture). Aside from their optical effects, fillers or filler blends can be used to improve aspects of product uniformity and

Table 3. World's 10 leading producers of paper and paperboard in 2003

Position	Company	Output, ktpy
1	Stora Enso	13,960
2	International Paper	13,844
3	UPM-Kymmene	10,232
4	Svenska Cellulosa (SCA)	9,725
5	Georgia Pacific	8,843
6	Weyerhaeuser	8,558
7	Oji Paper	7,900
8	Nippon Unipac Holding	7,835
9	Smurfit Stone Container Corporation	7,307
10	Abitibi Consolidated	6,421
Total		94,625

Adapted from Paperloop 2004.



Source: Harris 2004.

Figure 2. World pigment use in P&W paper (2002)

quality. An understanding of filler interactions with retentions aids, sizing agents, cationic starch, and the dynamics of the wet and forming systems is required (Jopson and Moore 2004).

The main driving force for filler in fine papers is to substitute more expensive fiber with filler. No filler is capable of producing maximum light scattering for brightness and opacity without having any detrimental impact on wet web strength and sheet physical properties. The best pigments for brightness and opacity debond fibers the most because of their inherent high surface area.

Kaolin, calcium carbonate (GCC and PCC), and talc are the most widely used mineral fillers, with regional variations depending on local resources available. Table 4 lists the pigments used as filler in different printing paper applications. In the United States, PCC is widely used as filler because of the wide availability of limestone; the lime produced from limestone is converted into PCC at a state lime plant adjacent to a paper mill. Filler pigments must have a high degree of whiteness, a high index of refraction, small particle size, low solubility in water, and low specific gravity. It is also important that the filler be chemically inert to avoid reactions with other components in the sheet and in the papermaking system. The filler should contain a minimum of impurities, and the grit content must be low to avoid excessive wear of the wire and other processing equipment such as cutting blades. Furthermore, unless the filler has very unusual properties, it must be inexpensive.

Hydrous Kaolin

Kaolin was the usual filler used in Europe and the United States up until the 1990s when the use of PCC in the United States and GCC

^{*} Newspapers and magazines require long runs on the printing presses, and several factors affect how well a paper will run on the press. Runnability describes a paper's ability to hold ink on its surface consistently and to absorb ink uniformly, along with its dimensional stability and its surface texture.

Table 4. Filler pigments in different printing paper applications

Type of Paper	Ash Content, %	Clay, %	GCC, %	PCC, %	Talc, %
Newsprint*	<15	<10	<10		Can be used
Machine-finished specialty (MFS)	<15	<10	<10		
Supercalendered offset (SCO)	<35	<35	<10	<20	
Supercalendered rotogravure (SCR)	<35	<35	<10	<20	<10
Lightweight coated offset (LWCO)†	<10	<10	<10	<10	<10
High-brightness lightweight coated (HB LWC)†	<12	<10	<10	<10	<10
Medium-weight coated (MWC)†	<10		<10	<10	<10
WFU†	<22			<22	
WFC†	<15		<15	<15	Pitch talc

Adapted from Haarla 2002.

* Most of the ash comes from recycled fiber in newsprint, if the main raw material is recycled paper.

† A part of the ash comes from coated broke in coated paper.

in Europe emerged. The main use of kaolin fillers in the last decade has been in engineered products. The new range of filler content for SCA paper is based on the production of a high-aspect-ratio (often >40) filler and a controlled particle-size distribution of about 50 wt % <2 µm and a minimum of 5% >10 µm. These high-aspect-ratio kaolin products, with a brightness of ISO 82, provide good opacity to the base paper. They are particularly useful in SCA papers where the platy kaolin with calendering gives a sheet that can compete with LWC papers. The development of a range of platy kaolins has been at the expense of the less expensive kaolin filler.

Over the past two decades, additional processes have been developed to improve the quality of the kaolin from the deposits in Cornwall in the United Kingdom. These deposits have been well documented in the literature (Exley 1959, 1976; Sheppard 1977; Halliday 1980; Allman-Ward et al. 1982; Alderton and Rankin 1983; Bray and Spooner 1983; Allman-Ward et al. 1985; Bristow and Exley 1994; Bristow 1995; Manning, Hill, and Howe 1996; Scott, Hart, and Smith 1996; Psyrillos, Manning, and Burley 1998; Psyrillos et al. 1999; Bristow et al. 2000; Thurlow 2001; Bowditch, undated). For brightness enhancement, superconducting magnets have been introduced alongside high-intensity magnetic separators (HIMSs), froth flotation, selective flocculation, and selective separation processes to remove abrasive materials such as quartz and feldspar. The most significant processing development over the last decade, however, has been the production of delaminated clays from vermiform or stacky kaolinites so that approximately 60% of the processed Cornwall kaolin is now delaminated. The flow process at low-abrasion plants involves flotation to remove contaminants (feldspar, quartz, and mica) and a sand grinder (known as such because it once used a round resistant sand as the grinding medium; a ceramic bead is now the preferred medium) for delamination.

The aspect ratio of the resultant delaminated kaolin is an important parameter, and Imerys developed a stop-flow conductivity measurement instrument that gives a shape factor (called a factor because aspect ratio is not actually measured). The method is known as PAN-ACEA (particle assessment [by] natural alignment [and] conductivity effect analysis). Measurements of shape factor are made online and help to control the process. Historically, aspect ratio was measured using the transmission electron microscopy (TEM) platinum shadowing technique, which was a very lengthy process relying on the particle thickness being proportional to the shadow length—the thinner the platelet of kaolin, the narrower the shadow.

The base paper pigment has an important bearing on the subsequent coating pigment application. The influence of the base paper structure is more noticeable when the paper is coated with

GCC because its particles pack less efficiently on the surface compared to the platy and broad particle distribution kaolin (Bown 1991; Lorusso 2002; Hiorns and Nesbitt 2003). Although it is clear that coating color formulation and coating conditions have potentially greater influence on the coated paper quality, the filler content of the base paper has a profound effect on coating runnability and paper quality.

Calcined Kaolin

Calcined clay is used in small amounts in newsprint and as an addition to other fillers to replace more expensive titanium dioxide to improve opacity. With the onset of calcined clay as filler in newsprint, it is common now to have newspapers with color photographs not visible through the sheet because of its increased opacity.

Calcium Carbonate

The conversion from acid to alkaline papermaking techniques and the demand for brighter and bulkier paper have been the main drivers behind the increased preference for calcium carbonate over kaolin. This switch has eroded the share of the market held by kaolin because paper producers partly substitute its use with calcium carbonate, which is less expensive and often brighter. Neutrally sized paper can have higher mineral filler loadings than acid-sized paper, so calcium carbonate slurries are preferred over kaolin slurries because of their higher solids content. Table 5 compares the properties of kaolin and calcium carbonate, both precipitated and ground. Although calcium carbonate is generally brighter than most commercial kaolin, new grades of kaolin for use in paper coating have a brightness of more than 90%.

Ground Calcium Carbonate

Table 6 lists some of the advantages of GCC compared to kaolin usage in alkaline woodfree papermaking. Kaolin was once the most widely used filler in paper manufacture, but the last two decades have seen a steady increase in the use of calcium carbonate. The conversion from acid to alkaline papermaking and the demand for brighter paper have been the main reasons for this change.

Precipitated Calcium Carbonate

World PCC capacity is approximately 6.2 Mtpy, of which almost three-quarters is used in paper. Nearly all of the PCC in paper is used as a filler, and the largest market is the United States. As papermakers transferred to alkaline technology, the number of satellite PCC plants has increased significantly since the first U.S. plant opened in 1986. By 2000, some 80 plants had been installed

Table 5. Comparison among properties of kaolin, PCC, and GCC in papermaking

Property	Kaolin	GCC	PCC
Brightness	80%–85% (some 90%)	>90%–96%	90%–97%
Particle size	Naturally 2 μ m	Requires grinding	Manufactured fine
Opacity	Excellent	Moderate at high load	High at high load
Loading levels	20%–30%	20%–30%	Limited to 20%
Sheet strength	Good	Excellent	Moderate
Bulking	Moderate	Good	Good
Absorption	Low	Low	High
Chemical reactivity	Inert	Unstable in acid environments	Unstable in acid environments
Flexibility	Filler/coating	Alkaline-only filler/coating	Mainly filler
Processing	Extensive	Grinding/sizing	Energy intensive
Availability	Restricted	Geologically plentiful	Satellite plants
Price	Low (North America)	Low (Europe)	Based on cost-effectiveness

Source: Harben 1998.

worldwide, with almost 50 in North America alone; the industry is dominated by MTI with 54 plants, followed by Huber Engineered Materials with 12 and Imerys with 6.

PCC manufacturing in Europe is shared between five major producers with an estimated total production capacity of more than 2.0 Mt py in 2003, including products for paper and other applications. The five companies are Huber Engineered Materials with 6 plants, Specialty Minerals Inc. (SMI) with 13 plants, Omya with 4 plants, Solvay with 6 plants, Schaefer Kalk with 3 plants, and Imerys with 1 plant. At the time of this printing, Huber is in the process of selling their 6 PCC plants. The competitiveness of an on-site PCC plant is primarily influenced by the size of the plant (economics of scale) and by the CO₂ content in the gas source from the host paper mill. This means that an on-site satellite PCC plant has to have a certain minimum size and be supplied with a gas of a certain minimum CO₂ content in order to be economically viable. For example, an on-site PCC plant has to process a minimum of 20,000 tpy to be economically justified, corresponding to the demand from paper production of 100,000 tpy of uncoated paper with a 20% filler level.

In Europe, PCC has shown by far the strongest growth rate and since 1995 has continuously taken market share from GCC and other fillers. The growth of PCC is likely to continue with further penetration as filler into the WFU paper segment, although at a slower rate as the market matures.

Some paper mills that had been using GCC derived from chalk in Europe were among the first to capitalize on the added brightness that could be achieved using PCC. Several PCC satellite plants have come onstream in Asia since the mid-1990s, including plants in Thailand, Indonesia, Japan, China, South Korea, and Malaysia. New satellite plants have also been built in South Africa and in South America.

PCC is now making some inroads as filler in groundwood (SC and LWC) papers, and this represents the largest remaining potential market. This market is currently dominated by kaolin and talc, however, especially in European rotogravure paper. MTI has invested much research into developing acid-tolerant PCC, allowing its entry into the groundwood paper sector, for which it now has several satellite plants.

Talc

The choice of filler in paper is driven by cost reduction and quality improvement. For talc, which is more expensive than some other pigments, improving the paper quality and the papermaking process itself is the dominant driving factor. The properties of talc—

Table 6. Advantages of GCC compared to kaolin in alkaline woodfree papermaking

Paper
<ul style="list-style-type: none"> Brightness—GCC has a higher brightness than clay; lower optical brightening agent (OBA) demand without alum Strength—tends to be higher without high amounts of alum; filler loadings higher Permanence—absence of alum benefits aging properties of paper
Process
<ul style="list-style-type: none"> Refining—30% energy savings in refining under slightly alkaline conditions Drainage—rhombohedral shape of GCC drains better than platy kaolin Drying—dries better than clay because of slightly more hydrophobic nature of GCC Water—better drainage and lower bacteriological activity reduce water demand pH stability—strong buffering action; GCC keeps pH level stable at 7.2 to 8.4

soft, organophilic, chemically inert, and platy—are reasons why it today is used as filler in many different kinds of paper. The organophilic surface helps reduce dye consumption and two-sidedness in colored paper. *Two-sidedness* in colored paper is the term used to describe the difference in color characteristics between the top side and the bottom side of the sheet. The difference can be either in shade or in strength, or both. Contributing factors are finish, chemical additives, points of addition, order of addition, and colorant characteristics. With careful control of all these factors, however, two-sidedness can be eliminated to result in a uniform sheet.

The relatively coarser particle-size distribution of talc (compared with other pigments) leads to better retention in the sheet and lower effect on the paper's strength properties. Improved dewatering, less wire abrasion, higher retention, a longer life of cutting knives, and fewer core breaks in SCR printing are typical advantages in the process provided by talc. In addition, the pitch and sticky control function reduces tacky deposits and improves paper machine runnability. The paper quality itself is influenced by talc with increased smoothness, better printability, deeper color in colored papers, and a lower impact on strength properties than other fillers.

Other Filler Pigments

Other mineral systems are employed—for example, titanium dioxide. Titanium dioxide is used more as a specialty chemical to impart

specific end-use properties rather than as filler because of its cost. It is used primarily for its opacity properties, particularly in lightweight papers such as paper used for bibles.

A new specialty filler in newsprint is Zeocros PF, produced by Ineos Silicas, a leading global supplier of silica, silicate, and zeolite products. Zeocros PF has a high ISO brightness of 97; small, angular particles with efficient light-scattering surfaces; and a tight particle-size distribution. In newsprint it raises opacity, improves printability, reduces print through/strike through, and enhances brightness. A 1% filler addition will give 0.6 points of opacity increase. Paper with Zeocros also prevents ink penetration into the paper.

Gypsum, or calcium sulfate, is an abundant mineral formed naturally and from industrial by-products (such as flue gas desulfured gypsum and phosphogypsum). It generally has the disadvantage of high solubility, and it also tends to plug machine felts. Calpak C20 is filler derived from gypsum in Spain and is being developed by Kemira. It is a bright filler for a wide range of pH and sizing systems. The production of filler gypsum, however, is limited in the world.

Diatomaceous earth is not filler in the sense of the other pigments but is normally used for pitch control (0.5%–1.5% on pulp), to improve formation, and to increase the rate of drainage, though one serious disadvantage is its abrasiveness.

THE ROLE OF PIGMENTS IN PAPER COATING

Application of Coating Pigments

A coating layer on a paper surface can bring the following improvements to the paper sheet:

- Cover the base paper fibers to give a uniform surface
- Make the paper whiter
- Contribute to the paper's opacity
- Give the desired finish—gloss, silk, or matte
- Give the desired printing properties

A coating mixture, known as a coating color, is normally a mixture of a mineral with a binder to stick the mixture to the paper, a viscosity modifier to assist in the application to the paper surface, and often other chemicals that improve the shade of the coating and its printing properties. An important characteristic for any coating color is good rheological response during metering and application and an ability to retain water during application. An ideal coating mixture needs to be fluid during application, yet immobilize quickly after metering. An ideal coating should cover all the paper fibers. Fiber coverage is often achieved by using high coatweights, coarse particles, platy particles, and coating mixtures that immobilize rapidly.

In paper coating, minerals are used as white pigments to conceal the fiber, thereby improving brightness, whiteness, and opacity, as well as smoothness. If applied by a blade coater, the pigmented layers impart a fairly constant surface layer, but of varying depth as the surface voids and pits of the base sheet are filled in. There is a growing understanding that the filler in the base paper can have a great influence on the behavior of the coating pigment. Application methods such as the air knife and, to a degree, the film press or metering size press provide a coating of more uniform thickness, which follows the larger-scale surface contours of the sheet to give a varying surface level. Such contour coating methods are particularly useful in applying a ground coat to uneven substrates such as folding carton board and corrugating liners.

Coating using the size press is a growing practice, producing paper that bridges the gap between uncoated and full-blown blade-coated products. An extension of this is using high surface area silica or calcium carbonate pigments to provide dye-receptive coatings for inkjet paper (pigment acts as an acceptor of the image

medium). Even in conventional offset lithographic grades, careful development has been undertaken over many years to optimize the ink transfer and drying characteristics of the coatings. In electro-photographic printing grades, controlling surface resistivity and toner adhesion is critical in coatings development. In the Indigo unit with its wet toner system, surface chemistry, specifically acid-base interaction, is critical in image transfer to the paper surface. Matching the pigment formulation to the imaging systems is an increasingly important part of product development, especially in higher value coated paper grades.

The coating formulation must also be optimized for runnability on a high-speed coating line. This requires careful attention to rheology (viscosity at high and low shear). Such parameters are important not only to coating transfer and metering but also to uniformity of the coating in terms of coverage of the fiber in the base sheet. This is vital to print quality. The rheology of the coating is determined by the interactions between the pigment particles themselves and between pigment and binder under the influence of coatings solids content and temperature. Common binders include styrene-butadiene rubber (SBR) latices, starch, acrylics, or vinyl polymers. The rheology can be manipulated by water-phase thickeners such as carboxyl methyl cellulose (CMC) and associative thickeners such as alkali-swellable acrylates or hydrophobically modified urethanes.

In most paper coating, the pigment concentration is higher than the critical pigment binder concentration (CPVC) that is familiar in paint formulations. A blade coating for offset lithographic printing would contain 100 parts pigment to 14 parts binder at 60%–65% solids. A coating for air knife or rod coater application would be about 30%–40% solids. The objective is to create a microporous coating that can facilitate ink transfer. For folding carton board, acrylic and polyvinyl acetate binders are used to increase porosity to permit the use of adhesives on the coated surface. Exceptions to the higher pigment binder ratio are found in barrier coating. Here pigments are used not for their optical properties but to increase the tortuosity of the diffusion path of oils, grease, or water through the barrier. Pigments with high aspect ratios such as platy clay and talc find applications in this area. The addition level is generally about 30–40 parts pigment to 100 parts emulsion polymer, well below the CPVC. A balance has to be struck between adding pigment to boost barrier properties and preserving coating elasticity, so that the paper and board can be folded without cracking the barrier layer.

Table 7 lists pigments used in the coating process and their basic properties. Kaolin and GCC are the major coating pigments, accounting for some 90% of the total. Basically, GCC and kaolin are blended in a wide range of differing coating formulations, depending on the type of paper being manufactured.

Kaolin

Kaolin has a platy morphology that is still required for a large number of paper applications, particularly in lightweight coated papers. The trend in recent years has been to combine different minerals in one coating formulation. Kaolin can be mixed with GCC, with PCC, and more recently, with talc, to obtain improved performance. If a choice is to be made between kaolin and GCC for coating, the papermaker considers the solids percentage (the higher the solids, the less drying of paper necessary), paper brightness, paper opacity, fiber coverage, paper gloss, and print gloss. For high-brightness paper, GCC is used; but for fiber coverage, paper gloss, and print gloss, the platy nature of kaolin is preferable. Kaolin is widely used in paint as an extender, and the calcined grades give higher opacity than a hydrous type. There are regional trends, with the United

Table 7. Properties of pigments used in coating paper

Pigment	Composition	Refractive Index	Specific Gravity	Dry Brightness, %	Average Particle Size D50, μm	Crystal Form
Kaolin	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	1.55	2.65	70–91	at least 70% <2	Pseudo-hexagonal
Calcined clay	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$	1.62	2.70	90	~2, aggregate	Chunky aggregate
Natural GCC	CaCO_3	1.49–1.66	2.72	90–96	0.8–1.5	Rhombohedral
PCC	CaCO_3			>95	0.1–0.2	Scalenohedral (C)
	Calcite (C)	1.49–1.66	2.72			Rhombic (C)
	Aragonite (A)	1.53–1.68	2.94			Acicular (A)
Talc	$3\text{MgO} \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$	1.57	2.75	85–90	~50% <2	Monoclinic, platy
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1.52	2.34	85–90	at least 70% <2	Monoclinic, prism
Titanium dioxide	TiO_2 , rutile (R)	2.70	4.20	97–98	0.2–0.5	Tetragonal
	TiO_2 , anatase (A)	2.55	3.90	98–99	0.2–0.5	Tetragonal
Alumina	$\text{Al}(\text{OH})_3$	1.57	2.42	98–99	0.3–1.0	Monoclinic, platy
Satin white	Calcium sulfo-alumina complex	1.46	1.55	>90	~90% <2	Acicular
Blanc fixe	BaSO_4	1.69	4.3–4.5	98	0.2–2.0	Orthorhombic
Zinc sulfide	ZnS	2.37	3.98	97–98	0.3–0.5	Generally hexagonal
Zinc oxide	ZnO	2.01	5.65	97–98	0.3–0.5	Hexagonal
Plastic pigment	Polystyrene	1.59	1.05	>97	0.1–0.5	Spherical

Adapted from Dean 1997.

States still relying dominantly on kaolin for coating, followed by PCC and GCC. In Europe and Asia, the trend has been toward GCC, no doubt because of the proximity of high-quality marble deposits in such places as Carrara in Italy and Ipoh in Malaysia.

The world kaolin market of high-quality beneficiated kaolin was estimated at 25 Mt for 2003 (Wilson 2003, 2004b). The major producing kaolin companies worldwide (Table 8) are led by Imerys with 25% of the market. Leading kaolin-producing countries are the United States, mainly based on the sedimentary deposits in Georgia, with 36%; United Kingdom, 10%; Brazil, 9%; and other countries, 45%. Brazil has shown the most significant growth and is expected to soon overtake the United Kingdom. Large reserves of high-quality coating kaolin discovered in the Amazon Basin have been developed over the past 20 years. These deposits are all sedimentary in origin and are widespread throughout parts of the Amazon Basin. The main operations in the Amazon Basin are CADAM (now owned by Companhia Vale do Rio Doce [CVRD], which is the largest exporter of iron in the world); Para Pigmentos SA (PPSA; now 100% owned by CVRD); and Rio Capim Caulim (RCC; 100% owned by Imerys). In 2005, these three companies had an installed capacity of 2.25 Mtpy, split between CADAM (0.8 Mt), PPSA (0.6 Mt), and RCC (0.8–1.5 Mt). Sales in 2001 brought in revenue of US\$200 million. Proven reserves of kaolin are put at >500 Mt, with CADAM having 270 Mt of ultrafine clay (98 wt % <2 μm); PPSA, 110 Mt of platy clay at 82–85 wt % <2 μm (excluding other reserves that CVRD controls in the same region); and RCC, with 120 Mt of platy-type kaolin at 78–94 wt % <2 μm . Future expansions based on these large high-quality reserves are planned with CADAM aiming to produce 1 Mtpy by 2007; with PPSA, 1 Mtpy; and RCC, 1 Mtpy by mid-2005. CVRD is emerging as the second largest kaolin company in the world, following Imerys.

The world coating clay market is estimated at 8 Mt, of which the major suppliers are the United States, Brazil, and the United Kingdom, with some production from Australia, China, the Czech Republic, Bulgaria, Germany, and France. Coating clays based on sedimentary kaolin sequences in the United States (Georgia), and in the Amazon Basin show a wide range of properties but generally

Table 8. Summary of some No. 1 and No. 2 properties based on brightness and particle size distribution of coating clays from the United States, Brazil, and Australia

Product	TAPPI Brightness, GE % (unless stated otherwise)	Particle Size, % <2 μm
U.S. Clays		
No. 1 high bright	90–92	90–94
No. 1 fine high bright	90–92	96–100
No. 1	86.5–88	90–94
No. 1 fine	87–89	95–99
Range of No. 1 products	86.5–92	90–100
No. 2 high bright	90–92	80–84
No. 2	85.5–87	80–84
Range of No. 2 products	85.5–92	80–84
Coarse delaminated	85–87	54–62
Delaminated	88–90	75–81
Delaminated high glossing	88–90	83 minimum
Range of delaminated clays	85–90	54–83
Brazilian (Amazon)		
CADAM—Premier clay	89 (ISO)	98
PPSA—Century	90–91	80
RCC (Capim)—Imerys		
Engineered pigments (fine)		
Capim DG	90.5	90
Capim GP	90.5	90
Coating high-brightness (delaminated)		
Capim NP	90.5	80
Capim CC	89	80
Australia (Pittong, Victoria)		
EckaPlate (HB) S—delaminated	86 (ISO)	85
EckaPlate HB—delaminated	85 (ISO)	85
EckaCote—delaminated	84 (ISO)	85

Table 9. Range of Imerys coating clays from the United Kingdom, United States, and Brazil

United Kingdom, ISO brightness %	United States, GE brightness %	Brazil, GE brightness %
Engineered pigments	Coating regular brightness	Engineered pigments
Suprastar—88.5	Fine #1 Astra Glaze—88.0	Capim DG—90.5
Supraprint—88.5	#1 Premier—88.0	Capim GP—90.5
Coating high brightness	Delaminated	Coating high-brightness delaminated
Suprawhite—95 88.0	Astra-Plate—86.0	Capim NP—90.5
Suprawhite—80 87.5		Capim CC—89.0
Coating regular brightness		
SPS—85.5		
Ultra platy coating		
Supraplate—86.5		
Suprasmooth—65 83.0		

Table 10. Range of Thiele Kaolin Company's calcined, coating, and filler clays from the United States

Grade	Description	TAPPI Brightness, GE %	Sedigraph, % <2 μ m	Viscosity*	Maximum Residue, % <325 mesh pH	†	% Moisture Solids, dry 1.5% maximum
Calcined Clays							
Kaoclay	Calcined high-brightness coating and filler	92.0 minimum 92.5 minimum	86–92	Not available	0.010	7.0–8.0	50–52
Kaoclay 80	Calcined low-brightness coating and filler	80–83	86–92	Not available	0.010	6.5–7.5 4.0–6.0	50–52
Coating Clays							
Kaogloss 90	No. 1 high bright	90–92	90–94	300	0.010	6.0–8.0	69–71
Kaobrite 90	No. 2 high bright	90–92	90–94	300	0.010	6.0–8.0	69–71
Kaofine 90	No. 1 fine high brightness	90–92	96–100	200‡	0.010	6.5–8.0	69–71
Kaogloss	No. 1	86.5–88	90–94	300	0.010	6.5–7.5	69–71
Kaobrite	No. 2	86.5–87.0	80–84	300	0.010	6.5–7.5	69–71
Kaofine	No. 1 fine	87–89	95–99	300	0.010	6.5–8.0	69–71
Kaowhite	Delaminated	88–90	75–81	450§	0.010	6.5–7.5	67–68
Kaowhite S	Delaminated high glossing	88–90	83 minimum	450§	0.010	6.5–7.5	67–68
Kaowhite C	Coarse delaminated	85–87	54–62	350**	0.020	6.5–7.5	62–64
Kaoprint	Top coat high bright	90.5–92.5	89–94	500††	0.010	6.0–8.0	68–69
Lopaque M	Base coat low bright	76–82	88–96	300	0.010	6.5–8.0	69–71
Filler Clays							
Kaofill HB	Delaminated filler clay	87–89.5	77–83	Not available	0.010	6.5–7.5	68–69.5
Kaofill	Coarse filler clay	83.0 minimum	50 minimum	Not available	0.15	6.5–7.5	69–71
EG-44	Fine filler clay	81.0 minimum	88 minimum	Not available	0.30	6.5–8.0	69–71

* Brookfield viscosity. No. 1 spindle, 20 rpm, typically @ 70% solids.

† Slurry as shipped, dry @ 20% solids.

‡ Number 2 spindle.

§ Number 3 spindle @ 67.5% solids.

** Number 3 spindle @ 63% solids.

†† Number 2 spindle. As shipped.

are clays with a high brightness and good runnability. There are also ranges of platier clays that are either found naturally or can be delaminated from stacky kaolinite found in the deposits.

A range of clays from the United States, Brazil, and Australia is shown in Table 8 and indicates the range of products, whether they have been delaminated or not, and the particle-size distribution.

Imerys, as the largest producer of kaolin with 25% of the world capacity of 25 Mtpy, is the only international kaolin company to produce coating clays from the United States, the United Kingdom, and Brazil; Table 9 shows their range of products.

Table 10 shows a full range of kaolin products covering calcined clays, coating clays, and filler clays for the U.S. producer Thiele Kaolin Company.

New kaolin deposits are being identified in many parts of the world, including Ukraine, Suriname, China, and Australia. Although the coating kaolin market will be dominated by Brazilian and U.S. clays, there is the opportunity for potential new ventures to enter the market. Australia is seen as a likely source of high-quality coating kaolin, with deposits in Western Australia being developed. W.A. Kaolin Holdings Pty (WAK) has acquired the

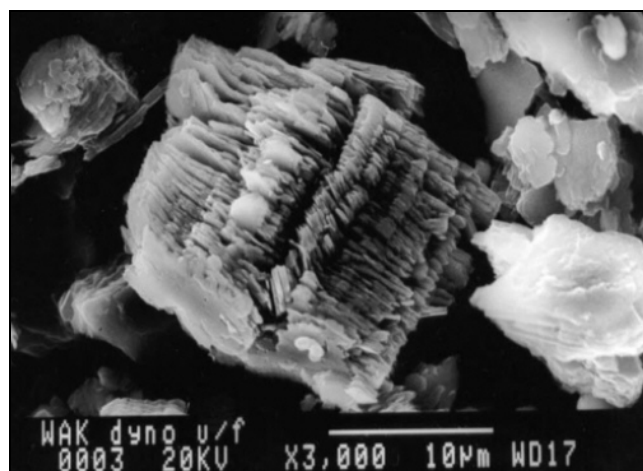


Figure 3. Scanning electron microscopy (SEM) of the WAK Australian kaolin dynocone underflow showing kaolinite stacks

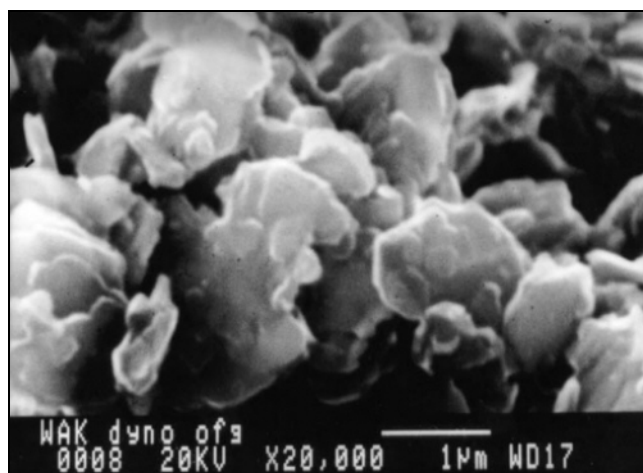


Figure 4. SEM of WAK-delaminated dynocone overflow platy kaolin

deposits evaluated in great detail by CRA/Rio Tinto in the Wickpin Area, 180 km southeast of Perth. The firm has drilled 621 boreholes in the area, amounting to almost 20,000 m of core. All of this core has been evaluated and models of the deposit prepared. Proved reserves of 100 Mt have been identified with the potential for an additional 300 Mt from 274 km². Full-scale pilot-plant trials were planned for late 2005, leading to a decision on whether a plant will be constructed. The deposit is kaolinized granite with a high kaolin yield of 50% at the <45-µm refining level; by comparison, kaolinized granite from Cornwall shows a 15% yield, reflecting the different levels of felspar in the basement granites-gneisses of Western Australia and the high-level granites of southwest England. Detailed characterization studies have been carried out in U.K., Japanese, and U.S. laboratories, and the potential for high-brightness coating clay has been evaluated in the licoating trials in Finland and elsewhere. This processing has involved cyclone and centrifuge separation with the coarse booklets of kaolinite from the underflows (Figure 3) being subjected to delamination to give a platy product (Figure 4).

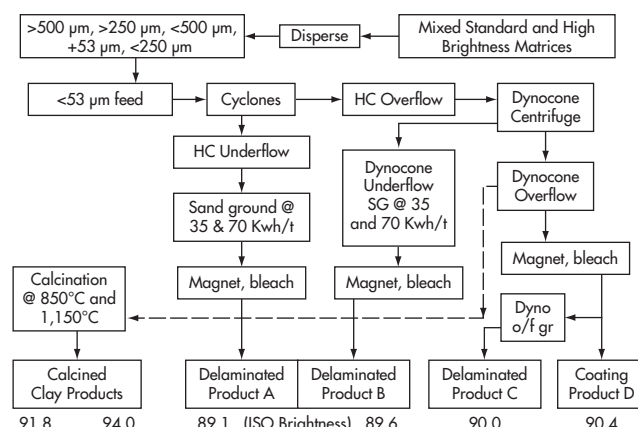


Figure 5. Processing of the WAK kaolin with brightness of various products

For the Chinese market, the high-brightness clays may be blended with GCC in a mix of 70% GCC and 30% kaolin. The Western Australian kaolin can be processed to give a high-brightness delaminated (HBD) coating clay and also as a high-brightness coating clay (Figure 5). Table 11 compares properties of the WAK with Brazilian and U.S. sources, showing the high-brightness values of the WAK clay.

Some Chinese kaolin is suitable for coating clay but, at present, it supplies only the coated board market, not coated paper. A deposit supplying the coated board market is Maoming in Guangdong Province (Zhang et al., 1982; Yuan and Murray 1993; Wilson, Halls, and Spiro 1997; Wilson 2004a).

Kaolin that has been carefully processed to give a controlled particle-size distribution is known as *engineered kaolin*. Ultrafine (less than 0.1 µm) particles are removed to improve light scattering (brightness). These particles are too fine to affect light scatter. Removing such particles does not affect sheet gloss because particles from 1 µm to 0.1 µm have the greatest influence on this property. The disadvantage with engineered kaolin is that the spaces left by the fine particles that have been removed must be filled with water, leading to lower weight-percent solids and less water retention. Because of its higher light scattering, engineered pigments will give improvements in coated sheet brightness and opacity (Table 12).

The shape of the kaolinite particle also influences the coated sheet properties. Pigment shape refers to aspect ratio: the ratio of particle height to width. For a pigment with the same average particle size as measured by a sedigraph, a platy or high-aspect-ratio pigment will impart more fiber coverage when coated. This improved coverage often will result in a smoother coated sheet, which is extremely important for holding dot quality in rotogravure printing. The disadvantage of platy pigments is that the large plate-like particles do not easily flow among one another, giving rise to lower weight-percent solids. The same plate-like characteristics mean, however, that under a coating blade, platy pigments do not lose their water easily.

Ground Calcium Carbonate

Roskill Information Services (2002) estimated that the demand for GCC in papermaking was 15 Mtpy in 2002, with Europe dominating at 67%, followed by Asia and Oceania (22%), North America (8%), and others (3% for Middle East, Africa, and South America).

Table 11. Comparison of Australian clays with Brazilian and U.S. coating products

HBD Coating Clays for Blending with GCC (HBD clays—fine particle size distribution, platy, glossy)				
	Australia		Brazil	United States
Product name	HBD	SBD	Capim SP	Hydragloss 90
Deposit	Wickein	Wickein	Capim	Georgia
Company	WAK	WAK	Imerys	Huber
Wt % <2 µm	94	94	91	98
Wt % <1 µm	76	81	70	98
Wt % <0.5 µm	41	56	42	92
Wt % <0.25 µm	13	28	19	61
ISO brightness	90.5	88.4	89.5	88.8
ISO yellowness	3.3	3.5	4.0	4.2
Shape factor	27	25	25	22

Non-Delaminated HB Coating Clays (HB clays—blocky)			
	Australia		Brazil
Product name	HB		Century
Deposit	Wickein		Capim
Company	WAK		PPSA
Wt % <2 µm	90		82
Wt % <1 µm	75		61
Wt % <0.5 µm	49		33
Wt % <0.25 µm	15		10
ISO brightness	89.5		89
ISO yellowness	3.5		4.0
Shape factor	12		11

Table 12. Effect on paper brightness and opacity of engineered kaolin and GCC

Coating Pigment (magazine paper)	Pigment Brightness	Paper Brightness	Paper Opacity
Kaolin	88	70.8	85.2
Engineered kaolin	88	72.8	85.8
Ground marble (GCC)	95	71.4	84.0
Engineered GCC	95	73.4	85.5

Adapted from Gentile 2003.

Table 13. Coating pigment choice between kaolin and GCC based on properties*

	Color Solids	Paper Brightness	Paper Opacity	Fiber Coverage	Paper Gloss	Print Gloss
Coarse GCC	++	+	—	+	—	—
Fine CC	G ++	+	—	—	—	—
Engineered GCC		++	+	+		—
Blocky kaolin	+	—	+		++	+
Coarse platy kaolin	—	—	+	++		+
Fine platy kaolin		—	+	+	+	++
Engineered kaolin		+	+	+	+	+

* Plus signs indicate most advantageous property in coating; minus signs indicate least advantageous property in coating. Blank cells indicate no particular advantage or disadvantage.

It can be seen that Europe is a major user of GCC based mainly on marble deposits and also some chalk. Most of the coating market is supplied by products derived from marble deposits, with Omya controlling 75% of the total market and Imerys, Provencale, Reverte, and others accounting for the rest. A major growth market for GCC is now Asia, of which China is at the forefront with many new projects involving satellite GCC plants (for example, APP has a 500,000-tpy GCC plant in Dagang).

Using GCC as a coating pigment gives technical and economic benefits such as high brightness, coating at higher solids, lower binder demand, good runnability, and improved printability. In some applications, the advantage of high-brightness coating pigments leads to lower hiding power and reduced opacity. Therefore, adding opacifying pigments to the coating color to reach the required opacity is common practice. Pigments with high brightness, broad particle-size distribution, and a average particle size of many of the GCCs currently used in coating are not optimal for opacity.

The larger companies such as Omya and Imerys are now producing a range of products for which the GCC is manufactured to optimize the opacity. The new products are produced by a slightly different processing technique: the particle-size distribution and the average particle size are moved according to the theory of light scattering toward that of the ideal opacifying pigment. The processing involves techniques to give steeper curves and in some cases removing finer particles. The percentage of solids at which the processing of the GCC is carried is also important.

Omya has developed a new pigment called Hydrocarb CC. Using the theory of light scattering, Omya designed a pigment with a tailor-made (engineered) mean particle size and particle-size distribution. For high opacity, the target is a narrow particle-size distribution with a mean diameter between 0.6 and 0.8 µm. Using a modified grinding technology, Hydrocarb CC has been manufactured with a narrower particle distribution than Hydrocarb 90. Comparing Hydrocarb 90 and the new pigment shows that the narrow particle size leads to a higher wet void volume and a lower specific surface for Hydrocarb CC. This difference is explained by the reduced amount of fine particles, which results in a more open and porous surface for an increase in ink receptivity. Hydrocarb CC produced from marble shows a higher brightness and opacity on the finished paper compared to Hydrocarb 90 produced from the same source of calcium carbonate.

The choice of mineral pigment used by the papermaker will depend on a number of factors related to the paper grade being produced. These include fiber production costs, mineral pigment price, paper optical properties, and strength. It is significant that the papers considered the best in relative quality terms have the highest mineral content, whether it is by filler content or coating or both. Minerals add value to paper.

Table 13 shows a choice between kaolin and GCC, based on the paper properties. Here GCC is clearly better for color solids and paper brightness but has poorer paper gloss and print gloss than kaolin. The platy nature of the kaolin gives better fiber coverage (especially the coarse platy type for SCA papers), and the fine platy kaolins give good paper gloss and print gloss compared to GCC.

Today the pigments used in paper coating are many and varied in their properties. Blending has become a common feature with precoat often being a coarser GCC (about 60–70 wt % <2 µm) followed by a topcoat with a fine GCC (90–95 wt % <2 µm) blended with either a blocky or platy kaolin dependent on the type of surface required. Very fine clays, such as Amazon Premium, are often blended with 20–50 wt % fine GCC to give a higher brightness surface with enhanced printing properties. Various blends from

Table 14. Typical blends of kaolin and GCC used in LWC and MWC paper

Paper Type	Blend of Kaolin and GCC		Comments
	Type of Kaolin	Type of GCC	
LWC	50% U.S. #1 (blocky) 80% Platy clay	50% 90 wt % <2 μm 20% 90 wt % <2 μm	Single coated, 60-gsm paper Single coated
MWC/woodfree—gloss			
Gloss, precoat	None	100% 60–75 wt % <2 μm	Base paper, 90 gsm
Gloss, topcoat	30% U.S. #1 blocky	70% 90–95 wt % <2 μm	
MWC/woodfree—matte			
Matte, precoat	None	100% 60–75 wt % <2 μm	Base paper, 90 gsm
Matte, topcoat	50% Fine platy kaolin	50% 90 wt % <2 μm	

Table 15. Soft calcined clay products for the paper industry

Product	Properties	Brightness, %	Size, wt % <2 μm	Product Form
Engelhard				
Luminex	Ultra-high brightness calcined	95.8–96.5	80–90	Dry
Ansilex 93	High brightness calcined	92.5–93.5	86–90	Dry
Ansilex	Standard brightness calcined	90.0–92.5	86–90	Dry, 51% solids
Excaliber	Standard brightness, high opacity	80.0–82.0	86–92	Dry
Huber				
Hycal	Calcined	92.0–94.0	86–96	Dry
Hubertex	Calcined	92.0–93.5	NR*	Dry, slurry
Hubertex D	Calcined, high solids slurry	92.0–93.0	NR	Slurry
Imerys				
Alphatex	Calcined	92.5	93	50% solids, dry
Alphatex HP	Calcined	92	91	50% solids, dry
Opacitex	Calcined	80	88	Dry
Deltatex	Calcined	92.5	92	59% solids, dry
Liner-fil 300	Calcined	92.5	91	50% solids, dry
Astra-Plex	Calcined composite	NR	NR	56% solids
Thiele				
Kaocal	High brightness calcined	92	86–92	50%–52%
Kaocal 80	Standard brightness	80–83	86–92	50%–52%

* NR = no results.

pigments such as GCC, PCC, kaolin, and talc are continuously being developed to give the papermaker a wide choice. Table 14 shows some typical blends of kaolin and GCC used for various types of paper.

Unlike the situation in other areas where large players such as Imerys, Engelhard, Huber, Thiele (United States); CADAM and PPSA (Brazil; for kaolin); Omya and Imerys (for GCC); and Specialty Minerals dominate, the Chinese paper pigment market has a larger number of producers for all pigments, with no single company having a sizeable market share. Development of PCC and GCC in China will be dependent on local sources of limestone and marble, respectively, and also the logistics of delivering marble for satellite GCC plants.

The largest paper mill in China is the APP operation at Dagang. Here the pulp is imported from Indonesia and the base paper is manufactured using PCC produced from lime from local limestone in a satellite plant at the paper mill. The precoat is a GCC at approximately 65 wt % <2 μm , followed by a topcoat that is 95 wt % <2 μm GCC, mixed with 30% imported kaolin from the

United States and Brazil. Calcined clay might well be used at the 10% level in the precoat.

Calcined Clay

Soft calcined clays are loosely aggregated as a result of fluxing that occurs on the edges of the particles. This aggregation results in particles of nominally larger sizes but with entrained air voids that give rise to good light-scattering characteristics. These properties are widely used in the paper industry to provide good opacity, ink immobilization, and light-scattering effects. Table 15 shows the main calcined products sold into the paper industry, which is the largest consumer of soft calcined clay products. These are all soft calcined products that are not reactive like metakaolins but have been agglomerated by heating. They have point-contact adhesion, which gives the kaolin platelets a three-dimensional structure; it is this structure that is of benefit to the papermakers: they enhance the optical and printing properties of paper. These products are used in rotogravure applications where low levels of calcined clay improve optics and structure the coating to provide good fiber coverage and

missing dot performance. Calcined clays are also used in newsprint applications to improve the opacity and reduce the consumption of titanium dioxide.

Talc

In Europe, the two main printing processes are rotogravure and offset. The offset process poses problems for the use of talc because the transfer of the image uses a hydrophilic/hydrophobic action, which is largely incompatible with an organophilic mineral like talc. The rotogravure process, however, prints by direct contact between the image cylinder and the paper. Producing printing cylinders is expensive, and, therefore, rotogravure printing is suitable only for large-volume magazines, mail order catalogs, or flyers. Key requirements for rotogravure papers are good spool formation and smoothness. Good spool formation is essential if the printing presses are to run without constant stops. In the early 1970s, papermakers exclusively used platy English and German clays, and then added U.S. delaminated clays. In the late 1970s, the research department at Finminerals (now Mondo Minerals) began working with large Finnish customers to develop talc grades suitable for coating; in 1981 they launched their product. This was followed by Luzenac introducing a rotogravure-coating talc. The talc works in two ways to improve rotogravure paper. First, its low coefficient of friction allows the large spools to be produced with a constant tension, which reduces paper breaks; and second, because talc is very platy, it helps improve the smoothness and therefore gives better printability. Talc has successfully established itself as a major coating mineral for rotogravure paper (Whiteley 2002).

Precipitated Calcium Carbonate

PCC is well accepted as a filler pigment and is now beginning to be used as a coating pigment. Currently, PCC accounts for less than 5% of coating pigments used but the market is developing, led by SMI, Imerys, and Omya. SMI, part of Minerals Technologies, pioneered the concept of the satellite plant for PCC and now has more than 50 plants in operation around the world. PCC is valued for its high brightness and light-scattering characteristic in paper filling and coating applications. PCC is produced through a reaction process that uses very pure calcium carbonate crystals and water. The crystals can be produced in a variety of different shapes and sizes, depending on the specific reaction process that is used. The two main raw materials required are quicklime and carbon dioxide. Because quicklime is readily available in many areas of the world, it can be delivered to the satellite plant at a reasonable cost. In most paper mills, carbon dioxide is available to be used from a mill flue gas. This makes PCC economically attractive for the paper mill.

For paper coating, SMI developed several PCC product lines—ALBAGLOS, OPACARB, and JETCOAT. ALBAGLOS has a precisely controlled particle-size distribution, good high-shear rheology, and good ink hold-out, and it can be used at high levels to improve paper brightness and opacity while maintaining sheet gloss. OPACARB has an acicular shape that provides good smoothness, gloss, brightness, and opacity owing to a narrow particle-size distribution and a mean particle size of 0.40 μm . JETCOAT is the latest PCC coating pigment and is designed specifically for coating inkjet and other nonimpact papers. SMI has developed six different commercial crystal shapes of PCC that give a wide variety of crystal structures that offer different performance characteristics (brightness, opacity, and bulk) to a sheet of paper. These shapes are scalenohedral calcite, spherical calcite, prismatic calcite, clustered acicular aragonite, rhombohedral calcite, and discrete acicular ara-

gonite. Using crystal-engineered PCC can also improve paper machine productivity.

Imerys produces a broad range of PCC products for filling, precoating, and top/single coating, applicable in all paper and board-manufacturing processes. Imerys's PCC coating products include Opti-Cal Print (rhombohedral), with a mean particle size (mps) of 0.5–0.7 μm and a brightness of 95–98 GE. Opti-Cal Matte is rhombohedral with an mps of 2.0–2.2 μm and Opti-Cal Gloss is aragonite with an mps of 0.3–0.5 μm and a brightness of 95–98 GE. Imerys was chosen by M-real, one of Europe's foremost producers of P&W papers (ranked first in WFC paper, and second in WFU paper), as the supplier of calcium carbonates for its paper mill in Husum, Sweden, which has a capacity of 620 ktpy. Under a long-term contract, Imerys completed construction in 2005 of a satellite PCC plant at M-real's Husum facility.

Blanc Fixe

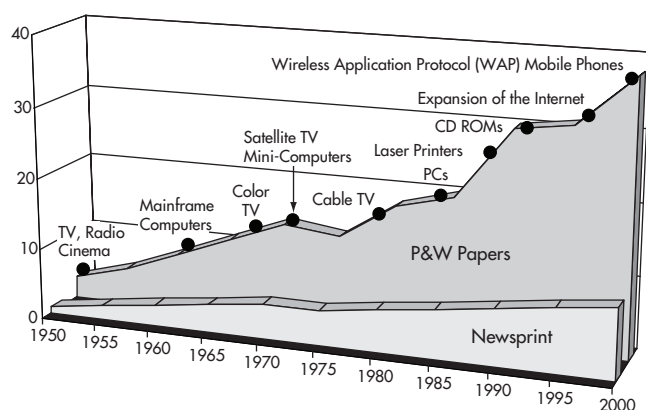
Blanc fixe (meaning *stable white*) is a synthetic barium sulfate that is precipitated with a defined particle size from highly purified solutions of barium salts and sodium sulfate. Because of its chemical production process, blanc fixe is free of impurities such as quartz. The feed material for the process is chemical-grade barite (BaSO_4), which is generally low in silica. Much of the chemical-grade barites used in Europe for blanc fixe production come from China. With its hardness of 3 on the Mohs scale, blanc fixe has low abrasion and exhibits an extremely high light reflectance in broad ranges of the spectrum, not only in the visible but also well into the ultraviolet and infrared ranges. Blanc fixe is generally 99% BaSO_4 with an average particle size of 3 μm , a lightness/color of 98.5 (on the International Commission on Illumination [CIE] $L^*a^*b^*$ color system), and a pH of 9. It is used both in pulp and as a pigment in coating because of its color and low binder requirements. It is used in small amounts in coated art papers and in photographic papers, where it was applied to the base to improve the surface before the light-sensitive photographic emulsion is applied. The development of extrusion coating involving special plastics that do not absorb the processing chemicals, however, has generally replaced this precoat, especially for color printing paper.

Satin White

Satin white, a calcium sulfo-aluminate, is one of the oldest known pigments for paper. Manufacture involves reacting alum with slaked lime at a controlled temperature. Satin white forms acicular crystals that are often 1–2 μm long and 0.1–0.2 μm in cross section. This shape imparts an open, bulky structure to the coating that has a major influence on its optical properties; in particular, it is responsible for high-gloss development during calendering as well as giving a high print gloss, high ink receptivity, high bulk, and good covering power. A 4-g/m² coating of satin white would have a similar covering power to a 10-g/m² clay coating. Satin white, however, has a very high dispersant demand because of calcium ions in solution. It also leads to high adhesive demand if the satin white level exceeds 10%. The main applications for satin white are in high-quality art paper and high-quality lightweight offset grades.

Titanium Dioxide

TiO₂ offers the highest opacity and hiding power of all coating pigments, giving good optical density, excellent brightness, and very low grit levels (0.0010–0.0050 wt % of <325 mesh). High brightness, combined with superior light scattering, provides excellent brightness and whiteness to paper and paperboard products. TiO₂ provides the best opacifying performance available to the paper industry because of highly efficient light scattering. The higher the TiO₂ g/m²



Adapted from Haarla 2002.

Figure 6. Western European newsprint and writing paper consumption, Mtpy

light scattering, the less TiO_2 needed to achieve the opacity target. The high refractive index of the rutile TiO_2 crystal proves an inherent light scattering advantage over anatase TiO_2 . The median particle size of TiO_2 coating pigments is very fine at just 0.30–0.60 μm .

THE FUTURE

Pigments for paper will continue to be a growth industry over the next decade, particularly in China, where production is expected to grow from 33 Mtpy to 80 Mtpy by 2015 (M. Sang, personal communication). In Western Europe, paper consumption increased significantly from 1950 to 2000, despite innovations such as television, computers, and the Internet that were expected to lead to a paperless society (Figure 6). Unless there is a dramatic shortage of fiber in the world for some unknown reason, papermaking, particularly the uncoated woodfree papers, is expected to grow.

Kaolin competes with GCC, PCC, and talc in the paper industry. In 1980, kaolin accounted for 87% of the pigment used in paper (10.2 Mt), whereas in 2000 this had fallen to 40% when the total pigment used in paper was 29.9 Mt. During the same period, GCC's market share grew from 9% to 33% and PCC use grew from virtually zero to a 14% market share (Haarla 2002). This trend toward calcium carbonate has mainly been a result of an alkaline papermaking system replacing an acid system, and also because of the requirements of higher brightness pigments for woodfree pulp.

These changes have been in a market that has grown significantly, however, so the tonnages that the kaolin companies supply have remained much the same over the last decade. The supply of kaolin has switched from the United States and the United Kingdom to Brazil with the discovery and development of world-class facilities based on the sedimentary kaolin deposits in the Amazon Basin.

There will be no shortage of pigments in the world for the next 100 years at least. New kaolin deposits in the Amazon Basin, Western Australia, and elsewhere are being discovered, and potential resources are very large. The Cornish kaolin deposits mined for more than 250 years have just another 40–50 years of reserves left. There is sufficient suitable limestone available to manufacture lime for PCC production, and the use of GCC, which relies mainly on good sources of marble, is expected to grow. Although there might well be some shortages of high-quality marble in some parts of the world, increased processing such as flotation to remove silicates, graphite, and iron pyrites will allow the use of lower quality marble

deposits. New deposits of anatase and rutile are being discovered and developed, which means no shortage of titanium dioxide.

The real value of minerals used in papermaking lies in their capability to further improve printing results and enable the paper or board substrate to be a good printing surface. Developing higher brightness, whiteness, and opacity remains a challenge, especially as papers and boards trend to lower basis weights and sheet thickness. The digital revolution has enabled almost everyone to access text and pictures that can then be used to produce an infinite variety of printed media. This capability has created new requirements for paper and board surface properties than can be satisfied not only by surface-applied pigments but also by the use of fillers to improve base sheet uniformity. Developing filled barrier coatings is also an emerging opportunity.

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Paint and Coatings

Peter A. Ciullo

At the dawn of the industrial revolution, artisans used paints and varnishes for both decorative and protective purposes. By the late nineteenth century, mechanization and the widespread use of iron and steel helped transform the production of coatings from an art to an industry. Ferrous fabrications required anticorrosive and protective coatings and the need for architectural coatings grew with the size of cities, so paint factories were established in industrial and population centers. Initially, very few scientifically trained personnel worked in the industry, but between the world wars of the twentieth century, the accelerating pace of technological development—particularly the manufacture of titanium dioxide (TiO_2), developments in alkyd chemistry, and the mass production of automobiles—catalyzed research into coatings of all types. The post-World War II era can be characterized as the gradual and ongoing conversion to solventless coatings technology. Although the first latex paint was introduced in the late 1940s to only moderate success, water-based systems have since undergone continuous improvement and are now as durable for many uses as their solvent-based counterparts. Today, industrial finishes that are free of both solvent and water are common.

The annual production of paints and coatings in the United States is approximately 1.3 billion gallons (Anon. 2002), and Table 1 compares the production volume of the major categories of coatings by type and form. Multinational corporations dominate the worldwide paint and coatings industry. More of the world's leading producers are headquartered in the United States than in any other country, but the size of the North America market for architectural and industrial coatings, particularly those for the automotive industry, has resulted in considerable participation by foreign companies, including their establishment of manufacturing facilities in North America (Anon. 2003). Of the approximately \$16 billion in annual U.S. shipments of paint, varnish, and lacquer, only 2.5% is imported and nearly 7% is exported (Anon. 2002).

RAW MATERIALS

The coatings formulator chooses raw materials from the following basic categories:

- **Extender pigments:** These are the minerals used to optimize the pigmentation efficiency of TiO_2 , improve film properties, and reduce cost.
- **Pigments:** Inorganic and organic pigments are added principally to impart a particular color.

- **Binders:** The binder forms the continuous coating film. It literally binds the pigment and extender particles within the film.
- **Solvents:** Solvents are needed in liquid coatings to solubilize or disperse the binder. The solvent is lost to evaporation during film formation.
- **Additives:** Additives is a broad category encompassing many chemicals and several minerals used to optimize coatings properties before, during, and after cure.

EXTENDER PIGMENTS

Traditionally, fine-ground minerals have been used in paints as inexpensive fillers—they extend the film formed by the generally more expensive binder. Most minerals are now more appropriately used as functional fillers. They are chosen to benefit coating stability, rheology, and application properties, and to enhance dry film properties. Very fine particle-size minerals are used as pigment extenders in a more literal sense, extending the optical value of TiO_2 , the predominant white opacifying pigment in coatings. These extenders effectively separate the individual TiO_2 particles and provide the optimum pigment spacing for maximum opacifying effect. Pigment extenders are used in this way to reduce the amount of relatively expensive TiO_2 required for a given level of opacification and whiteness. The major extender minerals are calcium carbonate, talc, kaolin, silica, barite, wollastonite, nepheline syenite, and mica. Lesser use is made of diatomite, feldspar, perlite, and pyrophyllite.

Important Properties

The performance properties of an extender pigment are influenced by its volume fraction in the coating matrix (pigment volume concentration [PVC]), its particle shape and particle size, and its adhesion to the binder.

Volume Fraction

The volume fraction of the extender pigment, or its PVC, is the volume it occupies divided by the volume of the dry coating film. These minerals usually exert their strongest overall influence on coating properties when there is just enough binder to coat all particles and fill interparticle voids. In coatings, this occurs at the critical pigment volume concentration (CPVC). Film properties change rapidly near the CPVC, where film density, tensile strength, and adhesion tend to reach a maximum. At PVCs above the CPVC,

Table 1. Annual coatings production, selected categories

Category	Gallons (x1,000)
Architectural Coatings	
Exterior, solvent-thinned	70,967
Exterior, water-thinned	182,423
Interior, solvent-thinned	48,947
Interior, water thinned	407,104
Lacquers	5,808
Other	1,981
OEM Product Finishes	
Automobile, truck, bus, and parts	66,111
Aircraft, railroad, other transportation	11,558
Construction, farm machinery, and equipment	18,865
Appliances, HVAC equipment	7,329
Metal building products	35,855
Furniture and fixtures	82,567
Wood and composition board flat stock	10,060
Marine Coatings	
OEM and refinish	13,565
Special-Purpose Coatings	
Construction and maintenance, interior	23,370
Construction and maintenance, exterior	34,207
Traffic marking paints	39,397
Transportation and machinery refinish	45,979
Other	4,233
Category	Pounds (x1,000)
Powder Coatings	
Appliance	59,445
Automotive	44,515
Architectural	10,310
Lawn and garden	12,170
General metal finishing	111,015
Other industrial finishes	192,425

there is not enough binder to completely fill the voids between the pigment particles. The film becomes more permeable, with consequent reduction in scrub resistance, stain resistance, rust inhibition, enamel holdout, and blistering. As the CPVC is approached and exceeded, the pigment particles progressively disrupt the smoothness of the film surface, causing light to be scattered and gloss to be reduced. CPVC usually occurs between 40% and 55% PVC.

Particle Size and Shape

Extender pigment particles can be described by three basic shapes: (1) blocky, as with calcium carbonate, silica, and nepheline syenite; (2) platy, as with talc, mica, and kaolin; and (3) acicular, as with wollastonite. Platy and acicular particles are further characterized by aspect ratio. For platy particles, the aspect ratio is the ratio of the mean diameter of a circle of the same area as the face of the plate to the mean thickness of the plate. For acicular particles, it is the ratio of mean length to mean diameter.

For a mineral to contribute to the mechanical properties of a coating film, stress, as from stretching or bending, must be transferred from the polymeric film to the strong and stiff mineral. The stress transfer is more efficient if the mineral particles are smaller, because for a given concentration, greater mineral surface is exposed to intercept the stress. Effective stress transfer also requires intimate mineral-binder contact and a certain minimum aspect

ratio. Once this ratio is exceeded, the efficiency of stress transfer increases with increasing aspect ratio.

Although small particle size and large surface area improve the durability of a coating film, they also promote high vehicle demand, which lowers CPVC and limits loading levels. The balance of film reinforcement and vehicle demand can be controlled by the choice of mineral, by the particle-size distribution of the mineral, and by the use of combinations of minerals. High aspect ratio particles tend to pack in such a way as to create larger interstices, which fill with binder, as opposed to low aspect ratio or blocky particles. Platy and acicular extenders, therefore, are generally produced with a broad distribution of particle sizes. The finer particles fill within the interstices of the larger ones, displacing binder and increasing CPVC, without compromising the mechanical properties of the coating film. With extenders of narrow size distribution and high aspect ratio (HAR), this purpose can be served by the primary pigments and by the inclusion of low-cost, fine-ground blocky fillers such as calcium carbonate and silica.

Binder-to-Mineral Adhesion

Intimate mineral-binder contact is important in optimizing extender pigment performance. The pigments may be well dispersed throughout a coatings film, but any gaps at the mineral-binder interface represent areas of zero strength and locations for the transmission or collection of moisture and other liquids. This is analogous to the effects on permeability and film strength of exceeding the CPVC.

Solvent- and waterborne coatings present significantly different considerations regarding the intimacy of binder-to-filler contact and adhesion. In the former, the mineral is already wetted by and dispersed throughout an organic medium. As volatiles are lost and the film contracts, the mineral particles become more closely packed and are ultimately encapsulated in the final binder film. In an emulsion coating such as a latex paint, the mineral particles are wetted by water that contains surfactants and dispersing agents designed to make the particles hydrophilic and resistant to agglomeration. The dispersed mineral particles share the aqueous medium with dispersed binder micelles. As volatiles are lost, the binder micelles coalesce into a continuous polymeric film. In so doing, they must deform around, displace water from, and coat the mineral surfaces. This process is consequently less conducive to intimate binder-mineral contact than that of solvent paints.

Surface treatments and modifications are used as necessary to optimize a mineral's compatibility with and adhesion to the binder matrix. Although a mineral to which any type of organic chemical has been added is commonly called "surface treated," a surface treatment can be differentiated from a surface modification on the basis of functionality. A surface-treated filler is coated with a processing aid. A processing aid may not bond to the filler and does not bond to the matrix. It acts as a wetting agent to make the filler surface hydrophobic and more intimately coated by the organic medium. Surface treatments improve deagglomeration and dispersion in organic media, promote better coating of mineral by binder, and allow higher filler loadings. Stearic acid is a common treatment on calcium carbonate. Organosilanes with nonreactive organic groups are sometimes used as treatments on silica and silicate extenders.

A surface-modified filler has a coupling agent covalently bonded to its surface. The coupling agent is in turn bound to the matrix through chemical reaction or chain entanglement. The coupling agents used as surface modifiers perform the same functions as surface treatments and, in addition, improve binder adhesion, film integrity, weathering, and service life. The most commonly used modifiers are the organosilanes with amino, epoxy, methacrylate, or

vinyl functionality. Silane treatment levels are typically 0.5% to 1.0% of mineral weight.

Oil Absorption

The oil absorption of an extender pigment is measured to reflect the composite effect of particle shape, particle-size distribution, surface area, the effect of mineral PVC on CPVC, and mineral-binder interaction. The coatings formulator often uses oil absorption values as a guide to selecting the optimum combination of pigments and extender pigments.

The spatula rub-out oil absorption test (ASTM D281) is used to indicate binder demand by determining the amount of linseed oil that is just sufficient to coat the mineral particles and fill the interparticle interstices. The first component of the test is the amount of oil required to wet and coat the mineral particles. This depends on surface area, which is affected by particle-size distribution; hydrophilicity, which can be adjusted by surface treatment or surface modification; and porosity, which is a result of mineral lattice structure. Surface treatment or modification, for example, can reduce oil absorption and raise the CPVC of a mineral that is otherwise an appropriate shape and size distribution. After the particles are coated with linseed oil, the second component of oil absorption is the additional oil that fills the interstices. In effect, this test measures the CPVC of the mineral-linseed oil composite and has some value in indicating the mineral's CPVC in a coating.

The following equation is often cited to relate oil absorption to CPVC:

$$\text{CPVC} = 1 \div [1 + (OA \times p)/93.5]$$

where *OA* is the oil absorption and *p* is the specific gravity of the mineral (Hare 1994). This is generally considered to be a good predictor of CPVC in solvent paints. This formula overstates somewhat the CPVC expected in latex films because of the different mechanism of filler integration, as previously described. From this equation, nevertheless, comes an appreciation of the effect of a filler's specific gravity, or weight per gallon, on CPVC: for a given oil absorption, a higher specific gravity results in a lower CPVC. This relationship is easily overlooked because the high specific gravity pigments and extenders, such as TiO₂ and barite, are often lower in oil absorption than low specific gravity alternatives. Because paints are sold by volume rather than by weight, specific gravity is taken into account along with cost per pound when the overall economics of the coating formulation are considered.

The oil absorption values of individual pigments and extenders can indicate the relative effects of these components on CPVC. When formulating for PVC versus CPVC with a particular combination of pigments and extenders, however, aggregate surface areas, specific gravities, and packing geometries must be considered. Oil absorption of the blend must therefore be measured because the contribution of the individual components is not additive.

Mineral Extenders

Table 2 compares the extender mineral basic properties of interest to the coatings formulator, and Table 3 compares their relative advantages in contributing to film mechanical and optical properties.

Calcium Carbonate

Calcium carbonates are more widely used in paint and coatings systems on a weight basis than any other mineral extender. The ground natural products have a long history of use because they are relatively inexpensive, are white, and have low vehicle demand. These attributes make high loadings both possible and attractive. These materials are used to reduce the cost of many formulations

Table 2. Extender pigment basic properties

Extender Pigment	Specific Gravity	Refractive Index	Mohs Hardness	pH
Calcium carbonate	2.7	1.66	3	8.5
Talc, platy	2.8	1.59	1	9.5
Talc, tremolitic	2.6–3.1	1.57–1.62	3.5	9.5
Kaolin, hydrous	2.6	1.56	2	4–8
Kaolin, calcined	2.5–2.6	1.62	3–4	5–6
Silica	2.6	1.54	7	7
Barite	4.5	1.64	3–3.5	7
Wollastonite	2.9	1.63	5–5.5	10
Nepheline syenite	2.6	1.53	5.5–6	10
Feldspar	2.6	1.53	6–6.5	8–9
Mica	2.8	1.6	2–2.5	7–9
Diatomite	2.2	1.45	5.5–6	7
Pyrophyllite	2.6–2.9	1.54–1.6	5	7
Perlite	2.6	1.49	5.5–7	7

while improving both the rheological and mechanical properties of the coating.

Ground natural products are used extensively in solvent-borne exterior house paints and interior flats and semigloss enamels. The higher vehicle demand of the precipitated calcium carbonates (PCCs) limits the use of these materials in nonaqueous systems, although small amounts are used as flow-control agents. In water-bornes, the hydrophilic nature and low water demand enable the easy incorporation of high levels of calcium carbonate with only minor increases in viscosity. High brightness ultrafine-ground PCCs are used as TiO₂ extenders and opacifiers in waterborne coatings. They have a higher binder demand than coarser grades but better dry hide and gloss retention. The alkalinity of calcium carbonate is an advantage for in-can buffering and in corrosion control coatings. It can be a disadvantage in protective coatings, however, because of its reactivity with acids and its consequent sensitivity to acid rain.

Talc

Talc products are perhaps the most broadly functional of the extender pigments. Although exterior house paint is the major coatings application for talc, talc is probably used in a wider variety of coatings than any other mineral. Talc products serve as extender pigments in solvent-borne and waterborne architectural and industrial primers and topcoats, and in powder coatings.

The products used in coatings are platy talc, containing predominantly (>90%) the mineral talc, and tremolitic talc, most often a natural blend of platy talc and serpentine, plus acicular/blocky tremolite and anthophyllite. Platy talcs can be further classified as microcrystalline or macrocrystalline. Microcrystalline varieties are naturally small in plate size and are the product of compact, dense ores. Macrocrystalline varieties contain relatively large, higher aspect ratio plates. Because talc is a very soft, platy mineral, the residual minerals in platy talc products can have a subtle effect on properties. Carbonates, for example, being nodular and relatively hard, might require more grinding than a softer, platy chlorite in order for a talc product to attain a particular Hegman fineness. Tremolitic talcs, however, exploit the properties contributed by the significant amount of accessory minerals that occur together with the talc.

The value of platy talc in coatings accrues primarily from its particle shape and surface properties. Talc is hydrophobic, but it

Table 3. Extender pigment selector*

Properties	Calcium Carbonate	Talc	Kaolin	Silica	Barite	Wollastonite	Nepheline Syenite	Feldspar	Mica	Diatomite	Pyrophyllite	Perlite
Mechanical												
Durability		x(tr)	x(dl)	x	x	x	x	x	x		x	
Weatherability		x(tr)	x	x	x	x	x	x	x		x	
Permeability										x		
Sandability		x(pl)			x					x		
Resistance to:												
Chemicals				x	x		x	x	x		x	x
Acid				x	x			x	x		x	x
Abrasion		x(tr)	x(cc)	x		x	x	x		x		
Scrubbing	x(gr)	x(tr)		x		x	x	x			x	
Wear		x(tr)		x		x						
Blistering	x	x(tr)		x		x	x	x		x		
Chalking				x			x	x	x		x	
Frosting		x(tr)	x					x			x	
Corrosion	x					x			x			
Staining							x	x				
Optical												
TiO ₂ extension	x(pt)	x	x(cc)	x	x						x	
Tint retention		x(tr)	x			x	x	x				
Low sheen		x(pl)		x(pt)		x			x	x	x	
Flatting		x(pl)	x(dl)	x(pt)						x		x
Dry hide	x	x(tr)	x(cc)								x	x

* gr = natural, ground; pt = precipitated; dl = delaminated; cc = calcined; tr = tremolitic; pl = platy.

disperses easily in aqueous as well as solvent-borne coatings. With its platy shape, talc has a beneficial effect on paint rheology. It generally contributes to improved brushability, leveling, and sag resistance. It is normally self-suspending in paint vehicles and assists in keeping other pigments suspended. When settling does occur, it is generally soft and readily redispersed.

Platy talcs improve the toughness and general durability of paint films. The talc plates tend to align with the coating's flow so that they are parallel to the substrate in the dry film. This creates a physical barrier to the transmission of moisture, improving water and humidity resistance. The relative impermeability, however, can increase the formation of blisters as any moisture or gases leave the substrate. Platy talc reinforces the dry coating film because of its alignment therein and its naturally high aspect ratio. Reinforcement makes the film more resistant to cracking or rupture in response to stretching and flexing, thus better insulating the substrate from the environment. The combination of barrier properties, alkaline pH, and reinforcement accounts for talc's contribution to corrosion inhibition. Its barrier properties also make platy talc well-suited for primers and sanding sealers used on porous substrates to control penetration. In exterior paints, platy talcs tend to chalk more readily than most extender pigments, although less than calcium carbonate.

In liquid coatings, 325-mesh or 4-Hegman talcs are most commonly used. The micronized talcs, 6 Hegman or finer, are used for TiO₂ extension, good low angle sheen, and good burnishing resistance. Macrocrystalline varieties are preferred for the ir excellent flatting.

Tremolitic talc is used as an alternative to platy talc in many coatings applications, with the heterogeneous mineral blend accounting for its functional differences. The combination of acicular, blocky, and platy particles, ranging in size down to the clay-like serpentines, allows for softer settling, easier redispersion, and

higher loading levels. These factors also allow for better light scattering and thus better color in oil and better dry hide. Flatting efficiency is generally inferior to that of platy talcs. The hardness of the nontalc constituents provides greater scrub resistance and durability (Ciullo and Anderson 2002). In primers, the variety of particle shapes provides more microroughness than do flat plates and thus better intercoat adhesion.

Tremolitic talc often provides better film reinforcement but somewhat greater permeability than platy talc. Barrier properties are generally not as good, but this reduces the tendency to blister. For corrosion control, greater permeability is compensated for by greater alkalinity in addition to film durability. Tremolitic talcs with 4 Hegman fineness are the most widely used grades in architectural, industrial, and marine coatings.

Kaolin

Kaolin has a platy structure, but unlike talc, its use in coatings derives more from its contribution to optical properties than to physical properties. Because of the importance of kaolin's effect on the optical properties of coatings, these clays are offered in more varieties than are other extender pigments to provide a range of particle sizes and shapes, controlled particle-size fractions, brightness, and opacification. For example, the thin, wide individual plates of delaminated clay, from a coarse water-washed clay fraction, provide improved brightness, opacity, and barrier properties. Low-temperature calcination of water-washed clay increases hardness, porosity, brightness, opacity, and oil absorption. High-temperature calcination maximizes brightness and opacity. The balance of opacity and sheen derived from calcined clays is further manipulated by the temperature, rate of heating, and fluxes used in the calcination process.

These clays are made even more versatile through chemical modification. Grades are available with dispersant coatings for easy

dispersion in water, as well as stearate or silane surface treatment or modification for improved compatibility with organic matrices. "Structured" clay products, in some cases also called SAMS (synthetic alkali metal aluminosilicates), are made by reacting kaolin with alkalies, such as alkaline silicates, under elevated temperatures and pressures. The resulting alkaline products are essentially kaolin plates with a rim of amorphous reaction product. The reaction and subsequent agglomeration can be conducted to provide products with increased but controlled levels of porosity, oil absorption, brightness, opacification, tinting strength, and flattening (Broom 1997). A different approach to structured pigments for better optical properties is to electrostatically bind oxide particles such as silica or titania to clay faces.

The primary use of kaolin in coatings is as a TiO_2 extender in water-based architectural paints. Calcined clays generally provide the best brightness, TiO_2 extension, and dry hide. Water-washed and delaminated grades also contribute to extension and dry hide, as well as covering power and gloss control.

Despite the fact that the coatings industry focuses primarily on the optical properties of kaolin clays, this mineral also serves as a functional filler (Stoneback 1996). Water-washed clays are used for their contribution to suspension stability, flow properties, leveling, film smoothness, film strength, and weather ability. Delaminated clays are preferred for improved barrier properties and for more controlled chalking and overall durability in exterior coatings. Because of their greater hardness, calcined clays provide better scrub resistance, which is otherwise not improved with kaolins.

Silica

Ground quartz is used in a wide variety of trade sales paints and liquid and powder industrial coatings as a relatively low-cost, high-brightness extender. It is produced in controlled particle-size distributions for low binder demand. It is chemically inert for good acid, chemical, and heat resistance, and its hardness improves abrasion resistance. Ground quartz is especially suited for primers where surface hardness and roughness are desirable. Its presence in exterior solvent-borne paints improves weatherability in a wide range of environments. It also improves the wear resistance of deck enamels and traffic paints. The particle shape of novaculite, a platy natural silica, imparts additional mar, wear, and weather resistance. Using micronized silica in interior and exterior latex coatings increases surface uniformity and provides efficient flattening. Precipitated silicas are used in coatings to provide flattening, mar resistance, and abrasion resistance. Synthetic silicas are also used as flattening agents in clear coatings because their low refractive index makes them transparent in the film.

Barite

Barium sulfate is used in coatings as barite (known as barites in the United Kingdom), in its natural mineral form, and as *blanc fixe*. *Blanc fixe* is made by reducing barite with coal to barium sulfide, which is then dissolved and reacted with sodium sulfate to precipitate barium sulfate. Barite is used for its low oil absorption; high density; low abrasiveness; chemical inertness; heat resistance; high brightness; lightfastness; low solubility in water, acids, and alkalis; and for its low absorbance over a broad spectral band from near infrared to near ultraviolet. *Blanc fixe* is the preferred form when higher brightness and purity and finer particle size are required.

Blanc fixe and finely ground barite are widely used in industrial coatings, particularly in automotive, marine, and aerospace primers and topcoats. Low oil absorption allows high loadings with a minimal effect on rheology. The high filling level results in a smooth nonporous primer surface with good sanding properties and

excellent gloss retention for subsequent topcoats. In topcoats, these extenders improve flow properties, surface hardness, and color stability. *Blanc fixe* is preferred for glossy topcoats and generally for TiO_2 extension. Barite is widely used for high wear resistance in powder coatings.

Blanc fixe and finely ground barite are also used as extenders for waterborne paints, particularly those requiring a high level of gloss and minimum color distortion. The high refractive index of these materials allows them to function as a translucent white pigment in latex paints, providing a moderate degree of hiding power while having a minimal effect on the color of the primary pigment. The chemical resistance of barium sulfate imparts good weathering characteristics to both solvent-borne and waterborne exterior paints. High specific gravity makes the barium sulfate extenders somewhat more difficult to maintain in suspension compared to other minerals.

Wollastonite

Wollastonite is unique among extender pigments, combining naturally high brightness for cleaner tints; needle-like particles for low sheen and film reinforcement; moderate hardness for wear resistance; moderate oil absorption for higher PVC contribution; and alkaline pH for in-can buffering and flash rust, corrosion, and mildew resistance. The most common use of wollastonite is in corrosion-resistant coatings, particularly waterborne epoxies, where it acts as a synergist with primary inhibitive pigments (Jackson 1990; Hare 1997). Silane-treated fine ground and micronized grades are preferred. In barrier-type formulations where corrosion resistance is achieved through means other than inhibitive pigments, wollastonite is effective on its own. In addition to providing alkalinity, surface-modified grades, typically with aminosilane or epoxysilane, control ionic permeability of the coating film by ensuring against voids at the binder-mineral interface, and by reinforcing the film, reducing film failure caused by mechanical stress, impact, and abrasion.

In addition to corrosion control applications, powder and HAR acicular grades of wollastonite are used in architectural, industrial, and marine coatings to ensure film integrity when exposed to physical and environmental assault. The hardness and acicular shape of wollastonite particles, even at low aspect ratios, reinforce coating films, providing durability and flexibility as well as good mar, scrub, and abrasion resistance. HAR wollastonite grades are used in thick build systems—asphalt coatings, coal tar coatings, texture coatings, and block fillers—for mechanical strength, mud-crack resistance, and durability. Wollastonite is also used in epoxy powder coatings because its low binder demand promotes smooth flow, water resistance, improved adhesion, and good chip resistance. Coarser, more acicular grades are used in primers because they provide a microtextured surface with good tooth for finish coats. In decorative powder coatings, fine-ground and micronized wollastonites are used to provide a smooth satin finish.

Nepheline Syenite and Feldspar

Nepheline syenite and feldspar are unique among low aspect ratio extender pigments for the combination of physical and optical properties that they provide. Milled nepheline syenite and feldspars are composed of angular blocky particles. This shape, with its attendant low surface area, accounts for easy dispersibility, low vehicle demand, and the ability to achieve high loadings. The shape and size distribution of these particles can significantly improve the integrity of dried film through their ability to interlock and pack more tightly and rigidly than smooth surfaced spherical or nodular fillers. The likewise promote flattening and uniform low-angle

sheen. Dry film durability confers crack resistance, and, in combination with relatively high mineral hardness, provides high abrasion, scrub, and burnish resistance. Coatings grades of nepheline syenite and feldspar products are differentiated primarily by particle-size distribution, which in turn determines surface area, oil absorption, and Hegman fineness.

Feldspar and nepheline syenite have very low tint strength, contributing minimal color at high loadings, thus allowing the maximum development of deep tone and pastel colors with minimal colorant. Film reinforcement, chemical stability, and resistance to chalking promote retention of tint and gloss on prolonged exterior exposure. A 4-Hegman grind of nepheline syenite is typically used to achieve the optimal balance of properties. The low refractive index of nepheline syenite and feldspar allows for higher loadings in clear and semitransparent coatings and stains.

Nepheline syenite is often favored over feldspar in coatings because it is silica-free and an effective alkaline in-can buffer. If an exterior latex coating is sufficiently permeable, however, the nepheline component is subject to attack by acid rain and acidic atmospheric moisture. This can eventually result in the frosting of deep tones. Feldspar is preferred in this case. An application of emerging interest for nepheline syenite is powder coatings, where hardness and low resin demand allow for high loadings, low-melt viscosity, and improved abrasion resistance (Keegan 1999).

Mica

The primary coatings use of mica is as nacreous pigment in automotive paint. The grades used as a platy extender pigment are generally higher in aspect ratio, more flexible, more hydrophilic, higher in binder demand, and inferior in color compared to platy talc. Because mica plates are generally stronger and less brittle than the particles of talc and clays, they are more resistant to breakage and reduction in aspect ratio under high-intensity mixing or milling. Mica does not delaminate quite as readily as talc, so it is somewhat harder, although still softer and less abrasive than most other extender minerals, minimizing its contribution to scrub and abrasion resistance. Its high aspect ratio and platy shape provide excellent film reinforcement.

Fine-ground and micronized mica is used as a functional extender in a variety of paint and coating formulations. As a platy mineral, it has beneficial rheological properties in liquid coatings, and also helps reduce sagging once the coating is applied. Mica reinforces the paint film during drying and curing, and as the film ages, it reduces the internal stresses from oxidation, and thermal expansion contraction. Mica increases the film's flexibility and reduces cracking and checking, resulting in improved adhesion and better weathering. Film reinforcement therefore accounts for mica's utility in a broad spectrum of coatings, from texture paints to exterior coatings.

Because its flakes align parallel to the substrate, mica is used in roof coatings, exterior wood stains, and exterior paints to control moisture and gas permeability and to reduce light penetration in the coating film. This makes the film more resistant to fading, weathering, and ultraviolet (UV) degradation. Mica's barrier properties are also exploited in primers, anticorrosion paints, and marine coatings. The ability of mica plates to overlap and bridge openings is used for penetration control in sealers for porous surfaces. Other typical filler uses are in floor and porch paints, heat-resistant paints, and traffic paints. Mica's relatively low brightness and high binder demand necessitate low loading levels in most decorative coatings.

Diatomite

White, flux-calcined diatomite is used as a functional extender and flattening agent. The varied size, shape, and high surface area of the

individual particles result in irregular texturing of the coating surface. This reduces surface gloss and improves adhesion of subsequent coats. Diatomite is used in coatings for uniform control of gloss on irregular surfaces, improved sanding properties, and increased film vapor permeability. The last promotes more rapid drying and reduced blistering and peeling. Diatomite's inherent absorbency reduces resistance to staining and soiling.

Pyrophyllite

Typical of commercial pyrophyllite, this mineral is not necessarily the major component of products sold under its name. Relatively coarse-ground grades are used to impart mud-crack resistance to high-build coatings such as textured paints and block fillers, and checking, cracking, and frosting resistance to exterior latex paints. The platy nature of the pyrophyllite, mica, and kaolin components promotes good dispersion by inhibiting the settling of pigments, helps film dry, and increases resistance to film cracking. The considerable quartz content of these products contributes hardness and wear resistance. Fine-ground grades have also been considered for use in powder coatings and traffic paints. The combination of soft platy and hard blocky particles in pyrophyllite products provides unique performance possibilities in coatings, but their generally off-white color and the safety concern relating to their high quartz content (up to 60%) inhibit widespread use.

Perlite

Perlite is a chemically inert flattening filler with high oil absorption and good dry hide. Expanded perlite is used in lightweight fire-resistant coatings for structural steel and concrete, as a filler in textured paints, and in auto underbody plastisol coatings to reduce weight and improve sound insulation. Expanded perlite is milled and sized to fine particles with jagged interlocking shapes that promote good film integrity and substrate adhesion.

PIGMENTS

In addition to color, important pigment characteristics are brightness, tinting strength, lightfastness, bleed resistance, and opacity. Tinting strength is the ability to color a white base. Lightfastness is the pigment's resistance to fading or color change from prolonged light exposure, especially UV. Bleed resistance is important when a topcoat is applied over a base coat. Some pigments in the base coat may bleed into the applied coat if they are soluble in the topcoat's solvents. Opacity, or hiding power, is a property of particular interest with white pigments such as TiO_2 . It is the pigment's ability in a dried film to obscure any color from the substrate.

A pigment's particle size and refractive index determine its degree of opacity—the smaller the particles, the greater the number of interfaces between the dispersed pigment and binder. This increases light scattering until the particle diameters are about half the wavelength of light, 0.2 to 0.4 μm . With even smaller particles, scattering power diminishes because light simply goes around them. Opacity is also proportional to the difference in refractive index between the binder and pigment. A greater difference results in a higher degree of light scattering and thus greater opacity. Flat paints have greater hiding power than high-gloss paints because they are typically so highly loaded with pigment that the pigment particles partially interface with the air. Because air has a very low refractive index, higher opacity is the result.

Chemical reactivity can also be an important consideration in pigment selection. Some pigments, for example, can react with air pollutants, causing discoloration. Different pigments can even appear to have exactly the same shade of color under indoor lighting but show differences in color in outdoor light. This phenomenon,

called *metamerism*, is caused by differing spectrophotometric absorption characteristics between the pigments.

There are two broad classes of paint pigments, organic and inorganic. In most cases, there will be several organic and inorganic pigments for the same color group.

White Pigments

The primary white pigment in coatings is TiO_2 , which is available with an average particle size close to half the wavelength of light, the optimal for light scattering. It has a relatively high refractive index (2.5 for anatase and 2.7 for the rutile crystallographic form) and is chemically inert. Titanium dioxide is the best general-purpose white pigment for hiding power.

Other white pigments are used, but all have shortcomings compared to TiO_2 . Zinc oxide can be chemically reactive with the binder resin and is not as cost-effective for hiding. Lithopone (barium sulfate/zinc sulfide) is generally too costly for high-volume use. White minerals such as talc and calcium carbonate are not effective compared to TiO_2 mainly because of insufficiently high refractive index.

Black Pigments

Carbon black is the most common black pigment in coatings, although it is one of the most difficult to adequately disperse. Carbon blacks are insoluble in all solvents but do have some affinity for aromatics. They have very high tinting strength and opacity. Three types of carbon blacks are available to the paint industry. Furnace blacks are the most commonly used and provide medium jetness (black intensity). Thermal blacks have larger particle size, are more expensive, and display a lower degree of jetness. Channel blacks provide the highest degree of jetness and are still used in paints even though they must be imported. Black iron oxides are available in a range of jetness and are preferred to carbon blacks in certain applications because of their lower oil absorption and relative ease of dispersion.

Colored Pigments

The inorganic colored pigments are generally less expensive and more widely used than their organic counterparts. The inorganics provide excellent heat stability and lightfastness but are more difficult to keep uniformly suspended because of their relatively high specific gravity. Many of the inorganic pigments are based on lead, chromium, and cadmium, and their use is limited by toxicity concerns. Some representative inorganic pigment types are

- Red (iron oxide): Fe_2O_3
- Yellow (hydrated iron oxide): $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$
- Yellow (lead chromate): PbCrO_4
- Yellow (cadmium sulfide): CdS
- Green (chromium oxide): Cr_2O_3
- Blue (iron blue): $\text{Fe}(\text{NH}_4)\text{Fe}(\text{CN})_6$
- Blue (ultramarine blue): $\text{Na}_6\text{Al}_6\text{Si}_6\text{O}_{24}\text{S}_4$
- Orange (chrome orange): $\text{PbCrO}_4 \cdot \text{PbO}$
- Orange (molybdate orange) $\text{PbCrO}_4 \cdot \text{PbMoO}_4 \cdot \text{PbSO}_4$

A spectrum of hues is obtained through hydration, coprecipitation, and blending of inorganic pigment compounds in various proportions.

Organic pigments are generally purer, brighter, and higher in tinting strength than the inorganics. The chemical nature of some organic pigments, however, makes them sensitive to heat, solvents, or pH extremes. Many organic structures absorb electromagnetic radiation in the UV portion of the spectrum but not in the lower

energy visible portion. Thus the vast majority of organic compounds are clear white powders. To obtain a selective absorption in a portion of the visible spectrum, conjugated organic structures consisting of fused aromatic rings, chromophore groups, or organo-metallic complexes are used. The organic pigments are categorized according to distinct chemical types as monoazo pigments, diazo pigments, phthalocyanine pigments, quinacridone pigments, acid dye pigments, basic dye pigments, and miscellaneous polycyclic pigments.

Metallic and Nacreous Pigments

Metal flake pigments are made from aluminum, stainless steel, and bronze. The most widely used are those of aluminum, made by milling a mineral spirits suspension of finely divided aluminum metal with a steel ball mill. The resulting thin flakes are produced in a variety of particle sizes. Aluminum flakes for coatings are produced as leafing and nonleafing. Leafing flakes are surface treated, usually with stearic acid, to minimize surface tension. This provides flake orientation at the surface of the coating film. The continuous overlapping of aluminum flakes acts as a barrier to oxygen and water vapor while providing a bright metallic appearance. Leafing aluminum flake is used in corrosion-resistant paints for steel structures and in roof coatings to improve weatherability and decrease heat absorption. Nonleafing aluminum flake is not coated and is formulated to be encapsulated within the binder film, but parallel to its surface. It is used most commonly with transparent color pigments in automotive topcoats to provide a metallic color that changes shade with the angle of viewing.

Nacreous (pearlescent) pigments are thin, transparent platelets of high refractive index that partially transmit and partially reflect light. The pearlescent effect results from specular reflection from the broad surfaces of the transparent platelets and the parallel orientation of those platelets at various depths within the binder film. Light transmitted through platelets near the film surface is partially reflected by deeper platelets. The dependence of reflection on viewing angle and the sense of depth created by reflection from many layers produce the pearly luster.

The first pearlescent pigment was derived from fish scales as platy crystals of guanine and hypoxanthine. This remained unrivaled in luster for approximately 300 years, until the refinement of crystallization processes for platy basic lead carbonate in the 1950s. Bismuth oxychloride was developed as a nontoxic alternative to lead carbonate, but the most widely used nacreous pigments in coatings today are the coated micas.

White nacreous pigments are made by forming a uniform coating of TiO_2 on mica platelets. The mica serves as a transparent template so that the high refractive index TiO_2 can assume the required platy shape. Pearlescence is optimized when the pigment optical thickness (platelet thickness \times refractive index) is in the 100-nm (blue white) to 140-nm (yellow white) range. Thicker platelets are produced to make interference colors. Light interference is created by interaction of the reflections from the upper and lower surfaces of the platelet. A reflection maximum occurs at the wavelength of light for which these two reflections are in phase. A reflection minimum occurs at the wavelength for which they are exactly out of phase and cancel each other. A transparent, colorless nacreous pigment platelet acts as a filter, separating light into two components: the reflected color and the complementary transmission color.

When coated on a white surface, the nacreous pigment provides a two-tone metallic effect. The reflected color (specular) is seen as a highlight. The background color at nonspecular angles is created by the diffuse reflection (from the white surface) of the transmission color. The complementary reflection/transmission

colors as a function of pigment optical thickness range in a continuous spectrum from blue-white at 100 nm, to magenta/green at 250 nm, to green/red at 370 nm.

The color effects of nacreous pigments are supplemented by overcoating the TiO_2 -mica platelets with a thin, transparent film of a light-absorbing colorant, for example, iron oxide for yellow, ferric ferrocyanide for blue, chromium oxide for green, and carmine for red. The combination pigments thus produced can have matched reflectance and absorption color, or these can be two different colors. When the colors are the same, the same color is seen at all viewing angles, with metallic highlights provided at specular angles. With different colors, a two-color effect is achieved. Combination interference/absorption pigments are made in the gold-to-red range by coating Fe_2O_3 directly onto mica.

The TiO_2 -coated and Fe_2O_3 -coated micas are used to provide metallic, two-tone, and two-color effects in industrial and automotive coatings. They are widely used in the latter with surface treatments designed to improve dispersability and weatherability.

BINDERS

Binders are the polymeric components in a coating formulation that form the protective film. The binder literally bonds the pigment particles together in the film. If the coating contains no pigments or extenders, then the binder will usually form a glossy transparent or translucent coating.

Drying Oils

Drying oils are vegetable or fish oils and chemically are triglycerides based on a blend of saturated, unsaturated, and polyunsaturated fatty acids. They form flexible films through oxidative cross-links between the polyunsaturated fatty acid groups of different triglyceride molecules. Linseed oil, tung oil, and fish oil are commonly used drying oils. Linseed oil, from flaxseed, was once widely used by the paint industry. More than 50% of its fatty acid component is triunsaturated linolenic acid. The high linolenic acid content tends to cause some yellowing, but in highly pigmented paints this is usually not a problem. Tung oil, from the nut of the tung tree, is 80% eleostearic acid. Because of this acid's conjugated, triple unsaturation, tung oil is faster drying than linseed oil, giving good film hardness and flexibility. Fish oil contains high levels of both reactive and nonreactive acids. It can impart an undesirable odor, and it dries more slowly than linseed oil and gives a softer film because of the plasticizing, saturated, nonreactive fatty acids present. Paints based solely on drying oils have been substantially replaced by alkyds, acrylics, and other synthetic polymers. Drying oils provide a softer film than synthetic binders, have a low gloss, and are used only in highly pigmented paints. These paints have relatively poor durability and chemical resistance, and today they are used in small volumes for limited applications.

Oleoresinous Binders

Oleoresinous binders are used principally in making varnishes. They are produced by "cooking" a resin with a natural drying oil, usually tung or linseed oil. This process dimerizes and oligomerizes the oil and renders the oil and resin mutually compatible and soluble in a thinning solvent. The ratio of oil to resin determines many of the final film properties. A higher ratio of oil to resin gives a slower drying speed, greater softness, increased flexibility, and reduced gloss. With a lower ratio of oil to resin, there is an increase in drying speed, high film hardness, and increased gloss. The ratio of oil to resin is commonly referred to in the varnish industry as oil length, which is defined as the number of gallons of oil to 100 pounds of resin, as follows:

Varnish Type	Oil Length
Short oil	5–15
Medium oil	16–30
Long oil	>30

The resins used in making oleoresinous varnishes include polyterpene resins, petroleum resins, coumaron e-indene resins, gum rosins, wood rosins, tall oil rosins, rosin soaps, rosin ester s, novolac phenolic resins, and rosin-modified phenolic resins. Most oleoresinous varnishes are made from gum, wood, and tall oil rosin esters or soaps and phenolic resins. In clear coatings, oleoresinous binders have been largely replaced by polyurethanes, which have superior hardness, chemical resistance, and water resistance.

Alkyd Resins

Alkyd resins are produced by the reaction of a dibasic acid with a polyol and a fatty acid. A common example of alkyd resin formation is the polycondensation of glycerin, phthalic anhydride, and monocarboxylic fatty acid. The resulting polymer is soluble in aliphatic solvents if the content of fatty acid is sufficiently high. Although fatty acids can be used directly, less expensive vegetable or fish oils are usually used. Many alkyd resins are available because of the wide variety of possible reactants. After glycerin, pentaerythritol is the most commonly used polyol because it improves water resistance, raises viscosity, increases film hardness, and accelerates drying of the alkyd. Because it is tetrafunctional and very reactive, it is commonly used with other polyols such as glycerin or ethylene glycol. Sorbitol, trimethylolpropane, diethylene glycol, and propylene glycol are also used in alkyd synthesis, depending on the particular resin properties desired.

Phthalic anhydride is the most common dibasic acid for producing alkyd resins. Alkyds based on isophthalic and terephthalic acid are often used in exterior coatings where improved hydrolytic stability is required. Maleic anhydride is used with other polybasic acids as a modifier to increase alkyd viscosity and film hardness. Trimellitic anhydride is used in making water-soluble alkyds for specific applications. Soybean oil is commonly used to produce nonyellowing alkyds. When discoloration is less important, linseed oil or tung oil are used for faster drying. Sometimes a nondrying oil such as cottonseed or coconut is used when the alkyd resin is to serve as a plasticizer rather than a film former.

Oil length also affects alkyd properties. The solubility of short oil alkyds is limited to aromatic solvents and other nonaliphatic solvents. They are baked to form a film and are generally restricted to industrial coatings. Long oil alkyds are readily soluble in aliphatic solvents and are air dried. They are easily applied by brush and are used extensively in architectural coatings. Generally, as oil length increases, viscosity decreases, hardness decreases, flexibility increases, and water resistance is reduced.

Alkyd chemistry lends itself to even further modification. Vinyl-modified alkyds, for example, are produced for more durable and quicker drying films, although with some sacrifice in cross-linking rate and consequent development of solvent resistance. Acrylics, silicones, phenolic resins, and natural resins are likewise used to tailor film gloss, flexibility, durability, and drying time for certain applications.

The ability of alkyds to be modified in so many ways accounts for their use in more types of paints than any other binder. Versatility is their primary advantage. A noted disadvantage is the lack of the alkyd film's chemical resistance. Alkyds, being modified polyesters, do not possess high alkali resistance and are subject to attack by hydrolysis. Conventional alkyds are also dependent on the use of organic solvents.

Solvent emissions are minimized with water-reducible alkyds. The simplest approach has been to emulsify the alkyd, although alkyd emulsion paints do not compete with synthetic latex paints in cost or performance. A more effective approach has been to attach carboxylate groups to the alkyd molecule. Such water-reducible alkyds are made by using low-molecular-weight styrene-allyl alcohol polymers as the polyol. These alkyds are maleated by reaction with maleic anhydride and then hydrolyzed to carboxylate salt groups with amine and water. The resulting maleated alkyds form stable aqueous dispersions. After the coating is applied, the volatiles, including a mine, evaporate and the film cross-links by auto-oxidation. The carboxylic acid groups remaining in the cross-linked film, however, generally provide inferior water and alkali resistance compared to the corresponding nonmaleated, solvent-borne alkyd.

Acrylics

Acrylic binders are widely used in both solvent coatings and latex paints for their inherent clarity, color stability, and resistance to yellowing. Of the thermoplastic acrylics, poly(methyl methacrylate) is the largest volume used. Alkyl groups can include methyl, butyl, isobutyl, 2-ethylhexyl, isodecyl, and lauryl. A combination of methacrylates and acrylates is sometimes used to balance film properties. For example, poly(methyl methacrylate) provides film strength and hardness whereas poly(methyl acrylate) improves film flexibility. A plasticizing monomer such as ethyl acrylate or ethylhexyl acrylate is therefore added with the methyl methacrylate monomer by the polymer manufacturer in an addition-polymerization process to produce a copolymer for use in coating formulations. The softer and more flexible polymer facilitates latex film formation.

Thermosetting acrylics incorporate functional carboxyl, hydroxyl, or amide groups. Acrylamide and acrylic acid are often used as functional monomers for this purpose. The thermosetting acrylics are formulated with other reactive resins, such as epoxies, to provide a thermally cross-linked film. These films are considerably harder, tougher, and more chemically resistant than those obtained from thermoplastic acrylics.

Acrylic latex paints dominate the trade sales market for both exterior and interior use because of their balance of film adhesion, durability, flexibility, color stability, alkali resistance, and ability to withstand blistering and chalking. Thermoplastic acrylic solvent-borne paints are used in high-volume applications like automotive finishes, whereas thermoset acrylics are used to bake a hard enamel finish onto large appliances.

Vinyl Resins

In the coatings industry, vinyl resins usually refer to either polyvinyl chloride or polyvinyl acetate (PVAc), which is widely used in interior latex paints. PVAc homopolymer is too hard to allow its colloidal latex particles to coalesce well at ambient temperatures, so most PVAc emulsions used in the paint industry are actually copolymers with a plasticizing monomer such as dibutyl maleate, 2-ethylhexyl acrylate, *n*-butyl acrylate, dibutyl fumarate, isodecyl acrylate, or ethyl acrylate. Copolymers of vinyl acetate and ethylene are also produced for latex paints. External plasticizers are used as well. All of these modifications soften the polymer to facilitate coalescence of the latex particles into a continuous film. PVAc emulsions are less expensive than acrylic emulsions but impart very good color stability and durability. This has enabled PVAc to penetrate a large portion of the interior house paint market.

As a halogenated polymer, polyvinyl chloride is used in specific coatings to provide low moisture permeability films. The major use of polyvinyl chloride, usually as a vinyl acetate copolymer, is in coatings where corrosion protection is a major function. Polyvinyl

chloride copolymers with high vinyl chloride content are used in thermoplastic powder coatings. They are limited in this application by the deficiencies common to thermoplastic binders: they are difficult to pulverize to small particle size, their high molecular weight gives high-melt viscosity and consequent poor flow and leveling, and they are restricted to applications that can accommodate a relatively thick coating.

Styrene-Butadiene Binders

Homopolymers of styrene are too hard to form a continuous film from a latex, but a plasticizing monomer can be copolymerized to produce a softer polymer. A ratio of two parts styrene to one part butadiene is commonly used to produce the styrene-butadiene latexes used in coatings. This is nearly the inverse ratio used to produce styrene-butadiene rubber (SBR). Styrene-butadiene latexes were the first practical latexes to be used in interior architectural applications in the 1950s, but they are not commonly used today. One advantage of styrene-butadiene emulsion paints is superior alkali and chemical resistance, which is greater than either PVAc or acrylic emulsion paints. A major disadvantage is the susceptibility to oxidation because of the unsaturation in the butadiene units of the polymer backbone. This oxidation leads to yellowing and ultimately film embrittlement.

Polyurethane Resins

Many solvent-borne finishes are based on polyurethane resins because they are characteristic ally tough yet flexible, and very resistant to abrasion. They also impart good film adhesion and can be made to harden at ambient temperatures. In the coating industry, any polymer containing the urethane linkage in the backbone, even if that same polymer may also contain many other linkages, is called a polyurethane. Generally, the polyurethane resins involve the reaction of a diisocyanate with a hydroxyl compound. Polyurethane coatings are used as a single-pack system or a two-pack system. There are three basic types of single-pack systems and two of the two-pack systems. More recently, waterborne urethanes have been developed to reduce solvent emissions.

Oil Modified

Oil-modified finishes are based on a polyurethane-modified alkyd. These are also called polyurethane-alkyds or simply uralkyds, and are prepared in a manner similar to alkyds, with a diisocyanate, usually toluene diisocyanate (TDI), replacing the polycarboxylic acid. Thus, the reaction product possesses urethane linkages instead of the ester linkages associated with traditional alkyds. The percent isocyanate, or conversely oil length, determines the properties of the resulting film. Higher isocyanate content (shorter oil length) reduces film flexibility and impact resistance, increases film hardness and solvent resistance, and reduces drying time. In certain commercial coatings, some of the isocyanate is replaced by phthalic anhydride to make phthalic-modified uralkyd. Uralkyds are cured through oxidative drying in the same manner as regular alkyds. Metallic driers can likewise be used to accelerate drying. Uralkyds are one of the most commonly used polyurethane resins, finding particular application in varnishes for floors, boats, and general use. Although these resins do not impart the best gloss, they do give excellent abrasion resistance and generally better water and alkali resistance than an alkyd.

Moisture-Curing Prepolymers

Moisture-curing prepolymers are single-pack polyurethane systems that cure from exposure to atmospheric moisture. Initially a diisocyanate such as TDI is reacted with a high-molecular-weight polyol

such as castor oil. The TDI reacts with a minimum of three hydroxyl groups per molecule to produce a trifunctional prepolymer. After application, the prepolymer is cured into a hard film from exposure to moisture in the air. Two isocyanate groups, in the presence of water, bond to form a urea. Cure rate is greatly dependent on relative humidity, and care must be taken that all pigments and mineral additives are free of moisture to avoid reaction before use. This system results in a tough film and is commonly used in floor coatings.

Blocked Isocyanates

In the blocked isocyanate system, polyol is reacted with a diisocyanate such as TDI to form a structure with isocyanate adducts. These adducts are then reacted with a blocking agent, usually phenol. The bond between the phenol and isocyanate is stable up to 150°C, so no reaction will take place while the coating is stored. After the coating is applied, it is baked, causing the phenol to split off and allowing the resin to cross-link.

Catalyzed Moisture Cures

Catalyzed moisture cure is a two-component system that is the same as the one-package moisture cure system except that a tertiary amine catalyst such as *N,N*-dimethylethanolamine is added just before application. This shortens cure time and increases the cross-link density of the film for better chemical resistance. As soon as the catalyst is added, there is limited pot life before gelation occurs.

Two-Pack Systems

In two-pack systems, one package contains a low volatility isocyanate, usually a polyisocyanurate (a polymerized TDI), and the other consists of the polyol component, which may be either a polyether or saturated polyester resin. The distance between the hydroxyl groups on the polyol relates to resultant film flexibility and hardness. If film flexibility for greater exterior durability is required, sufficient space between these hydroxyl groups is needed. If a high cross-link density is required for greater film hardness, the distance between these reactive hydroxyl groups is less. When the two packages are mixed, the isocyanate functional groups react with the polyol hydroxyls. It is also possible for atmospheric moisture to enter into the reaction, resulting in urea cross-links. Two-pack systems have a short drying time and are often used for coating floors, furniture, boats, metals, and concrete.

Water-Reducible Urethanes

One approach to incorporating polyurethane coating attributes into aqueous vehicles has been to prepare a hydroxyl-terminated polyurethane with 2,2-dimethylolpropionic acid as one of the diols. The carboxylic acid group is sufficiently sterically hindered to minimize amide formation, so that a polyurethane is formed with pendant acid groups. These are neutralized with amine and diluted with water to form a stable polyurethane dispersion. In use they are cross-linked with methylated monomeric melamine-formaldehyde (MF) resins. Another approach is to first prepare an isocyanate-terminated polyurethane in acetone. This is the ncha in-extended with a sulfonate-substituted diamine. The acetone solution is diluted with water, and then the acetone is removed by distillation, leaving an aqueous polyurethane dispersion stabilized by charge repulsion of sulfonate groups.

Epoxy Resins

The coatings industry uses approximately half of all the epoxy resins produced in the United States. Although epoxy coatings provide superior chemical resistance, high film adhesion strength, and tough

but flexible films, they are relatively expensive and slow to harden, with relatively poor gloss retention and UV resistance. The coatings industry has used many different types of epoxy resins. The most common are those produced from the reaction of bisphenol-A with epichlorohydrin. These are used in two-pack systems with amines, polyamines, polyamides, or acid anhydrides. Amine combines with an epoxy group in a ring-opening reaction, so the reaction of a trifunctional amine and diepoxide results in a three-dimensional cross-linked matrix. This forms the basis of industrial maintenance coatings and marine coatings, among others, with exceptional resistance to solvent and chemical attack.

Solvent and chemical resistance is even further improved by blending the epoxy with a phenolic resin and baking the coating. At elevated temperatures, the phenolic resin and epoxy groups react through a ring-opening mechanism. The secondary hydroxyl groups react further to form a tight, cross-linked network that imparts optimum solvent and chemical resistance. Flexibility of the film is reduced, however, compared to other epoxies, and discoloration can be a problem. If a lighter color is needed, urea-formaldehyde resins are reacted with the epoxy with little loss in chemical and solvent resistance.

Epoxy resin esters are formed by reacting an epoxy resin with fatty acids from drying oils. The fatty acids react with both the epoxide and hydroxyl groups of the epoxy resin to form the epoxy ester. Epoxy resin esters are less expensive than other epoxies because they are partially composed of lower cost fatty acid. They also have superior flexibility, but poorer solvent and chemical resistance, although generally better chemical and alkali resistance and better adhesion than conventional alkyds. As with alkyds, they are usually cured by auto-oxidative air drying with the aid of metallic driers. These resins are used in industrial and maintenance paints, automotive primers, and varnishes.

Amino Resins

Amino resins are rarely used as the sole binder in coatings because they form hard, brittle films with only fair adhesion. They are, however, the predominant cross-linking agents for thermosetting coatings. MF resins are most commonly used for these applications. Amino resins are prepared, in general, by reacting precursor and formaldehyde under alkaline conditions to form methylol groups. Alcohols are then reacted under acid conditions to yield ethers.

MF resins are most often used to cross-link resins having hydroxyl functionality such as alkyds, thermoset acrylics, hydroxy-terminated polyesters, and bisphenol-A epoxy resins. Cross-linking is through transesterification using an acid catalyst. MF resins will also cross-link carboxylic acid functional resins through esterification, although the reaction rate is slower than with hydroxyl groups. This is significant in the formation of water-based coatings based on hydroxy-functional binders that have been modified with carboxylic acid groups to improve dispersibility. The curing system for these binders is chosen to ensure a high degree of esterification, so that residual carboxylic acid groups do not increase the water sensitivity of the cured film. MF resins are also increasingly used with binders having both hydroxyl and urethane functionality.

Amino resin analogues to the MF types are produced from glycoluril, acrylamide, and methacrylamide, which provides greater film flexibility, and benzoguanamine, which provides greater alkali resistance, but the next most widely used are urea-formaldehyde (UF) resins. UF resins are generally the least expensive of the amino resins. They are also the most reactive. Coatings with UF resins can therefore be formulated for ambient or low-heat cures, but the

resulting films have relatively poor hydrolytic stability. Although the other amino resins are used in metal coatings, UF resins are used in coatings for temperature-sensitive substrates such as wood finishes, where corrosion resistance is unimportant.

Cellulosic Binders

The solvent-soluble cellulose esters, nitrocellulose and cellulose acetobutyrate, are used in coatings. Nitrocellulose is made by reacting cellulose with nitric acid. Cellulose hydrolysis and consequent molecular-weight reduction are a function of the small amounts of water present during the reaction. Greater hydrolysis results in lower molecular weight, lower solution viscosity, and lower film strength. The degree of nitration determines solvent compatibility. Polymers containing approximately 11% nitrogen are alcohol soluble and used in flexographic printing inks. Coatings grades contain about 12% nitrogen and are soluble in esters and ketones and in mixtures of esters and ketones with alcohols and hydrocarbons. Explosive grades contain about 13% nitrogen. Nitrocellulose lacquers provide thermoplastic films with high gloss and easy repairability but low durability. They were used for automotive finishes before acrylic lacquers were developed but today are used in wood finishing. The principal use of cellulose acetobutyrate has been as a component of acrylic-based metallic automotive finishes. The cellulosic component contributes to flow control and the orientation of aluminum flake pigment parallel to the film surface for maximum metallic effect.

SOLVENTS

Coatings solvents can be classified by function as active, latent, or diluent. An active solvent dissolves the binder. A latent solvent does not itself dissolve the binder but acts as a cosolvent when used with an active solvent. A diluent solvent has no solvency for the resin but is used to dilute the active solvent without precipitating the binder. Diluent solvents are used to reduce coating viscosity and cost. For each coating, solvent selection is guided by the required balance of solvency and evaporation rate. The solvent or solvent blend must keep the binder in solution throughout the drying process to optimize subsequent film properties. The evaporation rate must be appropriate for the application method, spraying versus brushing, for example; it must be initially relatively quick to avoid sag and then more controlled to allow proper leveling and adhesion. Coatings solvents are also classified according to chemical nature as hydrocarbons, oxygenated solvents, and "other," which are usually hydrocarbon derivatives.

Hydrocarbon Solvents

Hydrocarbons are the most widely used solvents and are typically subdivided as principally aliphatic, naphthenic, or aromatic. The most commonly used of these are aliphatic solvents, containing mainly iso- and normal paraffins. Some aliphatics contain naphthenes (cycloparaffins) and aromatics, which improve solvation power but increase odor. Mineral spirits is the primary aliphatic solvent, with several grades available based on evaporation rate and solvency. Low-odor grades contain mostly isoparaffins, although a lack of naphthenes and aromatics reduces solvency with many resins. Mineral spirits are widely used in architectural paints because their balance of moderate solvency and moderately slow evaporation impart good brushability, leveling, and wet edge. Varnish maker's and painter's (VM&P) naphthas are similar in solvency but evaporate much more quickly. They are used primarily in sprayed coatings.

The aromatic solvents provide stronger solvency but greater odor. The most common are toluene, mixed isomer xylenes, and

two high-flash-point aromatic naphthas. The fast-evaporating toluene is used in spray paints and industrial coatings. The mixed xylenes, with moderate evaporation rate, are used in industrial coatings, whereas the slow-evaporating aromatic naphthas are used in baked finishes.

Terpenes, unsaturated cyclic hydrocarbons from pine trees, represent the historically oldest coating solvents, although they are infrequently used today. Turpentine is the most common terpene solvent, although dipentene, with stronger solvency and slower evaporation, is also used. Turpentine offers greater solvency, although in a narrower range, faster evaporation rate, greater odor, and higher cost than mineral spirits, which has widely replaced it.

Oxygenated Solvents

The principal oxygenated solvents for coatings are ketones, esters, glycol ethers, and alcohols. These are high-purity synthetic compounds that provide much stronger solvency than hydrocarbon solvents and partial to complete water miscibility. They are widely used as active solvents for synthetic binders because they can be blended to provide tailored solvency and evaporation rate.

The ketones are characterized by their strong odor and range of evaporation rate and water solubility. The very volatile acetone is used in sprayed coatings, particularly nitrocellulose and acrylic lacquers, to reduce viscosity and then flash off during application. The fast-evaporating methylethylketone and moderately evaporating methylisobutylketone are widely used as active solvents in paints and lacquers based on synthetic binders, whereas the very slow evaporating isophorone is used in baked industrial coatings.

The esters provide solvency nearly equal that of ketones but with a more pleasant odor. The most common are the alkyl acetates, ranging from the very rapidly evaporating methyl acetate to the slowly evaporating hexyl acetate. One of the most widely used ester solvents, *n*-butyl acetate, has a medium evaporation rate and is used as a standard reference for expressing the evaporation rate of other solvents. In comparison to its assigned evaporation rate of 100, acetone has an evaporation rate of 1,160 and regular mineral spirits has an evaporation rate of 10. Glycol ether acetates are relatively slow to evaporate and are used as coalescents in latex paints and retarder solvents in solvent coatings. In the latter capacity, they maintain flow and leveling after the other solvents have evaporated.

Glycol ethers provide both alcohol and ether functionality and are characterized by mild odor, water miscibility, strong solvency, and slow evaporation. Ethylene glycol ethers have been widely used in water-based coatings as coupling solvents for water-reducible binders, and at low levels in lacquers as retarder solvents. More recently, propylene glycol ethers have replaced ethylene glycol ethers in many applications because of health and safety considerations.

Alcohols are used at low levels in waterborne paints as coupling solvents with glycol ethers and in certain solvent coatings as latent solvents. Denatured ethanol and *n*-butanol are the most commonly used, with the former also serving as an active solvent for shellac, PVAc, and several phenolics.

Organic carbonates and furan derivatives are specialty oxygenated solvents. Ethylene carbonate and propylene carbonate are cyclic esters with good solvency, very slow evaporation, and very low odor. Tetrahydrofuran, furfuryl alcohol, and tetrahydrofurfuryl alcohol are cyclic ethers with particularly strong solvency for vinyl polymers and certain other synthetic binders.

Other Solvents

N-methyl-2-pyrrolidone is a specialty solvent used in waterborne paints. It offers strong solvency, water solubility, biodegradability,

slow evaporation, and low toxicity. 1,1,1-trichloroethane is used as a fast-evaporating solvent in some spray coatings because it is not photochemically reactive and is thus not included in volatile organic compound (VOC) content, although health and environmental concerns over chlorinated solvents have restricted its use. Supercritical carbon dioxide is used as a diluent solvent in airless spray coating operations because of its high solubility in most formulations, low toxicity, low cost, viscosity-reducing effect, and behavior on application as a highly volatile solvent.

ADDITIVES

The chemical and mineral additives are typically used at less than 5% by weight, usually much less, to optimize coatings properties before, during, and after cure. Even with their relatively low concentration, they have a considerable effect on paint properties.

Dispersants and Surfactants

The dispersants commonly used in waterborne coatings include potassium tripolyphosphate, and sodium or ammonium salts of lignosulfonates, polynaphthalene sulfonates, and relatively short chain polyacrylates and polymethacrylates. These chemicals have little effect on surface tension or interfacial tension but align themselves so that their organic groups loosely attach to and coat the pigment and mineral surfaces, leaving their charged groups protruding into the water. This charged film renders the particles mutually repulsive, which retards settling and minimizes the viscosity contribution of particle-particle associations. Dispersants are therefore used to improve suspension stability and enable the inclusion of more pigment and extender without compromising rheological properties.

Surfactants reduce surface tension so that the liquid vehicle can effectively wet the pigment and extender surfaces. This is a particular requirement for hydrophobic solids such as talc. Surfactants also facilitate the application of coatings by allowing the paint to better wet and spread on the substrate. Anionic surfactants are typically sodium salts of alkyl sulfates, alkyl sulfonates, alkylaryl sulfonates, and sulfosuccinates. They often serve simultaneously as dispersants, although it is not uncommon for a paint to contain both surfactants and dispersants for optimum effect. Nonionic surfactants such as nonylphenol ethoxylates contain a pigment/mineral compatible group, a long chain alkyl or alkylaryl group, and a hydrophilic group such as polyethylene oxide. The long chains bond loosely to the pigment and extender surfaces, creating a film of hydrophilic groups that ensures wetting by the aqueous vehicle. Nonionic surfactants can also provide a dispersant effect by providing steric hindrance to particle flocculation.

Dispersion aids for solvent-borne paints function primarily as wetting agents and are typically nonionic. They contain an anchor group, selected for its affinity to the particulates in the paint formulation, and a polymeric or high-molecular-weight group selected for its compatibility with the binder and solvent.

The surfactants used to stabilize binder lattices in latex paints are properly considered emulsifying agents, with an organophilic component that is at least partially soluble in the binder droplets and a hydrophilic component that allows the droplet to be wet by the aqueous vehicle. Emulsifying agents can be either anionic or nonionic and inhibit droplet coalescence by charge repulsion or steric hindrance.

Rheology Modifiers

Adjusting paint rheology for optimal in-can stability and application properties requires the use of thickeners, thixotropes, and rheology modifiers of various types. Liquid paints for brush, roller, or

spray application are pseudoplastic (shear-thinning). Paint viscosity decreases as the shearing rate increases. Undisturbed in the can, high viscosity inhibits settling and flocculation of pigments and minerals. The shear caused by brushing or spraying reduces the viscosity so that a thin film is easily applied. Once on the substrate, the paint rethickens so that sagging is avoided. Pseudoplasticity, however, implies an immediate recovery of viscosity after shearing stops. This is not always desirable because rapid viscosity recovery impedes leveling and retains brush marks, roller marks, or orange peel. The proper balance of antisag and good leveling is usually attained by using cellulosic thickeners and mineral thixotropes, which impart the desired degree of thixotropy to the paint. A thixotropic paint is shear-thinning, for easy application and good coverage; but after shear is removed, viscosity recovers over a short period of time. When properly formulated, this provides just enough time for the paint film to level while developing enough viscosity to prevent sagging.

Roller application involves an additional consideration—control of spattering. At the point of contact between roller and substrate, the paint is under pressure. As the roller moves, the pressure is released and small bubbles are formed between the substrate and the receding roller edge. As the roller continues, the bubbles expand and their walls are stretched from roller to substrate until they resemble fibers. These paint “fibers” are eventually stretched to their breaking point. Ideally, part of the fiber retracts into the substrate coating and the rest onto the roller. In reality, the fiber generally breaks in two places, releasing free paint droplets that fly off as spatter.

Spattering is a particular problem with latex paints that contain conventional water-soluble, high-molecular-weight thickeners. Paint fibers stretching between roller and substrate experience elongation flow rather than shear flow. The corresponding elongation viscosity arises from the stretching and aligning of the thickener polymer chains. The long-chain, high-viscosity polymers impart the high elongation viscosity that promotes spatter. Spattering is minimized by the use of low-molecular-weight (short-chain) grades of these thickeners, but at the expense of shear viscosity.

Adequate low-shear viscosity is required to promote product uniformity. High-shear viscosity is an important factor with regard to spreading rate and hiding. The most widely used conventional thickeners are very shear-thinning, so that very thin paint films can be applied. If the applied film is too thin, however, the dried film will give poor hiding. One-coat paints require a relatively elevated high-shear viscosity so that an optimally thick wet paint film is applied. In paints using conventional polymeric thickeners, a balance among viscosity, wet film build, spatter resistance, sag resistance, and leveling is often achieved by using intermediate viscosity polymers and mineral thixotropes.

Conventional Thickeners

The most commonly used thickeners in waterborne coatings are the naturally derived nonionic celluloses. Medium- and high-viscosity hydroxyethylcelluloses dominate this group. Hydroxypropylmethylcellulose is the only other cellulosic with significant use in coatings. The only conventional synthetic thickeners used in substantial amounts in water-based coatings are the acrylic alkali-soluble emulsions (ASEs). These are supplied in liquid form as low-viscosity, water-insoluble latexes at low pH. In use they are neutralized with ammonia or a volatile aminoalcohol to provide thickening. Some are lightly cross-linked with a small amount (<1%) of a polyfunctional monomer to enhance viscosity. The ASEs are similar to the celluloses in rheology, but are more bioreistant and somewhat more water-sensitive.

Mineral Thixotropes

Smectite and hormite clays provide thixotropic aqueous dispersions and impart a controlled degree of thixotropy to paints thickened with the conventional polymers. The most widely used mineral thixotrope in aqueous coatings is the hormite clay palygorskite, which is better known as attapulgite. The micronized attapulgite used in paint is composed of low aspect ratio needles that deagglomerate in water in proportion to the amount of shear applied. When shear is removed, these needles form a loosely cohesive random colloidal lattice that provides suspension and emulsion stabilization. With shear cycling, it is shear-thinning and thixotropic. Because attapulgite deagglomeration is mechanically rather than ionically driven, as for smectite clays, it is insensitive to most solutes and can be added at any point in paint manufacture. Concentrated, predispersed aqueous suspensions of attapulgite are available because optimum deagglomeration and dispersion is energy intensive.

Hydroclassified natural smectite clays and synthetic smectites are used instead of attapulgite in coatings where finer adjustment of rheological properties is required. The hydration and dispersion of a smectite clay into individual colloidal platelets is driven by shear and osmotic swelling. Once separated, the absence of shear allows these platelets to form a more uniform and cohesive structure than that of attapulgite through ionic attraction of slightly positive platelet edges to negatively charged platelet faces. Solute present during hydration can inhibit osmotic swelling, but solutes introduced after hydration can improve the cohesion of the colloidal structure. Despite this relative lack of processing versatility compared to attapulgite, the smectites are used for their higher efficiency and the controllable synergism they provide with polymeric thickeners.

Precipitated silicas find some use as thixotropes in water-based coatings. The functional particles are clusters of strongly agglomerated, primary, amorphous silica particles. Dispersed in a liquid, these clusters are chained together by weak hydrogen bonds into three-dimensional networks. In highly polar liquids, bridging additives ensure this network structure; in aqueous coatings, certain nonionic surfactants serve this function. Silica gels and fumed silicas are used in water-based coatings for flattening rather than rheology control.

Associative Thickeners

Associative thickeners are relatively low-molecular-weight, water-soluble polymers with hydrophobic groups capping polymer and pendant chain ends. These thickeners provide little or no conventional thickening. They instead form a network based on hydrophobe-hydrophobe affinity. Hydrophobe groups associate among the polymer chains, and they adsorb onto hydrophobic surfaces in the dispersed phases of the paint. These surfaces are primarily those of the latex binder but can include hydrophobic pigments and extenders such as talc.

Associative thickeners generally provide solution rheology that is less pseudoplastic than conventional thickeners. This allows greater high-shear viscosity on paint application for optimal film build and hiding, and lower low-shear viscosity for good leveling. Associative thickeners also generally impart lower elongation viscosity, and are therefore preferred for spatter resistance. Hydrophobically modified celluloses, the first commercial associative thickeners, are relatively low-molecular-weight grades of hydroxyethylcellulose and ethylhydroxyethylcellulose modified through backbone hydroxyl groups. Hydrophobe substituents are one or two ethylene oxide units terminated with an alkyl or alkylaryl group. The hydrophobe modification makes these celluloses less pseudoplastic for better film build and leveling.

Among the first acrylic associative thickeners were hydrophobically modified analogues of the ASEs. These are lower in molecular weight than the conventional ASE thickeners, but on neutralization they do provide some viscosity. Subsequently developed ASE-based thickeners have as associative side chains polyethylene oxide segments joined by urethane linkages, with terminal hydrophobe groups. These side chains mimic the structure of the most popular class of associative thickeners, the hydrophobically modified ethoxylate urethane polymers (HEURs).

The HEURs have a backbone and side chains composed of urethane-linked polyethylene oxide segments, terminated at all ends with hydrophobe groups. These products impart the least pseudoplastic rheology and generally provide the best flow, leveling, film build, and spatter resistance. Their use as the sole rheology modifier, however, comes at the expense of sag resistance, suspending ability, and thickening efficiency. The HEURs are pourable aqueous solutions with an organic cosolvent added to suppress viscosity and ensure flowability. In products analogous to the HEUR structure, the polyether segments include ethylene oxide-propylene oxide block copolymer in place of polyethylene oxide, and amide or ether linkages instead of urethane.

Solvent Thickeners

Hydrogenated castor oil is used as a thixotropic thickener in paints based on nonpolar aliphatic solvents. Hydroxyl groups on the fatty acid chains of the castor oil triglyceride form a colloidal network through hydrogen bonds. Polyamide-alkyd resins function as thixotropic thickeners in nonpolar solvents through polar attraction among functional groups.

Precipitated and fumed silicas thicken solvent-borne paints and are most efficient in nonpolar systems. Both can be used in polar solvents, although higher levels are generally required, with fumed silica providing somewhat better efficiency. Organoclays, purified smectite clays that have been cation-exchanged with quaternary ammonium salts, are widely used in solvent-borne coatings. Several grades are available for aromatic or polar solvents and nonpolar solvents, depending on the organic treatment. The conventional organoclays require a polar activator such as methanol or propylene carbonate to facilitate delamination and the formation of a thixotropic colloidal structure through hydrogen bonding. Self-dispersing grades are modified to eliminate the need for a polar activator.

Driers

Paint driers are catalysts for the oxidation and polymerization reactions that provide binder film formation after application. Most driers are soaps of transition metals, providing catalytic activity based on the ability of the metal cation to be oxidized from a stable lower valency to a less-stable higher valency. The organic acids used to form these soaps provide compatibility in solvent-borne paints and enable emulsification into waterborne systems. The earliest driers were linolates, rosinsates, and tallates. These have been mostly replaced by naphthenates and particularly 2-ethylhexanoates. Neodecanoates and so-called synthetic acid (similar to 2-ethylhexanoate) soaps are favored for their higher metal concentration.

Primary driers directly promote oxidative film curing. They catalyze oxygen absorption into the film and accelerate the decomposition of the peroxides that are formed into free radicals that propagate the cross-linking mechanism. The most widely used primary driers are based on cobalt and manganese, and cobalt driers are by far the most reactive. They are surface driers in that they quickly dry the outermost layer of the paint film, preventing further drying—"through drying"—beneath. Cobalt used alone can

consequently result in film wrinkling. Zirconium soaps are used with cobalt driers to retard surface drying, accelerate through drying, and provide harder cured films. Manganese driers are slower than cobalt and provide some through drying, although they are, like cobalt, usually used with secondary driers to properly balance drying properties.

Lead driers used to be the most common secondary drier, their sole function being to catalyze oxygen uptake. This and their relatively low reactivity made them good through driers. Lead toxicity and atmospheric sulfide staining have now all but eliminated their use. Zirconium driers have generally replaced lead; they are not discoloring and are not considered toxic. Aluminum driers are also used in place of lead, but the substitution is not straightforward. The paint must be formulated specifically to promote their activity. Iron driers are used in heat-cured paints where their poor color can be accommodated. Temperatures greater than 100°C are required for catalytic activity, but high film hardness is obtained.

Nonmetallic drier accelerators are commonly used to improve the efficiency of primary driers and to maintain catalytic activity during in-can aging. Metallic soap driers, especially those with cobalt, typically lose some activity between the time of manufacture and use, primarily through pigment adsorption. The heterocyclic compounds 1,10-phenanthroline and 2,2'-diipyridyl form complexes with cobalt and manganese through their nitrogens, acting in effect as chelating agents. The metal-organic complex protects the metal against deactivation through adsorption during storage and modifies the metal's catalytic activity such that through drying is enabled. Proprietary metallic driers are available as another means of preventing the loss of efficiency of cobalt and manganese soaps during paint storage. These "feeder" driers dissolve gradually into the paint vehicle to replace drier metals lost through adsorption.

Coalescing Agents

The dispersed polymer particles in a latex paint must coalesce after application to form a continuous film at room temperature or below. Hard and high glass transition temperature (T_g) polymers must be temporarily plasticized to enable film formation. Coalescing agents serve this function by softening the resin particles and lowering their minimum film formation temperature, but slowly volatilizing after application to allow the polymer film to attain final hardness. Slow-evaporating ester-alcohol solvent is the most common coalescing agent because it efficiently lowers the minimum film-forming temperature of a wide variety of resins, has good hydrolytic stability, and is insoluble in water. The latter is important in preserving coalescent efficiency by preventing loss of solvent from the polymer phase to the aqueous medium. Low-volatility glycol ether ester and glycol ether solvents are also used as coalescing agents.

Plasticizers

Plasticizers are used primarily to improve the flexibility and toughness of the final coating film. They are used more often in industrial, appliance, and automotive coatings than in architectural paints. Plasticizers form strong polar associations with polymer molecules, but because there is no chemical bond, they can be lost through extraction or volatility. Plasticizers are therefore typically very low volatility, water-insoluble liquids that are selected based on compatibility with the resin. The major coatings plasticizers are the phthalic, trimellitic, or adipic acid esters of 2-ethylhexanol or isononanol. The single most commonly used plasticizer is dioctyl (i.e., ethylhexyl) phthalate. The response of dry film properties to plasticizer addition level is not necessarily linear, so in most cases optimal concentration must be determined. In general, increasing the concentration of

plasticizer increases film elongation and permeability and decreases tensile strength. Film toughness and adhesion, however, increase to a maximum and then decrease.

Biocides

Biocides are used in both solvent and aqueous coatings as fungicides and algicides to keep the dried paint film free of discoloring mildew and algae. Biocides are used in waterborne paints as preservatives as well. Here they prevent the bacterial growth that can result in off-gassing in the can, and the enzymatic degradation of cellulosic thickeners that can result in loss of viscosity. Paint biocides are preferably colorless, free of objectionable odors, nonyellowing in the paint film, of low toxicity, environmentally acceptable, and cost-effective. Few, if any, of those in common use today meet all these criteria. Certain biocides are used exclusively as in-can preservatives, others as in-film fungicides, and yet others can serve both purposes. In the last case, the spectrum of biocidal activity is usually related to concentration and solubility. Some biocides, for example, are effective against bacteria at one concentration and effective against fungi at a much higher concentration. Preservatives are usually water-soluble for best effect, whereas in-film fungicides need to have very low water solubility to resist leaching.

In the past, organomercury compounds were the most widely used paint biocides, functioning at very low concentrations as both preservatives and film fungicides. Because of their high toxicity, they have been replaced in most cases by the less toxic but also less cost-effective organotin compounds, particularly tributyltin oxide and zinc oxide. Toxicity and environmental concerns have more recently restricted the use of these tin compounds as well. As the trend in favor of aqueous products continues, the variety of available preservatives has kept pace. These can be generically described as nitrogen or sulfur-containing organic biocides. Many of these are formaldehyde releasers, which largely accounts for their effectiveness but in some cases limits their use.

Broad-spectrum biocides are generally preferred for waterborne paints, but environmental, toxicity, and cost considerations often necessitate tailoring of the biocide system for maximum effectiveness at minimum use levels. This involves identifying the particular types of microorganisms requiring control in both the manufacturing and end-use environments. To avoid development of resistance to a biocide in the manufacturing environment, it is not uncommon for producers to periodically alternate between preservative systems with different biocidal mechanisms.

Antifoams

The surfactants and thickeners used to stabilize water-based paints also stabilize air bubbles entrapped during manufacture or application. Even so, solvent-borne coatings develop bubbles under shear. Bubbles that remain in the applied coating result in cratering in the dried film. Vehicle-insoluble liquids—silicone oils, alkyl (C_6 – C_{10}) alcohols, and mineral oils—are used to destabilize the air bubbles so that they break. In aqueous systems, silicone/amorphous silica combinations are often used. Because antifoams can be emulsified and lose effectiveness on prolonged paint processing, they are sometimes added twice during manufacture—a silicone antifoam during pigment dispersion to prevent air entrapment and a nonsilicone antifoam in the letdown to ensure performance during use.

Glycol

A slow-evaporating glycol is added to latex paints to serve as both antifreeze and humectant. Ethylene glycol is most commonly used, followed by propylene glycol. As water freezes, its volume

expansion can push the latex particles together with sufficient force to cause coagulation. Glycol depresses the freezing point, but even those paints that become cold enough to freeze tend to freeze to a slush that exerts less force on the latex particles. As a humectant, the glycol controls evaporation from the paint film to facilitate wet lapping. When paint is applied by roller or brush, each brushful or rollerful of paint overlaps the wet edge of the preceding area of coverage. Without glycol, evaporation can quickly render the previously applied film edge very viscous, although very weak because of limited latex coalescence. The brush or roller shear from the subsequent application can break up this film, leaving irregularities along the lapped edge.

Antiskinning Agents

The driers used in air-drying paints can also cause oxidative cross-linking at the surface of the paint in its container. This is prevented by adding a small amount of volatile antioxidant such as methylethylketoxime or butyraldoxime. Volatility and use level (<0.2%) are selected so as not to interfere with the drying of the applied paint film, although they may not be adequate to prevent the formation of a skin in a container of paint that has been opened, partially used, and resealed for storage.

Corrosion Inhibitors

Corrosion of metallic surfaces requires moisture, ions, and oxygen. Corrosion inhibitors are most often added to paints to prevent rusting of ferrous metals. Rusting is an oxidative process that occurs through an electrochemical mechanism. For example, a drop of water on steel, which is in effect a conductive electrolyte solution from ambient salts, will create an electrolytic cell. Electrons will flow from the anode at the center of the drop to the cathode at the edge. At the anode, iron is oxidized to Fe^{2+} , and at the cathode, oxygen is reduced to OH^- . The cationic iron migrating toward the cathode and the anionic hydroxyl migrating toward the anode form soluble ferrous hydroxide, $\text{Fe}(\text{OH})_2$. If sufficient oxygen is available, this is oxidized to the insoluble hydrated ferric oxide (rust), $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

Coatings can inhibit rusting in proportion to their impermeability to water, oxygen, and electrolyte. Solvent-based coatings provide generally less permeable polymer films than water-based coatings, but none is impermeable. Lamellar metals and minerals are used in coatings to reduce film permeability by physically inhibiting diffusion through the film. Platy minerals such as talc and mica are used for this purpose, although micaceous iron oxide (MIO) and aluminum flake are more widely employed.

Primers containing high levels of zinc dust are used to protect steel by a sacrificial cathodic mechanism. The less noble zinc acts as the electrochemical anode and corrodes instead of the steel substrate. The concentration of zinc powder in the dry primer film must be sufficiently high to allow the particles to make contact and allow an electrical current to be established between these particles and the steel.

Certain inorganic compounds, usually as their zinc salt, are used in paints as passivators to control rust formation. These inhibitors are slightly soluble in water and are slowly dissolved from the paint film through moisture permeability. The ions formed are carried to the film-metal interface by moisture diffusion. There they cause the corrosion electrical potential to be elevated to the passive potential at which the corrosion rate is dramatically reduced by polarization at the anode. Chromates have been the most widely used passivating inhibitors in coatings, although toxicity and carcinogenicity concerns have prompted their replacement by molybdates (zinc and calcium zinc) and zinc phosphate in certain cases. Alkaline

extenders such as wollastonite are used as synergists with passivators in some applications, providing a beneficial pH buffering effect.

Flash Rust Inhibitors

When water-based paints are applied over exposed ferrous metal, the drying film may develop a scatter of light brown spots. This "flash" rusting is prevented with alkaline inhibitors such as sodium nitrite, sodium benzoate, or 2-amino-2-methylpropan-1-ol (AMP). Basic alkaline earth alkylaryl sulfonates are used as both flash rust and corrosion inhibitors. Alkaline minerals, wollastonite in particular, are also used to prevent flash rusting.

Photostabilizers

Many paints are prone to fading and film degradation from exposure to sunlight, particularly UV light. UV absorbers are used to reduce UV absorption by the binder polymer and the resultant photoinitiated oxidative degradation. UV absorbers for exterior coatings ideally have high absorption at 280 nm through 380 nm, with no absorption above 380 nm to avoid color effects. The UV absorber should also be nonvolatile and soluble in the coating film. Hydroxybenzophenones, hydroxybenzotriazoles, and hydroxyphenyltriazines are commonly used, with the last generally providing the lowest volatility and best permanence. Optimum photostability, for example, in clear automotive topcoats, is obtained with synergistic combinations of UV absorbers and hindered amine light stabilizers (HALS) based on 2,2,6,6-tetramethylpiperidine. The UV absorber reduces the rate of generation of free radicals, and the light stabilizer reduces the rate of oxidative degradation by free radicals.

TYPES OF COATINGS

Paints and coatings can be classified in several ways: by application area, as with architectural versus industrial coatings; by the nature of the binder delivery system, as with evaporative versus nonevaporative coatings; or by the thermochemical properties of the ultimate dry film, as with convertible versus nonconvertible. Arguably, the most basic classification of paints and coatings is according to functionality: sealers, primers, and topcoats. A sealer is used to inhibit capillary action in a porous substrate such as masonry or wood, and is clear or only lightly pigmented. It provides a uniform base for the primer and prevents the migration of extractives from the substrate into the primer and to topcoats. A primer is usually highly pigmented, providing a dense and relatively inflexible film. It assists in protecting the substrate, provides a physically and optically uniform base for the topcoats, and ensures the adhesion of the coating system to the substrate. The top or finish coats are less dense and more flexible than the primer coat, providing the final protective and aesthetic layer.

Architectural Coatings

Architectural coatings are the paints used to protect and decorate the exterior and interior of buildings. They are also called "trade sales paints" when sold through retail outlets. These coatings are most often applied to wood and drywall to control moisture absorption, swelling, and degradation while providing a durable, flexible, and decorative film. Interior and exterior paints are produced in both solvent- and waterborne formulations yielding a flat, semigloss, or gloss finish. Waterborne latex paints dominate trade sales markets because of their ease of handling, application and ease of cleanup, nonflammability, and low hydrocarbon solvent exposure. Within the collective architectural coatings are those formulated for more specific performance. Masonry coatings, for example, are used to prevent surface deterioration, to block the passage of moisture and

extractables, and to improve the appearance of concrete, brick, stone, and tile.

Industrial Coatings

Industrial coatings are designed primarily to protect metal surfaces. Exposed ferrous surfaces oxidize rapidly to a nonprotective oxide coating. Liquid coating systems for ferrous metals are therefore typically based on primers containing a linseed oil or alkyd binder and anticorrosion pigments such as red lead, lead chromate, zinc chromate, potassium zinc chromate, and zinc dust. Primerless, direct-to-metal, protective latex coatings are also used. Although nonferrous metals tend to form an oxide layer that protects against further deterioration, they may require a coating to protect the surface from deterioration other than oxidation or, with a clear coating, to preserve the appearance of the unoxidized metal. Coil coating refers to a continuous process of applying a coating to a coil of steel or aluminum strip or sheet. The coated metal is formed into many colored metallic products such as appliance and electronics housings, roofing and siding materials, window blinds, and furniture components. The common coil coatings are based on amine alkyds, epoxies, vinyl alkyds, solution vinyls, thermoset resins, solvent-type and water-reducible polyesters, and fluorocarbon resins. Many items, particularly appliances, which were once coil coated are now powder coated.

Marine coatings are used on marine vessels and equipment. They are formulated to retard corrosion and fouling and generally to protect against the harshness of the marine environment. A ship coating system typically consists of a preconstruction primer with corrosion-inhibiting properties, a multipurpose repair primer, a ship bottom coating, antifouling coatings, topside coatings, and deck coatings. The environmental conditions in which the vessel or equipment is required to operate determine the composition and use of marine coatings.

Automotive finishes provide a high level of protection to the vehicle's substrate and an aesthetically appealing appearance, so that the vehicle retains its original look for as long as possible. Because of the consumer expectation of high-finish-coat quality, the primer coat must provide excellent adhesion and corrosion resistance as well as a uniform, smooth surface for the topcoats. The finish coats must be compatible with the prime coat and form a final hard, protective, blemish-free film that can be polished and repaired.

Convertible and Nonconvertible Coatings

Coatings are also classified as convertible or nonconvertible, according to the nature of the dried or cured film. A convertible coating reacts chemically during film formation, converting the polymeric binder into a three-dimensional cross-linked network. Cross-linking may be effected through an oxidative mechanism, as with oil and alkyd paints; catalysts, as with UF coatings; amine curing agents, as with epoxy systems; or UV radiation. The film is permanently altered and cannot be reliquified by heat or contact with most solvents.

Nonconvertible coatings form thermoplastic films, usually through the evaporation of organic solvent or water. Solvent coatings, in simplest terms, are made by dissolving a polymer of suitably high molecular weight at sufficiently low concentration to obtain the appropriate coating viscosity. As the solvent evaporates, the resin concentration increases, forming first a tacky film and then the final polymer film after the solvent is completely released.

Aqueous coatings are typically a latex emulsion consisting of colloidal polymer particles, usually smaller than 0.5 μm , that are

stabilized with an emulsifier to prevent flocculation and coalescence. After a latex paint is applied, water begins to evaporate and the polymer particles become increasingly concentrated. The particles eventually touch and pack together, leaving voids filled with water, which must eventually be lost to evaporation or porous absorption by the substrate. Eventually, the particles completely coalesce and fuse into a continuous film. Coalescing agents are used as temporary plasticizers, so that as the water evaporates, they have an increasing softening effect on the polymer particles, helping them coalesce more easily.

Evaporative and Nonevaporative Coatings

Yet another way to consider coatings is according to whether or not film formation depends on the loss of volatiles, either water or solvent.

Evaporative Coatings

Evaporative coatings include the conventional solvent-borne and aqueous emulsion types described in a previous section. For solvent coatings, high-solids systems, containing less than 30% volatile organic solvents, are generally preferred for environmental reasons. The viscosity of these systems is maintained sufficiently low for acceptable application properties by using oligomeric binders with carefully controlled molecular weight distributions and reactive diluents such as unsaturated monomers. Coatings with water-soluble binders are made with convertible resins modified with carboxylic, hydroxyl, or amino groups. These are essentially solvent coatings with water as the solvent. Polymeric film formation occurs in a sequence similar to that described for solvent coatings, with the final film oxidatively cross-linked.

An important factor in the production of an evaporative coating is the dispersion of the primary and extender pigments in the vehicle. To provide a uniform film with the desired surface characteristics, agglomerates must be broken down by mechanical shear into finely divided particles coated with the vehicle. Deagglomeration, particle-size reduction (if necessary), and dispersion are accomplished in a variety of equipment, from the conventional roller mills, ball mills, and pebble mills to high-shear media mills and dispersers. High-shear media mills are the most common type used in the production of paint and coatings. These mills can process high volumes of a wide range of coatings formulations, from very fluid compositions to high-viscosity materials, at relatively low operating cost. They consist of a hollow cylindrical shell with a rotating vertical or horizontal shaft and discs or pins located intermittently along the shaft length. These drive the grinding media through the coating formulation at very high velocity. The grinding media can be specially sized sand or, more commonly, small steel or ceramic balls. Media mills can be incorporated into either batch or continuous production processes.

The high-speed disperser is used in batch operations because of its relative ease of operation and cleanup. The viscosity of the formulations appropriate for this type of equipment must be in a well-defined range. If the viscosity is too low, no shearing action will occur, and if the viscosity is too high, the movement of the particles will not be rapid enough to break the agglomerates.

Evaporative coatings are typically produced in two steps: the "pigment grind" and "letdown." For example, with a waterborne coating, the pigments and extender pigments are first thoroughly dispersed into a portion of the water and glycol to which surfactant, dispersant, and defoamer have been added. This pigment concentrate is then diluted or "let down" with the balance of water plus binder, coalescent, thickener, and other additives.

Nonevaporative Coatings

Two component catalyzed systems are used as nonevaporative liquid coatings. One component contains a reactive polymer such as an epoxy, and the other contains the cross-linking agent. After the two parts are mixed, the coating has a limited pot life during which it must be applied before reaction and hardening occur. Thicker films can be obtained from this type of coating than are practical or possible from evaporative coatings.

Radiation cure coatings are typically solvent-free, high-solids systems based on acrylated epoxy or urethane oligomers with multifunctional acrylate monomers as diluent. These coatings cross-link rapidly at ambient temperature on exposure to UV or electron beam radiation. This makes them particularly suitable for heat-sensitive substrates such as paper, wood, and certain plastics. Because radiation intensity varies significantly with distance between the radiation source and the coated substrate, this technology is used almost exclusively on flat or rotatable cylindrical objects. Infrared and microwave cured coatings are sometimes also considered radiation cured, but in these systems the radiation is simply converted to heat, which initiates thermal curing.

Electrodeposition coatings for metal use water for its electrolytic properties rather than for its volatility. Binder particles, usually thermoset resin, are dispersed in an aqueous vehicle. The metal part can serve as either anode or cathode. In anodic systems, current causes the negatively charged paint particles to deposit on the anode through precipitation by the hydrogen ions generated there by electrolysis of the water. In cathodic systems, the positively charged paint particles deposit on the cathode through precipitation by generated hydroxide ions. Film thickness is essentially self-limiting because as film thickness increases, electrical resistance increases and deposition rate decreases until the film thickness at which deposition stops is reached. The coated article is removed from the electrodeposition bath, rinsed, and baked to cure. Because the entire surface of the metal object acts as an electrode, electrodeposition coatings are used to provide complete, void-free coverage. This is of particular value in the application of anticorrosion coatings.

Powder coatings use air as the medium through which resin is applied. Powder coatings are most often applied to bare metal as an electrostatic spray. The metal is grounded and the powder is given a negative electrostatic charge by the spray gun. The powder particles coat the metal surface through electrostatic attraction. Coverage tends to be uniform but self-limiting because the coating of powder acts as an insulator. The powder-covered article is baked, allowing the powder particles to fuse to a continuous film, flow, level, and cross-link. Heat-tolerant plastics and previously coated metal can be powder coated after preparation with a conductive primer. Powder coatings are widely used as industrial finishes on appliances, machinery, and outdoor fixtures and furniture because they provide a hard durable coating with essentially no VOC emissions and nearly 100% powder utilization—any overspray is easily collected and reused.

The coating powders are actually more like formulated plastics than like paint resins. They are prepared by premixing all ingredients (resin, pigments, extenders, reinforcements, and additives), melt extruding, and then pulverizing. Powder coatings are generally based on epoxy or polyester binders, although acrylic binders are used for particular applications such as for superior detergent resistance on washing machines. Thermoplastic powders, based on vinyl chloride copolymers, polyamides, fluoropolymers, and thermoplastic polyesters, are less commonly used because they are difficult to pulverize to fine particle sizes, resulting in relatively thick films, and because they provide relatively poor flow and leveling.

Thermoplastic powders are used in fluidized bed coating, although the resultant films are still relatively thick. The article to be coated is heated above the T_g of the binder resin and then suspended in an air-fluidized bed of coating powder. Powder particles fuse onto the hot object until the powder layer becomes thick enough to act as a thermal insulator and prevent additional fusing. The operation is completed in a separate oven, since the surface may contain incompletely fused particles. Electrostatic fluidized beds are also used, with charged powder and grounded substrates, which may or may not be preheated.

Flame spray technology is also used to apply thermoplastic powder coatings. A flame spray gun instantaneously melts the powder as it is sprayed so that the molten plastic flows and fuses onto the article. This process can be used on nonconductive, heat-tolerant surfaces such as concrete, wood, and certain plastics in addition to metals. It has the advantage of portability over the other powder-coating techniques, which require a large-scale, carefully controlled industrial setting. Flame spray apparatus can be used in the field to coat objects and to repair previously applied thermoplastic flame spray coatings.

TEST METHODS

The test methods employed in the evaluation of paints and coatings fall into two basic categories:

1. Those tests used to evaluate the properties and characteristics of a coatings formulation for a particular application
2. A selected subset of these tests used for the quality control of production material

The most widely used quality control tests for paints and coatings are described in the sections that follow.

Solids Content

The “solids” of a paint include all nonvolatile components that remain in the dry paint film. Measuring solids is important to ensuring control of the manufacturing process. Paints that deviate from the specified solids content may have variations in color and film durability. The solids content is also important in calculating the amount of coverage a paint will provide.

Specific Gravity

Specific gravity is an important, easy-to-measure property that indicates the weight of the paint for a given volume. Specific gravity is used as an in-process quality control test and as an end-product test to determine if all the major components were added in the correct amounts. It can be measured simply by filling a tared container of known volume and then weighing. For a higher level of precision, pycnometers are used.

Fineness of Grind

During the dispersion process, it is important to be able to measure the degree of breakdown of agglomerates and aggregate particles. If the grind is not fine enough, poor color uniformity, gloss, or hiding power can result. A convenient tool for measuring the “fineness of grind” is the Hegman gauge. This is a steel plate having a channel of declining depth from 0 to about 100 μm . Samples are drawn over the gauge with a straightedge. The depth of the channel at which particles are evident is taken as the Hegman reading for particle size. Table 4 lists Hegman fineness and corresponding channel depth. Hegman fineness of grind is commonly used as a specification test for mineral extenders to ensure that they do not contain any particles that are too large for the intended coating film.

Table 4. Hegman fineness and size (as channel depth)

Hegman Fineness	Channel Depth, μm
0	101.6
½	95.3
1	88.9
1½	82.6
2	76.2
2½	69.9
3	63.5
3½	57.2
4	50.8
4½	44.5
5	38.1
5½	31.8
6	25.4
6½	19.1
7	12.7
7½	6.4
8	0

Viscosity

Viscosity measurements are taken as in-process tests and end-product tests. Simple viscosity tests such as the Ford cup and Zahn cup tests measure the time required for a given volume of sample to pass through a standard size orifice. The Brookfield viscometer measures viscosity from shear resistance on a standard spindle rotating at a constant speed. A Stormer viscometer measures the time required for a standard paddle to revolve 100 revolutions from a constant force provided by a weight and pulley. The Gardner-Holdt bubble viscometer is used for varnishes. It quickly indicates varnish viscosity by measuring the time required for a bubble to rise to the top of a standard tube after being inverted under standard conditions. The problem with most viscometers is that they measure viscosity at relatively low shear. They can be used as good production control tests, but they do not necessarily relate well to the paint's rheology when applied under high-shear brush, roller, or spray application.

Wet Hiding Power

To measure the ability of the wet coating to produce an opaque film, it is uniformly brushed onto an impervious, black-and-white striped surface until complete hiding is achieved. The weight of the coating required to do this is determined and the hiding power in square feet is calculated. Wet hiding power is inversely proportional to coverage: the more paint needed, the less area that can be coated per gallon.

Dry Hiding Power

The dry hiding test uses the same striped panel and coating procedure previously described. Five brushouts are made, however, applying a different amount of paint each time. After each brushout, the panels are allowed to dry for 24 hours, and then the contrast ratio is measured. Contrast ratio is equal to the reflectance over the black area divided by the reflectance over the white area. The weight of the paint is plotted against the contrast ratio, and the amount of the paint required to give a contrast ratio of 98 is read from the resulting curve. The dry hiding power is calculated accordingly.

Specular Gloss

A 60° gloss reading on a standardized test panel is used to determine film smoothness and thus visual gloss. Increases in surface

roughness or imperfections promote diffuse reflection and lower gloss.

Color

The color of a finished coating can be qualitatively evaluated by visual comparison to an established standard. Most color comparisons, however, are made quantitatively by measuring test panels on color measurement instruments that calculate color coordinates and determine the color difference.

Table 5 lists the recognized American Society for Testing and Materials (ASTM) procedures used primarily for evaluating coatings formulations and determining coating characteristics.

TRENDS AND OPPORTUNITIES

Improved coating properties and lower emissions of volatile organics have been concurrent goals of the coatings industry for many years, with the latter often frustrating progress toward the former. Lowering VOCs is an ongoing process of replacing solvent-borne coatings with waterborne and solventless (organic solvent and water-free) alternatives. Because mineral extenders exert considerable influence on the rheological, optical, and performance properties of coatings, manipulation of particle size, shape, and surface properties remains a challenge and an opportunity. Low extender vehicle demand is preferred, for example, when formulating high solids and 100% solids coatings. This is an opportunity for the producers of naturally low demand extenders and a challenge to the producers of conventionally high-performance but high-demand extenders.

An appreciation of particle-packing phenomena is increasingly important as the coating formulator strives to optimize the extender loading for the required balance of application properties, optical properties, durability, and substrate protection. Emphasis is accordingly placed on manipulating the distribution of particle shapes and sizes of the minerals sold as extenders. The surface properties of extenders are likewise subject to further customization. Because most mineral extenders have hydrophilic surfaces, modification with additives such as silanes and titanates becomes more important to ensure compatibility with and reinforcement of the coating polymer film. This is reasonably straightforward for nonaqueous coatings, but less so for waterborne alternatives. The mineral surface must be sufficiently hydrophobic or even reactive for greater functionality in the binder film without being unduly difficult to disperse intimately in the aqueous vehicle.

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Table 5. ASTM test methods for coatings

D281	Standard Test Method for Oil Absorption of Pigments by Spatula Rub-Out
D344	Standard Test Method for Relative Hiding Power of Paints by the Visual Evaluation of Brushouts
D523	Standard Test Method for Specular Gloss
D609	Standard Practice for Preparation of Gold-Rolled Steel Panels for Testing Paint, Varnish, Conversion Coatings, and Related Coating Products
D610	Standard Test Method for Evaluating Degree of Rusting on Painted Steel Surfaces
D660	Standard Test Method for Evaluating Degree of Checking of Exterior Paints
D661	Standard Test Method for Evaluating Degree of Cracking of Exterior Paints
D662	Standard Test Method for Evaluating Degree of Erosion of Exterior Paints
D714	Standard Test Method for Evaluating Degree of Blistering of Paints
D772	Standard Test Method for Evaluating Degree of Flaking of Exterior Paints.
D869	Standard Test Method for Evaluating Degree of Settling of Paints
D870	Standard Practice for Testing Water Resistance of Coatings Using Water Immersion
D968	Standard Test Methods for Abrasion Resistance of Organic Coatings by Falling Abrasive
D1006	Standard Practice for Conducting Exterior Exposure Tests of Paints on Wood
D1014	Standard Practice for Conducting Exterior Exposure Tests of Paints and Coatings on Metal Substrates
D1210	Standard Test Method for Fineness of Dispersion of Pigment-Vehicle Systems by Hegman-Type Gage
D1308	Standard Test Method for Effect of Household Chemicals on Clear and Pigmented Organic Finishes
D1474	Standard Test Method for Indentation Hardness of Organic Coatings
D1475	Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products
D1735	Standard Practice for Testing Water Resistance of Coatings Using Water Fog Apparatus
D2197	Standard Test Method for Adhesion of Organic Coatings by Scrape Adhesion
D2486	Standard Test Method for Scrub Resistance of Interior Latex Flat Wall Paint
D2793	Standard Test Method for Block Resistance of Organic Coatings and Wood Substrates
D2805	Standard Test Method for Hiding Power of Paints by Reflectometry
D2832	Standard Guide for Determining Volatile and Nonvolatile Content of Paint and Related Coatings
D3170	Standard Test Method for Chipping Resistance of Coatings
D3258	Standard Test Method for Porosity of White or Near White Paint Films by Staining
D3359	Standard Test Methods for Measuring Adhesion by Tape Test
D3450	Standard Test Method for Washability Properties of Interior Architectural Coatings
D3730	Standard Guide for Testing High-Performance Interior Architectural Wall Coatings
D3794	Standard Guide for Testing Coil Coatings
D3960	Standard Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings
D4062	Standard Test Method for Leveling Characteristics of Paints by Draw Down Method
D4400	Standard Test Method for Sag Resistance of Paints Using a Multinotch Applicator
D4414	Standard Practice for Measurement of Wet Film Thickness by Notch Gauges
D4707	Standard Test Method for Measuring Paint Spatter Resistance During Roller Application
D4946	Standard Test Method for Blocking Resistance of Architectural Paints
D4958	Standard Test Method for the Comparison of Brush Drag of Latex Paints
D5150	Standard Test Method for Hiding Power of Architectural Paints Applied by Roller
D5178	Standard Test Method for Mar Resistance of Organic Coatings
D5324	Standard Guide for Testing Water-Borne Architectural Coatings
D6736	Standard Test Method for Burnish Resistance of Latex Paints

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Plastics

George Hawley

INTRODUCTION

Plastics can be defined as a mixture of polymers with additives. The polymer is a long twisted chain made up mainly of methylene groups, but it may also contain some amino and carboxyl groups. Side chains and substitute groups for hydrogen are also common. Industrial minerals and their derivatives are used as additives to overcome some of the deficiencies of the properties of plastics when compared to metals and cementitious materials. These additives may be roughly divided into a filler, which contributes some bulking and cost-reduction properties but is mainly used to improve some physical property, and an extender, which is used to augment the hiding power of a primary pigment and reduce cost. Favorable properties conferred by these additives are enhanced stiffness, strength, hardness, impact resistance, surface appearance, opacity, dimensional stability, thermal stability, service temperature, fire resistance, permeability to gases and liquids, chemical and solvent resistance, dielectric properties, thermal conductivity, electrical properties, resistance to ultraviolet (UV) and other radiation, and processability. These same improvements may be achieved through the use of specialty polymers or by chemical additives, but at much higher cost (and often the mineral confers a balance of several different property enhancements). At the same time, mineral additives may have an adverse effect on certain properties such as flexibility and impact resistance.

The leading mineral additive used in the plastics industry is dry or wet ground calcium carbonate (GCC) or dolomite, followed by talc, kaolin, mica, wollastonite, natural and synthetic silicas, aluminum hydroxide, and precipitated (synthetic) calcium carbonate (PCC).

Some of the more common polymers used in the plastics industry are

- Polyolefin—polymer composed of chains of carbon atoms with hydrogen or methyl side groups (e.g., polyethylene, polypropylene)
- PVC—polyvinyl chloride polymer
- PP—polypropylene
- PE—polyethylene (HDPE, high-density PE; LDPE, low-density PE; LLDPE, linear low-density PE)
- PA—polyamide (nylon)
- PS—polystyrene

- ABS—acrylonitrile-butadiene-styrene copolymers
- SMC—sheet molding compound
- BMC—bulk molding compound
- RRIM/PU—reinforced reaction-injection molded polyurethane

TYPES OF PLASTICS

Plastics are generally divided into two classes: thermoplastics and thermosetting. Thermoplastics are solid polymer pellets that can be melted and molded into specific shapes. They can also be recycled by remelting and remolding. Although there is some degradation with each melt cycle, up to 30% of a recycled thermoplastic can be used in a final product with no significant effect on properties, providing that stabilizing additives are used. Typical thermoplastics are PVC, PP, PE, ABS, and PA.

Thermosetting polymers are usually liquids at room temperature (because heat causes decomposition). They require the addition of catalysts to convert the polymer into a solid by cross-linking reactive groups on the chain. Once “cured,” the polymer is infusible. Thermosetting polymers are not usually recycled, unless pulverized and used as a filler. Typical thermosets include epoxy, unsaturated polyester, and polyurethane.

Plastics are further divided into amorphous, crystalline, and semicrystalline types. Amorphous polymers tend to be low in cost and to have more flexibility and good impact resistance, but they also exhibit low strength and stiffness characteristics. Typical amorphous polymers are LDPE (as used in agricultural and packaging films), PS, and ABS. In contrast, crystalline polymers tend to have higher strength and stiffness but lower impact properties. Crystalline polymers include PP, HDPE, and LLDPE.

MINERAL FILLERS IN PLASTICS

In general, when minerals are incorporated in plastics, they reduce shrinkage on demolding and speed up the molding cycle. Negative effects are the lowering of strength, impact resistance, and flexibility. Filler content usually increases plastic density to a specific gravity (SG) of about 1.5 compared to that of unfilled polymer, which ranges from 0.9 to 1.1. Although this is generally deleterious, the improved plastic properties may make it possible to substitute for steel at SG 7.0, leading to substantial weight savings. This is a major factor that is spurring the automobile industry, for example, to switch to plastics.

Table 1. World consumption of major fillers in plastics (2002)

Filler	kt	%
GCC	7,250	66
Talc	660	6
Kaolin	660	6
Wollastonite	330	3
Mica	110	1
Other*		18
Total	11,000	100

Courtesy of USGS.

* Includes silicas (natural and synthetic) and alumina hydrate.

Table 2. U.S. consumption of major fillers in plastics (2003)

Filler	kt	%
GCC	1,500	66
Talc	30	6
Kaolin	50	6
Wollastonite	50	3
Mica	20	1
Other*		18
Total	2,250	100

Courtesy of USGS.

* Includes silicas (natural and synthetic) and alumina hydrate.

Table 3. Consumption of ground calcium carbonate in plastics, by country

Country	Mt	%
Asia/Oceania	3.2	43
China	2	27
Japan	0.5	7
South Korea	0.3	4
European Economic Community (EEC)	1.7	23
United States	1.5	20
South and Central America	0.4	6
Middle East and Africa	0.6	8
Total	7.4	100

Mineral fillers act as true reinforcements only in crystalline polymers. One of their beneficial functions is to catalyze crystallization. In addition to their generic effects, mentioned previously, they increase strength, stiffness, and heat resistance. These plastics tend to warp on cooling because of the orientation of the crystallites in the flow direction, which results in a substantial differential in thermal contraction in the flow and cross-flow directions. This problem is worsened by fibrous fillers but is improved by using flake minerals such as mica, talc, kaolin, and graphite.

PROCESSING OF MINERAL-FILLED PLASTICS

Mineral-filled plastics are processed by the same machines as the unfilled versions. The main processes used are extrusion, blow molding, and injection molding.

In extrusion, the largest volume process, the plastic is melted, forced through a die to give the correct profile, and then cooled to set it. Typical products are pipes, tubing, siding, door and window

profiles, and window blinds, and typical filled polymers used are PVC, LDPE, PP, HDPE, and ABS. In a variation of this process, a pipe is extruded and then blown by internal air pressure to a bubble of the correct thickness, making film. Films of LDPE, LLDPE, PP, and HDPE are not generally filled, except in specialty applications such as diapers (see section on GCC in Microporous Films in this chapter). These films represent a huge market.

In blow molding, a variation of extrusion, a pipe section is extruded into a mold where internal gas pressure forces it to take its shape. All plastic bottles and drums are made by this process, as well as toys, air-conditioning ducts, and seat backs in cars. Typical filled polymers used are PVC, PP, LDPE, HDPE, and ABS.

In injection molding, the molten plastic is injected into a closed mold that is then cooled to set the plastic. This is the most common way to make three-dimensional plastic objects ranging from tiny computer contacts to 1,500-lb. truck cabs. Although all thermoplastic types are used, the most common are PVC, PP, PE, PA, and ABS.

One variation of this process is thermoset injection of filled sheet and bulk molding compounds where the mold is heated to cure the polymer. This process is used with unsaturated polyesters to make BMC plumbing fixtures (such as laundry sinks and shower pans) and SMC automobile parts (such as hoods and trunk lids). BMC and SMC contain high levels of GCC.

Another variation is RRIM/PU, in which mica- or wollastonite-filled polyurethane or polyurea liquid polymers are forced into molds. Very large parts such as truck cabs can be made with this low-pressure process. The largest end use is for front and rear fascias and wraparound fender assemblies on most cars.

Supply and Demand

The size of the market for minerals used in plastics is small relative to the large-scale commodity markets often served by the same suppliers. In fact, the fines from the production of mineral products used for the metallurgical, ceramics, and glass industries are often the starting point for production of mineral fillers. Overall, the supply of mineral fillers exceeds demand. To counter the relatively small tonnage of minerals required, however, the plastics market is important in that it requires more specialized products that command higher prices and generate higher profits. It is estimated that the total tonnage of mineral products used in the plastics industry worldwide exceeds 10 Mt (see Tables 1–3).

Prices

Prices range from \$0.02/lb to \$0.05/lb for coarse commodity-like powders and up to \$4.00/lb for sophisticated, high-tech products such as nanoclays (see Table 4).

Classification

Natural Fillers

Carbonates are by far the largest volume of minerals used. In this class, calcium carbonate with some dolomite predominates because its higher hardness lends increased durability to floor tiles. Silicates are the next largest class, mainly as talc, followed by kaolin. Wollastonite and mica, although relatively low-volume minerals, command high prices because of their unique reinforcing abilities. Magnesium minerals such as brucite, huntite, and hydromagnesite are used in small amounts as a flame retardant. Silica is used for its high hardness, chemical resistance, and thermal conductivity. Graphite consumption is currently small but has great potential for increased use in electrically conductive plastics—in particular, in fuel cell plates and antistatic plastics.

Synthetic Fillers

Alumina hydrate, the largest of the synthetic mineral products used in plastics, is used as a flame retardant in carpet backing and plumbing fixtures. Synthetic silicas are mainly used as thickening agents in liquid polymers, as reinforcements in silicons, and as antisticking agents in films. Precipitated calcium carbonate is used in plastics, but to a much lesser extent than GCC. Some magnesium hydroxide is also used but in small volumes, although this should increase because competitive fire retardants are being banned.

General Considerations

The demand for and value of industrial minerals increases with enhancements in the following characteristics:

- Purity—Heavy metals, toxins, and environmentally undesirable impurities are absent.
- Color—Generally, the highest whiteness or blackness is preferred.
- Fineness—The finer, the better. The trend is to submicrometer and increasingly, to particles that have their larger dimension in the nanometer rather than the micrometer region (with a narrow range).
- Surface modification—This improves particle dispersion and optimizes property enhancement by improved bonding.

INDUSTRY STRUCTURE

Infrastructure

Although it is obvious that a mine may not be sited near the end user, secondary processing can and should be located near the point of consumption. The use of minerals in plastics is highly technical, requiring a highly trained staff, and R&D is often conducted in concert with university and government laboratories. Fine grinding is energy intensive, necessitating that a significant power source be nearby. Technological requirements are for fine comminution, control of agglomeration, surface chemistry, and awareness of current status and future directions of the plastics industry.

Barriers to Entry

Supplying the plastics industry is a marketing-driven business. Technological expertise is mandatory, as is a deep purse, because penetration into markets such as automotive, aerospace, and medical/dental supplies may take 4 years or more. User confidence is hard won and ISO (International Organization for Standardization) certification is a must. The producers tend to be a small number of global suppliers of a suite of minerals that are supplied to all the markets, including plastics. These producers have sophisticated special-purpose laboratories that are equipped for plastics R&D work; these laboratories also enable producers to furnish the specialized technical services required by their customers.

Economic Factors

For the lower-value industrial minerals, the freight costs may be as high as the mineral value. For this reason, location near the markets or near low-cost transportation avenues such as waterways may be vital. Markets are now global and it may be less costly, for example, to supply Europe by sea than to truck product to a North American user. Major suppliers seek out mines and locate processing facilities as near to their customers as possible.

Specifications

The end user sets the specifications—even in the same application, different end users may specify products that vary widely in charac-

Table 4. Pricing of major minerals used in plastics

Mineral	Specification	\$/t
Calcium carbonate		
	GCC	
	45 μm	50–100
Fine PCC	5–7 μm	110–160
	0.5–2.0 μm	140–290
	0.4–1.0 μm	250–270
Ultrafine treated PCC	0.02–0.36 μm	375–750
Talc		
	20–25 μm	185–195
Kaolin	10–20 μm	200–205
Wollastonite	Hydrous filler	80–185
	Calcined	320–375
	200 mesh	205
	325 mesh	248
Mica	400 mesh	275
	High aspect ratio	345–1,000
Mica	Dry ground	210–400
	Micronized	535–930
	Wet ground	535–1,300

Adapted from Anon. 2004.

ter. Particle sizes range from 140 μm down to submicrometer and even nanometer sizes.

PRODUCTION TECHNIQUES

Raw and Intermediate Materials

Originally, filling plastics was regarded as a way to dispose of unwanted fines—for instance, fines from marble, soapstone, or calcium carbonate aggregate operations. Subsequently, user requirements became more restrictive and, because the prices commanded were orders of magnitude higher than those of the original end use, it became normal practice to produce fillers directly from ore. Ores are sought that are high in purity; preferably little or no beneficiation should be required. This is possible with carbonates, talc, silica, and some clays. With other silicates such as mica and wollastonite, however, beneficiation is normally required.

Mining and Processing

In general, mining methods used are conventional; carbonates and silicates require drilling and blasting, and clays are commonly mined using scrapers or loaders. Small amounts of large sheet mica and lump graphite are mined by hand for high purity, to produce larger-size flakes or lumps, or to preserve the character of the deposit.

Initial size reduction is generally by jaw crusher followed by hammer mills. Beneficiation may be by flotation, but residual reagents may interfere with performance in plastics. Dry processes such as gravity and magnetic and electrostatic separation are preferred and are also less harmful to the environment. Low-value products may be made by ball milling, but this process generally reduces the quality of minerals such as mica, wollastonite, and graphite. Hammer and cage mills are used to make products down to 20 μm . Air-swept mills reduce these products down to 2–10 μm . Fluid-energy milling is the standard method for producing finer particles, but it is costly in capital expense and operations. Stirred-media

Table 5. Surface modification and treatment

Chemical Type	Fillers	Wt % on Filler
Stearic acid and stearates	Calcium and magnesium carbonates	1–3
Silanes	Silicates (mica, wollastonite, kaolin, and talc); natural and synthetic silicas; oxides (titanium dioxide and iron oxides)	0.25–2.0
Titanates, zirconates, zirco-aluminates	Silicates, silicas, and oxides, plus carbonates	0.5–3.0
Carboxylated polymers	Mica, wollastonite, talc, kaolin	5–25
Chlorinated hydrocarbons	Mica, wollastonite	1–5

milling and vibro-energy milling are less expensive and are being used increasingly to make the finest particle sizes.

The filler surface is commonly treated. This may involve surface modification whereby the filler is reacted with a chemical that in turn reacts with the polymer to form a large molecule, ensuring that the polymer bonds to the filler (see Table 5). Or surface treatment that encourages wetting of the filler by polymer may be applied to the filler, improving dispersion and reducing viscosity. Surface treatment does not form any chemical bonds and is reversible.

Other treatments include pelletization or granulation to reduce dustiness and air entrainment and to facilitate feeding into plastics-compounding equipment.

FINISHED PRODUCTS

Specifications

Specifications always include particle-size analysis that is given as a curve or as quoting a average and top size. Surface area is commonly quoted because it is a measure of particle size. Moisture content is a required measurement, because moisture is deleterious to most plastics. Brightness is often quoted for white fillers. Other common measurements quoted are refractive index, pH, specific gravity, bulk density (loose and compacted), oil absorption, and water-soluble salts. Chemical composition is sometimes quoted but is of no real interest to the plastics end user.

Uses and Applications

As previously discussed, industrial minerals and their derivatives are used as low-cost functional additives in plastics to overcome some of the deficiencies of the properties of plastics when compared to metals and cementitious materials. The more common minerals are outlined in the following sections.

Ground Calcium Carbonate

GCC in PVC

GCC, by far the most important filler mineral used in the plastics industry, is used in large volumes in PVC. The main functions are as

- A low-cost opacifier, substituting for titanium dioxide
- A stabilizer against thermal degradation during processing
- An agent to increase service temperature to protect against weathering
- An agent to increase stiffness and surface hardness
- An agent to reduce shrinkage out of the mold
- An agent to increase chemical resistance
- An agent to improve impact properties
- A processing aid to increase throughput

GCC is used extensively in PVC sewer, pressure, and potable water pipes; fittings; floor tiles and other flooring; outdoor furniture; window and door extrusions; automobile plastics; leathercloth; wallpaper; and blinds. GCC is used at levels of 20%–30% by weight of products ranging from 1 to 5 μm . The level is much higher in flooring (up to 70%) using coarser particles (325 mesh and larger).

GCC in PP

The second largest use of GCC is in polypropylene—approximately 500,000 t of filled polymer in each of the EEC countries and in the United States. The filler level is 20%–60% of 1–3- μm GCC. End uses include

- Automotive (interior and exterior trim, under-the-hood parts)—53%
- Appliance parts—24%
- Garden furniture—8%

GCC in Microporous Films

Although polyolefin film is a huge market, it has not used much filler in the past except some GCC, PCC, talc, and diatomaceous earth at levels of 2%–5% as antiblocking agents. A new market has developed and grown rapidly—the production of microporous films, which hold liquid water but allow water vapor to pass through. These have become an industry standard in diapers, with a 65% market share in the United States, 50% in the EEC, and 40% in Asia. GCC content is 43%–70% by weight, with particles 1–2 μm in size. Another growing market is film underlay for walls and roofing. Current consumption is about 100,000 t and growing.

Other Minerals

Talc is mainly used in PP and HDPE where its hydrophobic nature ensures good compatibility without surface treatment. Talc-filled plastics tend to scratch easily and are being supplanted by GCC in wear-prone applications. End uses are automobiles, appliances, housewares, and business machines.

Kaolin is largely limited to use in electrical wire and cable, and calcined kaolin is the preferred type. Calcination converts the kaolinite to mulite, spinel, and cristobalite. Because it is anhydrous, it has excellent electrical properties. Surface treatments are used to improve adhesion and thus mechanical and electrical properties. Mica and wollastonite are used—mainly in polyolefins, polyamides, and polyurethanes—to increase stiffness, strength, and surface hardness, as well as to reduce shrinkage and warping. The main end uses are in the automotive industry (i.e., interior/exterior body parts, under-the-hood parts, glove boxes, and fender liners), and in dishwashers, washers, tubs, and pumps. Silane treatments are common for enhancing mechanical properties.

Competitive Alternatives

Ironically, industrial minerals tend not to reduce the cost of a plastic article because their high specific gravity (2.5–3.0) versus that of polymers (0.9–1.1) means that it takes 2.5 to 3 times the weight of filler to replace the same volume of polymer. Thus, to compete with PP at SG 0.9 and a cost of \$0.45/lb, the competitive price of a calcium carbonate filler would have to be about \$0.15/lb. This also ignores the cost of compounding the filler into the polymer, which may be \$0.15/lb or more.

Because the only true cheap filler is air or another gas, plastics may be foamed, but this reduces the mechanical properties greatly and some additional filler is required. With improved vehicle fuel efficiency (Corporate Average Fuel Economy [CAFE])

standards for U.S. passenger cars and light trucks invariably mandating weight reductions, the use of dense fillers is a problem for the automotive industry. This has encouraged the use of wood fillers in nonstructural applications. Synthetic wood for decks and benches are fast-growing markets for wood-filled HDPE. Glass fibers are by far the largest reinforcing filler used in plastics. But the growth of carbon fibers has increased with its reduction in cost, and with an SG of 2.0 (versus 2.65 for glass) and much higher reinforcing properties, carbon fibers will find more applications in automobile end uses.

MARKETING AND DISTRIBUTION

Use-Specific Marketing and Transportation

Because it is common for grades of minerals to be produced that are specific to a certain segment of the plastics industry—such as automotive, PVC profiles, and packaging—use-specific marketing is the dominant force in the industry. These are almost commodities, but there is enough variation among individual plastics end users that special subgrades must be tailor-made for a user's specs or even for that user's particular plant. The result is that the filler producer must make dozens of grades from each ore body. Selling to these markets is highly technical, and sales engineers with plastics experience are the norm and are supported by major investments in technical service and research laboratories.

The filler manufacturer normally has its own sales force. Small orders are often handed off to distributors who stock small amounts and service small accounts for a commission fee of 10% or so.

The regular packaging in the filler industry is 25-kg or 50-lb multiwall paper bags on pallets, but the industry is moving toward packaging in cardboard Gaylord boxes or woven plastic semibulk bags that contain 500–2,000 lb of product. The decision is one of economics. Paper bags are cheaper and need no special handling, but they are labor intensive. Bulk bags need special handling equipment, but the product is not prohibitively expensive. Very large compounders buy in bulk, and they find putting in bulk tanks and distribution systems to be cost-effective. Bulk handling, however, creates special problems for the filler supplier.

Just-in-time delivery is the norm and, in North America, this is best supplied by trucking. Vans carrying 40,000-lb loads are preferred for protection against the weather. Over a long haul, some cost advantages may be realized by piggyback road/rail transportation. Boxcars may carry up to three times the amount of material, but the load must be bulk-headed to prevent damage because of the poor quality of the track in some areas. Overseas shipments are handled by 20- or 40-ft containers, or by bulk bags carried in bulk carriers on top of the regular large-volume bulk commodity.

GOVERNMENTAL, ENVIRONMENTAL, AND HEALTH CONSIDERATIONS

Since the 1970s, the health effects of the unintelligent use of industrial minerals have become apparent, with the correlation of, for example, exposure to asbestos fibers with cancer. Regulations that control the production and utilization of fibers in the workplace are now in place. This affects not only asbestos itself but also any mineral that contains asbestiform fibers. Minerals where such fibers have been found or may be present include talc, vermiculite, and wollastonite.

The World Health Organization has classified fine crystalline silica as a carcinogen, triggering regulation that controls its use in the workplace. Silica is a very common impurity in most industrial minerals.

Lead has also been classified as a serious health hazard, as have other heavy metals such as chromium and toxic elements such as arsenic.

Minerals producers must determine that their products do not contain any of these compounds in regulated amounts, and also ensure that they are not releasing such agents into the atmosphere or into groundwaters.

TRENDS AND OPPORTUNITIES

The trend is toward substitution of plastics for conventional materials, not only because of cost but because the final products can be made very rapidly and much more cheaply, with less energy and more design flexibility. Wood products are becoming scarcer and more expensive. Cement-based products are very energy intensive and much more polluting than plastics; about 5% of all Canadian carbon emissions, for example, come from cement production. Metals are heavy, energy intensive, limited in design potential, have to be protected or decorated, and are more expensive on a volume basis than plastics. Plastics growth, which is virtually recession proof, is expected to continue at an average rate of 2%–3% per year.

Trends in filler production are toward finer particles down to submicrometer size and below. Opportunities exist in the production of nanometer-sized particles, which generally are much more effective as reinforcements for plastics. World production of nanocomposites was estimated in 2004 at only 104,000 t but has high growth potential. Modified montmorillonite clay, vermiculite, and graphite confer the same reinforcement characteristics at 2%–10% by weight that normally require 30%–40% of glass fibers, mica, or wollastonite. This increases product weight only slightly, a big advantage for the automotive and aerospace industries as well as the personal electronics industry. Other benefits include enhanced fire resistance without the toxicity of the conventional bromine-, chlorine-, and antimony-based additives—which are being classified as carcinogenic—plus reduced permeability to gases, especially oxygen, which is an important consideration for film packaging of meat.

USEFUL WEB SITES

- *Industrial Minerals* journal, monthly: <http://www.indmin.com>
- Kline & Company: <http://www.klinegroup.com>
- *Modern Plastics World Encyclopedia*, annual: <http://www.modplas.com>
- *Modern Plastics* magazine, monthly: <http://www.modplas.com>
- Society of Plastics Engineers: <http://www.4spe.org>
- U.S. Geological Survey (USGS) Minerals Information, Commodity Statistics and Information: <http://www.minerals.usgs.gov/minerals/pubs/commodity>

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Rubber

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INTRODUCTION

Elastomers are amorphous polymers that when mixed with various ingredients form a compound that can be “vulcanized” to produce rubber. They are elastic in that they can be stretched to several times their original length and can return or “bounce” back into their original shape without permanent deformation. In addition to being elastic and rubbery, these materials also dissipate energy because of their viscoelastic nature. They are further characterized by a great toughness under static or dynamic stress, an abrasion resistance that is higher than that of steel, an impermeability to air and water, and often a high resistance to swelling in solvents and attack by chemicals. Polymers that are elastomers include polyisoprene or natural rubber (NR) plus a host of synthetic elastomers, including synthetic isoprene rubber (IR), styrene-butadiene rubber (SBR), ethylene-propylene rubber (EPR), ethylene-propylenediene monomer rubber (EPDM), and nitrile rubber (NBR) (see Table 1).

Natural Rubber

Natural rubber exists as a colloidal suspension in milky white latex. This latex is the protective fluid made up of small particles of rubber dispersed in an aqueous medium and contained in tissue beneath the bark of rubber-producing plants such as the tree *Hevea brasiliensis* of the spurge family and other species in the same genus. These species constituted the sources of the original South American Para rubber, a commercial term that was applied to the rubber produced in the plantations of the tropics. Latex is collected as it exudes from a diagonal cut angled downward through the bark of the plantation trees that yield, on average, 450 kg/ha (400 lb/acre) of dry crude rubber per year with about 250 trees planted per hectare (100/acre). The gathered latex is strained, diluted with water, and treated with acid to cause the suspended rubber particles within the latex to clump together. After being pressed between rollers to consolidate the rubber into 0.6-cm slabs or thin crepe sheets, the rubber is air- or smoke-dried for shipment.

The resulting pure crude rubber is a white or colorless hydrocarbon with the simplest unit being isoprene (C_5H_8). The physical characteristics change as the temperatures change: rubber is a hard, transparent solid at -195°C (the temperature of liquid air); brittle and opaque from 0° to 10°C ; soft, resilient, and translucent above 20°C ; plastic and sticky when mechanically kneaded or heated above 50°C ; and decomposes above 200°C . Crude rubber is

insoluble in water, alkali, and weak acid, but soluble in benzene, gasoline, chlorinated hydrocarbons, and carbon disulfide. It is oxidized readily by chemical oxidizing agents and slowly by atmospheric oxygen. Crude rubber such as gutta-percha and balata from other plant sources is generally contaminated by an admixture of resins that must be removed before commercial use.

Synthetic Rubber

Synthetic rubber, defined as any artificially produced substance that resembles natural rubber in essential chemical and physical properties, is produced by the condensation or polymerization of certain unsaturated hydrocarbons. The basic units of synthetic rubber are monomers, which are compounds of relatively low molecular weight that form huge molecules called polymers.

Table 1 lists the main commercial synthetic rubbers. Neoprene, which was developed in 1931 and became one of the first successful synthetic rubbers, is the polymer of the monomer chloroprene [$\text{CH}_2\text{:C}(\text{Cl})\text{CH:CH}_2$] formed from acetylene and hydrochloric acid. Because neoprene resists heat and various chemicals such as oils and gasoline, it is used in hoses for gasoline and as an insulating material for cables and in machinery. In 1935, the buna-type rubber group was developed through the polymerization of two monomers including butadiene. (The name *buna* was derived from the initial letters of butadiene, used as one of the co-monomers, and natrium [sodium] used as a catalyst). One of the most popular buna rubbers, Buna-N, is based on acrylonitrile [$\text{CH}_2\text{:CH}(\text{CN})$] as the second co-monomer. Buna-N is resistant to the action of oils or abrasion. In 1940, butyl rubber was prepared by copolymerizing isobutylene with butadiene or isoprene. Although not as resilient as natural rubber and other synthetics, butyl rubber resists oxidation and corrosion and has low permeability to gas. Specialty synthetic rubbers include Koroseal, a polymer of vinyl chloride ($\text{CH}_2\text{:CHCl}$), which is heat-, electricity-, and corrosion-resistant and unaffected by exposure to light or long storage. Another is Thiokol, produced by copolymerization of ethylene dichloride (CHCl:CHCl), and sodium tetrasulfide (Na_2S_4), which when compounded and vulcanized like natural rubber is resistant to the action of oils and to organic solvents used for lacquers. Thiokol is useful for electrical insulation.

Other types include synthetic foam rubber, used mainly for upholstery, mattresses, and pillows, and cellular-crepe rubber, used by the shoe industry.

Table 1. Selected types and properties of rubber

Chemical Name	Common Name	Abbreviation	Properties
Isoprene, natural	Natural rubber	NR	Offer a good balance of properties with resilience and flexibility at lower temperatures. NR superior to most synthetics, but less resistant to chemical attack than some synthetics.
Isoprene, synthetic	Polyisoprene	IR	
Styrene-butadiene copolymer	SBR	SBR	Similar to NR
Terpolymer of ethylene, propylene, (with a small amount of diene)	EPDM	EPDM	Outstanding resistance to aging, weathering, and chemical attack. Low-temperature stability. Resistant to steam and water. Good resistance to glycol-ether hydraulic fluids, but not suitable for contact with petroleum liquids.
Isobutene isoprene polymer	Butyl	IIR	Very low gas and moisture permeability with excellent resistance to heat, aging, weathering, and ozone and chemical attack. Good electrical insulation properties. Not suitable for use with petroleum oils and fluids.
Chloroprene	Neoprene	CR	More resistant than NR to sunlight, ozone, and oxidation. Good resistance to heat, and softens less than NR under severe exposure. Not suitable for use with gasoline. Can be compounded to add flame-retardant properties.
Acrylonitrile-butadiene copolymer	Nitrile	NBR	Resistant to water, oil, fuel, and other petroleum products. Superior to most elastomers in compression set, cold flow, and abrasion resistance. Poor resistance to ozone, sunlight, or weather.
Chlorosulfonated polyethylene	Hypalon	CSM	Resistant to water, ozone, abrasion, flex cracking, acids, and weather. Good flame-resistant properties.
Polysiloxanes	Silicone rubber	"Q" Group	Resistant to temperature extremes (up to 2,000°C). Poor tensile strength, tear, abrasion, and steam resistance. Very good resistance to sunlight, ozone, and gases. Good electrical insulation and water repellent properties.
Polyesters	Polyurethane	AU	Abrasion resistant at moderate temperatures. Very high tensile strength, tear strength, and load-bearing capabilities. Resistant to oils, certain solvents, greases, ozone, sunlight, and weather. Poor resistance to acids and alkalis.
Fluorinated hydrocarbon	Viton	FPM	Resistant to most chemicals and commercial fluids. Retains strength at elevated temperatures and withstands embrittlement during long-term heat exposure.

PRODUCTION PROCESSES

Compounding

Raw rubber undergoes a mechanical grinding process called mastication that renders it soft, plastic, and sticky (i.e., it is plasticized). Commercial applications for uncured rubber, however, are limited to certain specialized cements; various adhesive, insulating, and friction tapes; and crepe rubber used in insulating blankets and footwear. Therefore, most rubber undergoes a process of curing or vulcanization, which imparts a permanent change and renders the rubber heat stable. Chemicals known as "curatives," which include vulcanizing agents, accelerators, and activators, facilitate this curing process when they are added during the compounding process. At the same time, to broaden the range of properties required to meet the demands of modern manufacturing, raw rubber is combined with an appropriate range and quantity of additives such as plasticizers, antioxidants and anti-ozonants, and functional fillers and pigments. The amount of additives introduced in compounding varies from just 2%–3% by weight for simple rubber bands to more than 60% for some highly specialized and sophisticated rubber products. The resulting compound, then, is unvulcanized rubber based on a particular formulation or "recipe" of rubber and compounding ingredients. Additives introduced in compounding are classified into the following categories:

- **Curatives:** Active chemicals that bring about the cross-linking of the long-chain rubber polymer (vulcanization). Sulfur is the traditional curative.
- **Accelerators and activators:** Chemicals such as zinc oxide that vary the speed and timing of the curing reaction.
- **Plasticizers:** Chemicals added to aid processability or to produce specified properties.
- **Antioxidants/antiozonants:** Chemicals added to help the compound resist surface attack, especially by ozone.

- **Process aids:** Substances that include resins, soaps, and low-weight polyethylene.
- **Reinforcing fillers:** Materials that increase the strength of the material. Carbon black and specialty silicas are the most common.
- **Fillers:** Relatively inert ground minerals used to increase the bulk of the compound. Ground calcium carbonate (GCC) and kaolin are the most common.
- **Pigments:** Minerals and chemicals added to produce specified colors. Only used with compounds that do not contain carbon black.

Curing or Vulcanization

Back in 1839, Charles Goodyear in the United States and Thomas Hancock in England found that heating a mixture of natural rubber and sulfur to 130°–140°C formed an elastic, nonsticky material with good mechanical strength that was insoluble in all solvents and did not soften further when heated. This process turned out to be the cross-linking of polymer molecules (i.e., the process in which the entangled chains are chemically linked together to form a network) known as curing, or, in more picturesque terminology, hot vulcanization. In the curing process, the compound is transformed from a plastic to elastic state, accompanied by the modification of the physicomaterial properties of the cured or vulcanized material. In particular, the product exhibits increased strength and elasticity and greater resistance to changes in temperature. At the same time, vulcanized rubber is impermeable to gases; resistant to abrasion, chemical action, heat, and electricity; and exhibits high frictional resistance on dry surfaces and low frictional resistance on water-wet surfaces (this in turn led to the invention of the pneumatic tire in 1877).

Subsequently, cold vulcanization (at room temperature) in the presence of sulfur chloride (S_2Cl_2) was discovered, along with a range of other chemical vulcanizing agents that can irreversibly

convert raw rubber from a plastic into an elastic material. These agents include selenium, tellurium, nitroderivatives, peroxides and hydroperoxides, diazoderivatives, or organometallic compounds, oxides, and modified phenol-formaldehyde resins. These vulcanizing agents have specific applications so that sulfur is a vulcanizing agent for natural rubber, polybutadiene, and butadiene-styrene copolymers, but it is not required in the vulcanization of polychloroprene or some specialty elastomers.

In the common hot vulcanizing process the vulcanizing agent is ground and mixed with the rubber and other dry ingredients; the proportion of sulfur to rubber varies from 1:40 in soft rubber goods to as much as 1:1 in hard rubber. In addition, most rubber products can be vulcanized under high temperature and pressure, often during the molding process. In some cases, the high pressures necessary for effective vulcanization are achieved by subjecting the rubber to external or internal steam pressure during heating (for example, garden hose may be clamped into shape and vulcanized by passing high-pressure steam through the opening).

Modern rubber curing systems vary both with the polymer type and with the property requirements of a particular application. Although native sulfur was the original curing agent, it now has a variety of competitors, including other forms of sulfur, peroxides, metal oxides, amines, and phenolic resins. In addition to the wide range of rubbers now in use, the rubber manufacturer has to deal with prevulcanization inhibitors (PVI) and antireversion chemicals.

Sulfur is the traditional and main vulcanizing agent. Utilization is mainly in the form of rubbermaker's sulfur, which is ground sulfur available in a range of purity with a uniform small particle size, generally in the range of 44–74 μm . Coarsely ground grades tend to be less dusty; finely ground grades have dispersion advantages. Additives may be included—for example, up to 2.5% of a conditioning agent may be added to improve flowability, handling, and dispersion characteristics of finely ground sulfur, and between 0.5% and 1.0% oil may be added as a dust suppressant to reduce the risk of a sulfur dust explosion. In cold vulcanization of soft, thin rubber goods such as gloves and sheeting, however, vulcanization is accomplished by exposing the uncured articles to the vapor of S_2Cl_2 manufactured by heating molten sulfur and chlorine gas to 240°C, followed by distillative purification.

Compounds that contain sulfur in a heat-labile form are used because they liberate sulfur at the vulcanization temperature. These so-called sulfur donors are subdivided into those that (1) exhibit an accelerator activity and can be substituted directly for sulfur without drastic change of the vulcanization characteristics [dithiodimorpholine, DTDM(I), and caprolactamdisulfide CLD(II)], and (2) are simultaneously vulcanization accelerators [2-morpholino-dithio-benzothiazole, MBSS (III); dipentamethylene thiuramtetrasulfide, DPTT(IV); and tetramethyl thiuramdisulfide, TMTD(VI)].

Accelerators and Activators

On its own, sulfur is a slow vulcanizing agent and increasing the amount of sulfur, temperature, and heating periods generates cross-linking inefficiencies. But through his research on rubber recycling in the early part of the twentieth century, the American chemist George Oenslager discovered that adding certain organic chemicals such as aniline and thiocarbanilide reduced the curing time and cut back on the oxidative degradation of the elastomers during vulcanization, thus improving the properties of the products or *vulcanizates*. Initially, these so-called vulcanization accelerators were confined to metallic oxides such as white lead and lime but they have since been expanded to include five major categories: guanidines, thiazoles, dithiocarbamates, xanthates, and thiurams. Of these, the guanidine-

type accelerators give the lowest rate of vulcanization as well as a relatively slow onset of vulcanization (scorch).

In general, these organic accelerators require activators to increase the efficiency of the accelerators by increasing the vulcanizing rate, reducing the vulcanization temperature, and improving the mechanical properties of the vulcanizates. Zinc oxide (ZnO) or zinc white is a popular and efficient activator because it leads to a decrease of the sulfidic cross-links while encouraging the formation of C–C bonds. The formation of these bonds in turn increases the thermal stability of vulcanizates. The very fine grades of zinc oxide in use contain a minimum of 99.5% ZnO and process a high surface area.

Product is manufactured by one of three processes: (1) the American process, where zinc oxide is obtained from the direct smelting of zinc ingot and the resulting zinc fumes are oxidized; (2) the French (or indirect) process, where zinc ash or dross is produced and sulfuric acid is used to vaporize it to zinc fumes that are then oxidized; and (3) the wet process, using precipitation from a carefully purified zinc-salt solution. In addition to activating sulfur cures, when dispersed into latex emulsion compounds, zinc oxide acts as a cross-linking agent for polymers containing halogen or carboxyl groups, such as chloroprene rubber (CR), brominated isobutylene-isoprene rubber (BIIR), chlorinated isobutylene-isoprene rubber (CIIR) or carboxylated nitrile butadiene rubber (XNBR), and carboxylated styrene-butadiene rubber (XSBR). Zinc oxide also has some pigmenting qualities.

Other compounds used as activators in rubber vulcanization are

- Magnesium oxide (MgO), which is mainly used with neoprene-type elastomers
- Litharge (PbO), which is less popular but still used along with thiazole-, dithiocarbamate- or thiuram sulfide-type accelerators
- Fatty acids, used as such or as zinc salts; these also improve the dispersion of zinc oxide. Examples include stearic acid, oleic acid, and dibutyl ammonium oleate.

Vulcanization Inhibitors/Scorch Retarders

Vulcanization inhibitors or scorch retarders such as MgO, salicylic acid, benzoic acid, acetylsalicylic acid, phthalic anhydride, N-nitroso-diphenylamine, or stearic acid are used to prevent premature vulcanization or scorching during processing. The concept is that the addition of a scorch retarder in the concentration range of 0.2%–1.0% extends the scorching period without decreasing the rate of the vulcanization process. This is particularly applicable where high-efficiency accelerators trigger the vulcanization process prematurely during processing; that is, mixing, preheating, extrusion, and calendaring (for the most part, scorching occurs during extrusion or in inner mixers where temperatures exceed 100°C).

Caustic calcined magnesia formed at 700°–1,000°C is chemically active and functions as an acid acceptor, vulcanizing agent, stabilizer, and curing agent in a variety of rubber and elastomeric compounds including neoprene, hypalon, natural rubber, styrene-butadiene rubber, viton, butyl rubber, chlorobutyl rubber, and fluoroelastomers. In addition, micronized, high-activity grades are used as scorch retarders in chloroprene and fluoroelastomers. Moderate-activity MgO is a scorch retarder and acid acceptor in diamine-cure fluoroelastomers.

Processing Aids

Processing aids used in the manufacture of rubber include plasticizers or softeners, antioxidants and antiozonants (antidegradants), and tackifiers.

Because the mixing of rubber compounds requires considerable energy, plasticizers or softeners are used to lower viscosity and thus reduce the energy required in fabrication. At the same time, these plasticizers—divided into chemical peptizers and physical plasticizers—may increase processing speed by improving melt stability. Typically added at 1–3 parts phr (by weight per hundred rubber), chemical peptizers such as sulfonic acids and pentachlorothiophenol reduce molecular weight by increasing the rate of oxidative chain scission. These chemical peptizers are used in the initial grinding or mastication of natural rubber. Physical plasticizers such as animal and vegetable oils, wool grease, fish oil, pine tar, and soya oil act to soften a compound by reducing entanglements and decreasing internal friction.

Other processing aids include mica used as a mold lubricant; magnesium sulfate used as a coagulating agent; ammonia used to prevent the coagulation of raw latex; salt to promote coagulation in emulsified latex derived from chlorinated butadiene and used in the production of neoprene, white, and buna rubber; and carbon disulfide (CS₂), used as a solubilizer.

Oxygen and ozone can react with elastomers and alter network structure by causing chain scission and/or cross-linking. Antioxidants and antiozonants inhibit the action of the degradants (and are therefore termed antidegradants) through a chemical or physical process. Chemical protectants such as amines, phenolics, and phosphites react with the degradant or interfere with the chain of reactions that causes degradation. Physical protectants such as various waxes function by migrating (i.e., blooming), thus forming a barrier to degradant attack.

Tackifiers are materials added to elastomers to improve tack; that is, the ability of two materials to resist separation after being in contact for a short time under light pressure. The function of tackifiers such as rosin derivatives that are typically added in the range of 1–10 phr is to increase initial tack and to prevent tack degradation after a stock has been processed.

Reinforcing Fillers

Reinforcing fillers increase the stiffness of unvulcanized compounds and improve a variety of vulcanizate properties such as tensile strength, abrasion resistance, and tear resistance. At the same time, stress values and hardness may be increased while elongation at break, rebound, and other properties (depending on the property) are lowered. A reinforcing filler has the ability to change the viscosity of a compound and the vulcanizate properties with an increasing amount of filler loading, whereas a nonreinforcing or nonactive filler such as GCC or kaolin (see section on Nonreinforcing Fillers in this chapter) slightly increases the viscosity of the compound and actually diminishes the mechanical properties of the vulcanizate.

To add significant reinforcement, filler particles must be of a small particle size (less than 1 mm), which generates a large surface area that can interact with the rubber and diminish particle-to-particle distance. At the same time, structure (irregularity in the shape of filler particles) and surface chemistry of the filler are critical because the extent and type of interaction between the filler and the rubber depends on functional groups on the filler surface. A filler with high structure has a large “void volume” within its structure, allowing rubber molecules to become “occluded.” This results in an occluded rubber-filler microcomposite that effectively becomes the reinforcing entity. Generally, high structure and strong bonding between the filler and the rubber increase reinforcement.

The two main commercial reinforcing fillers are carbon black and silica. Carbon black has an organic surface chemistry that makes the interaction between carbon black and the elastomer possible. In

contrast, silica has an inorganic surface chemistry that lacks a good interaction with the elastomer; therefore, silica fillers may be treated with silane coupling agents to chemically bond them to rubber. These fillers are available with a primary particle size as low as 100 Å.

Carbon Black

The traditional reinforcing filler in modern industrial rubber and tire manufacture has been carbon black, an intensely black, finely divided form of amorphous carbon in the form of spheres and their fused aggregates with sizes below 1,000 nm. This product is usually obtained by decomposing a hydrocarbon feedstock under precisely controlled conditions. For example, oil is heated above 2,000°F in a specially designed furnace where it “cracks,” producing a gas stream laden with carbon black powder. The gas stream passes through a series of filters, where the carbon black is separated as a powder, bound with water to create larger beads or granules, and dried. There are more than 100 commercial grades of carbon black characterized by spherical particles ranging from 10 to 100 nm that agglomerate into powders, pellets, and dispersions.

An estimated 70% of the world’s consumption of carbon black is used in the production of tires and tire products for automobiles and other vehicles, with an additional 20% going into sundry rubber products such as hoses, belting, mechanical and molded goods, and footwear. In general, carbon black accounts for about one quarter of the weight of a standard automobile tire. Tires used on vehicles requiring minimum electrostatic buildup, such as oil trucks and hospital operating carts, have even higher loadings. Nonrubber uses include plastics, ink, paper, and paint.

Precipitated Silica

Traditionally, precipitated silicas are used as reinforcement fillers in rubber applications. These products are made from a mixture of sodium silicate, sulfuric or hydrochloric acid, and metallic ions agitated to form precipitated silica with high brightness (97%), a 20-nm average particle size, and low porosity. Precipitated silica’s ultimate fine particle size generates a high surface area (25–700 m²/g) that allows for interaction with polymer chains. Precipitated silica is physically reactive when dispersed in silicone rubber, forming physical bonds with the polymer chains to enhance the vulcanized compound’s properties.

The rubber industry is the largest single consumer of precipitated silica, with the bulk used in the manufacture of tires plus a variety of industries including aerospace, appliances, medical, transportation, construction, electrical, and electronics. Rhône-Poulenc and Michelin pioneered the development of the so-called “green” tire in which between 5% and 25% of the carbon black is replaced with a highly dispersible silica (HDS, sometimes called “white carbon”) together with a bonding agent, usually a sulfur-bearing silane (i.e., silica-silane). The use of precipitated silica in the manufacture of tires as well as other technical rubber goods is based on the strengthening properties of silica, which provide tear and wear resistance. In tire manufacture, precipitated silica is used to

- Promote adhesion between brass-coated wire and fabric cord
- Alter stiffness in the bead area and thus increase the structural integrity of tires
- Reduce the tendency for “chunk out” of off-road tire treads through improved compound tear resistance (the chemical nature of the lattice structure is such that silica increases the energy required to propagate the tear, so adding 5%–8% silica increases the tear strength by 25%)
- Improve rolling resistance, wet traction, and other dynamic properties

It is claimed that green tires improve fuel efficiency by 5%–8% by reducing rolling resistance by up to 30%, compared with conventional tires filled with carbon black. This efficiency is achieved without sacrificing tread life, traction, or other properties. Silica-silane, however, costs approximately three times as much as carbon black, and there are increased compounding and processing costs. In addition, green tires tend to generate static buildup, although this can be countered through compounding and engineering modifications.

In the footwear industry, reinforcing silicas increases abrasion resistance and tear strength in rubber footwear and shoe soles. Because it is white, precipitated silica allows the formulator to produce either colored or translucent nonmarking soles. The silica provides superior durability and resilience while improving compound stiffness and modulus for all types of rubber-soled footwear. In industrial rubber, precipitated silica confers superior strength and durability on industrial belts and hoses, together with improved heat resistance and tear strength. The filler also improves adhesion in wire and fabric coat compounds and allows for rapid and easy processing, resulting in smooth finished surfaces in molded and extruded products.

In a related use, precipitated silica is used as a carrier to convert, for example, liquid plasticizers, process oils, and other rubber compounding ingredients to free-flowing powders for introduction into rubber compounds. This provides consistent loading performance and high absorption capability, making precipitated silica a more cost-effective carrier than mined products such as diatomaceous-earth-based calcium silicate.

Fumed (Pyrogenic) Silica

Formed from the hydrolysis of silicon tetrachloride in a hydrogen/oxygen flame reactor at 1,000°C, fumed or “pyrogenic” silica is a fine, particulate, amorphous silica composed of 7- to 20-nm spherical particles. This structure provides a high surface-area-to-volume ratio, and close control of the process parameters allows for the production of a number of grades that have specific particle sizes and particle-size distributions. Fumed silica is used for thickening, viscosity control, thixotropy, and reinforcement purposes in the rubber and other industries. For example, a loading of 6%–12% in silicone rubber products improves the mechanical strength of footwear, and 0.25%–3.00% in latex rubber increases the tear resistance of gloves, condoms, and the like.

Asbestos

In some asbestos paper, group 7 asbestos that is fiber coated with latex rubber via a chemical precipitation method forms a continuous sheet on a paper machine. This may be used as an underlayment for vinyl rolled floor covering or it can be densified for gasketing. Group 4 to 5 asbestos fiber blended with natural or synthetic rubber, plasticizers, and other ingredients in a high-shear mixer may be calendered to form sheet packing.

Nonreinforcing Fillers

The main nonreinforcing mineral fillers used in the modern rubber industry include the following:

- GCC and precipitated calcium carbonate (PCC)
- Kaolin and special clays
- Talc
- Mica
- Wollastonite
- Natural silica

- Barite and barium chemicals
- A variety of minerals such as diatomite, feldspar, nepheline syenite, gypsum, pyrophyllite, and zeolites

In addition to the minerals, oil extension of rubber, especially in tire treads, is common. Oil levels of 30–40 phr permit the use of elastomers with higher molecular weight and higher filler levels than would otherwise be possible.

Calcium Carbonate

Generally regarded as the most common and cheapest white mineral filler, GCC is used to reduce the cost of production. Dolomite may also be used and is preferred in certain circumstances, such as when there is a need for greater abrasion resistance. Ultrafine PCC adds strength without stiffness; acts as a white pigment; and generates smooth extrusions for wire and cable coating, footwear, and sporting goods.

Clays

Air-floated kaolin is a common function filler used in rubber products. This clay is processed dry simply by crushing, drying, and pulverizing, as well as by air flotation where kaolin is pulverized and separated from its abrasive “grit” mineral impurities on a moving column of air. Processing does not improve brightness and whiteness nor make significant improvements to particle size. Water-washed grades of kaolin are suited for extrusions where a low grit content is important and calcined kaolin is used in making heavy-duty insulation rubber. Overall, kaolin helps to stiffen uncured rubber and reinforce cured rubber, improving resistance to abrasion and tear and tensile strength, as well as to increasing the stiffness of the vulcanizate. The amount of reinforcement increases with smaller particle sizes of the filler so that the main characteristic of filler used as a reinforcement agent is a small particle size. There is a general division into hard kaolin used in nonblack rubber goods where high abrasion resistance is important, such as in shoe heels and soles, floor tiles and mats, wire and cable insulation, conveyor belts, and bicycle tires; and soft kaolin used in molded goods such as household products, toys, and rubber clothing.

Micronized sepiolite is a reinforcing filler in rubber compounds and acts as a processing aid by avoiding deformities during rubber extrusion when the rubber is in the green state.

Barite

Fine-grained (virtually all passing 325 mesh) barite is used as a filler in rubber and other products such as brake linings and clutch facings. As a functional filler, barite is white and relatively bright, chemically inert, relatively nonabrasive, resists weathering, has low oil absorption, and is dense. Related products are *blanc fixe* (reprecipitated chemically pure barium sulfate [BaSO₄]) and lithopone (a blend of 70% BaSO₄ and 30% zinc sulfide).

Barite is used as a filler in certain rubber products that must be weighty (automobile mud flaps, floor mats, rollers and their coverings, traffic cones) and/or chemically resistant (tank linings, industrial belts and hoses), or to impart sound-deadening qualities (insulation in automobile engine compartments). Rubber and rubber-covered rollers are used in numerous industries including paper, steel, textile, leather, and lithography, as well as for pressure functions such as inking or wringing and in typewriter platens. Loadings with barite may be around 20% by weight.

Silica

Silica sand ground to specific particle sizes forming ground silica or silica flour is used in certain rubber formulations, based on

whiteness, brightness of 84–91, hardness, inertness, low oil absorption, and low cost. Similarly, in the United States, tripoli (or the misnomer amorphous silica) is a friable microcrystalline silica with a natural average particle size of 0.1–0.5 μm . It is white (dry) to gray (wet) with an index of refraction of 1.550 and an oil adsorption (rubout method) of 17%–20%, making it useful as a filler in rubber and other products.

Other Fillers

Other functional fillers in the rubber industry include diatomite, talc, pyrophyllite, mica, wollastonite, nepheline syenite, and magnesite.

Diatomite's brightness of up to 90%, refractive index of 1.42–1.49, low bulk density, inertness, moderate refractoriness (softening range 1,400°–1,600°C), high absorptive capacity, and high surface area allow it to be used as a functional filler in rubber.

Talc is an extremely soft, nonabrasive, inert mineral that can be ground easily to form a low-cost, white and bright (>78 GE brightness), fine to micronized powder that acts as a white functional filler in rubber including carpet backing, valve rubber, and cable insulation. Additional advantages include its flaky habit (which allows for the ease of grinding), structural strength, pigmentation, opacity, rheology, viscosity, corrosion weathering resistance, and enhanced thermal properties. In addition, talc is used as a dusting agent and as a mold release agent for wires, cables, and in tire manufacture where it acts as a processing aid that lubricates molds and prevents surfaces from sticking together.

Pyrophyllite may be sufficiently white to be finely ground and used as a filler in certain rubbers. Agalmatolite, mainly produced in Brazil, is white, cream, or gray to greenish in color; is chemically inert; and has a brightness of up to 95%, a specific gravity of 2.7–3.0, and Mohs hardness of 2.5–3.0. These properties make it a useful filler in rubber.

Wet-ground and micronized mica in the 90- to 45- μm range retains its characteristic laminar crystalline structure. It is used as a specialized filler in rubber, as an antisticking and antifriction powder between the inner tube and casing of tires, and as a dusting agent and mold lubricant in rubber.

Wollastonite is used as a functional filler based on its acicularity, high brightness (90%–93%), chemical inertness, pH of 9.9, thermal stability and high melting point (1,540°C), good electrical insulation, and low moisture and oil absorption. It is particularly useful for increasing resistance to abrasion.

Nepheline syenite is used as a filler for improving resistance to staining, abrasion, and chemical attack, plus it has a high brightness and low tint strength and exhibits low viscosity at high pigment loadings. Specific examples of its use include silicone rubber automobile parts and neoprene rubber gaskets. It is categorized as generally recognized as safe (GRAS) for indirect food contact.

Ground natural magnesite and synthetic magnesium carbonate (MgCO_3) are white, relatively soft, and chemically inert powders used as fillers/pigments in rubber.

Fire Retardants

A number of minerals and chemicals used as fillers in rubber also serve as a flame retardant, smoke suppressant, afterglow suppressant, and/or antiarc/antitracking agent. For example, aluminum trihydrate or ATH [$\text{Al}(\text{OH})_3$], is a bright white powder produced as a by-product of the Bayer alumina process. ATH may be dried in hot air to form a white, bright, fine, and platy powder with good oil and water absorption properties and the ability to absorb UV light. Boron compounds melt during a fire to form a glass char barrier between oxygen and the burning surface. For example, zinc borate

($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$; trade name Firebrake ZB) is a leading fire retardant for interior uses such as carpet backing and exterior uses such as wire and cable covering.

Antimony oxide acts as the synergistic agent with halogens (chlorine and bromine), forming halogenated compounds with excellent fireproofing and fire-retardant properties with rubber and other products. Antimony oxide alone is not a fire retardant and the halogens are weak fire retardants, but a combination of approximately 3–4 parts of halogenated flame retardants to 1 part of antimony oxide on a weight basis generates a synergistic and extremely effective flame-retardant system for plastics. Styrene butadiene rubber, ethylene propylene rubber, and other elastomers can be flame retarded with halogenated compounds and 5%–30% antimony oxide. Polyurethane is flame retarded with a brominated hydrocarbon and up to 10% antimony oxide.

Pigments

Certain minerals and chemicals are added to rubber compounds that do not contain carbon black to produce specified colors. Most of the white functional fillers outlined previously—titanium dioxide, iron oxide, zinc oxide, lithopone, and a number of organic dyes, for example—are also pigments.

Titanium dioxide is regarded as the premier white pigment based on its high refractive index of 2.55–2.80, which provides good opacifying strength or hiding power, and its reflectivity, which generates brightness and whiteness (or “lightening power”). Other attributes include inertness and nontoxicity, chemical stability, resistance to UV degradation (color retention), tinting strength, and thermal stability over a wide range of temperatures.

Natural and synthetic iron oxides can be used as a pigment in rubber. Natural hematite, Fe_2O_3 , is a brown to red earthy mineral that is ground to a low-cost red pigment used in rubber. Natural reds such as Spanish, Indian, or Persian red, the most common of the iron oxide pigments, contain about 50% iron oxide as hematite with tinting strength increasing with $\alpha\text{-Fe}_2\text{O}_3$ content (up to 95%). Compared with natural iron oxides, synthetic iron oxide has superior uniformity, color purity (i.e., chroma), tinting strength, and tighter control over color consistency. Synthetics are used in rubber because the manganese content of naturals accelerates aging.

Chromic oxide green, a dark-green powder consisting of about 99% chromic oxide mixed with small amounts of cobalt oxide, is the most stable green pigment known, with strong resistance to light, heat, acids, and alkalis.

Forming

After compounding, the rubber may undergo calendering where it is squeezed between rollers, forming sheets of the desired thickness, with or without impressed designs such as tire-tread markings. Some times “blanks” are cut from the sheet, like pasty cutting. Alternatively, the warmed rubber compound may be squeezed or extruded through a shaped die to form flat, tubular, or specially shaped pieces such as window and door sealers. Any reasonable length of shaped material can be produced and fed, once cooled, into direct injection presses. At the same time, rubber can form a coating on fabric and be molded.

In contrast, foam rubber is manufactured directly from latex by mixing in emulsified compounding ingredients and whipping mechanically in a frothing machine to produce a foam comprising millions of air bubbles. The foam is poured into molds and vulcanized by heating to form mattresses, seat cushions, and so forth. In addition, latex toys or gloves may be manufactured by dipping porcelain or plaster-of-paris forms into concentrated latex that adheres to the form and is stripped off after vulcanization.

The basic processes of molding are compression, transfer injection, and direct injection. In compression molding, uncured rubber of a given size is placed between two halves of a heated mold that is closed in a press under a pressure of about 1 st/sq in. and the rubber is forced into the exact shape of the cavity. The rubber gains heat by conduction from the mold surfaces and, given sufficient time, “cures.” This is a relatively simple process used for components with simple shapes required in fairly low quantities. Some secondary finishing is required, however, to remove the flash or excess rubber formed by the blank in a process known as “deflashing.” In transfer injection, the heated mold is closed in a press and the rubber injected by a hydraulic cylinder through a feed hole in the cavity that has a means to allow air to escape. This method yields high-precision parts produced in moderate quantities without high tooling costs. In the simplest case, the mold can be the same as a compression mold with the addition of a feed hole. With direct injection, a screw injection system delivers a metered quantity of rubber into the closed mold from a continuous strip or a reservoir of uncured rubber, then is cooled to a void premature curing. This process, which is utilized for multicavity molds, can produce hundreds of components per press cycle, and is also suitable for relatively large quantities of products that have a large number of cavities and infrequent changes of materials or molds. Parts are repeatable and can be made to a high level of precision.

Finishing

Where necessary, the method of deflashing depends on the shape and size of the component and the type of rubber used. For example, in subzero finishing that uses modern cryogenics, parts are frozen to temperatures as low as -120°C and then tumbled and/or bead-blasted to remove the brittle flash. In tear finishing, the system is set to produce flash sufficiently thin to be torn off at the press during demolding. Hand-finishing includes buffing, in which the parts are smoothed using a variety of abrasive belts, wheels, and mops; and cutting, in which a range of tools from precision steel knives to scissors are used to die-cut parts.

PROPERTIES OF RUBBER

Although most commercial applications of rubber are based on the ability to provide elastic properties across a wide range of temperatures, the combination of various types of rubber and compounding gives a diversity of properties:

- Utilization over a temperature range from -80°C to $+300^{\circ}\text{C}$
- Availability in a wide range of colors
- Electrically insulating, conductive, or antistatic
- Withstands extremes of weather and outdoor environments indefinitely
- Withstands exposure to fuels, oils, and chemicals while retaining its properties
- Ability to be rendered flame-retardant and self-extinguishing, with halogen-free and smoke-suppressant types available
- Maintains tension and compression forces indefinitely; e.g., in seals
- Conformable, adaptable, and accommodating of movement, shock, thermal changes, tolerances, and roughness
- Absorbs vibration and noise and acts as an insulator
- Can be gas tight and used as a fluid seal or separator
- Possesses low thermal conductivity and can be used to reduce heat transfer
- Friction properties similar to human skin and comfortable to grip

- Surface may be clean and smooth, which is nonstick and suitable for hygienic applications
- Compatibility with other engineering materials such as metals, plastics, and ceramics, and can be combined with these through bonding.

USES

Although native South Americans used rubber before the Spaniards arrived, the first widespread commercial application was the opening of a waterproof cloth and rainproof garment plant in Glasgow in 1823 by the British inventor and chemist Charles Macintosh; hence the name for the practical garments. Since then, the types of rubber and compounds have increased dramatically along with the range of everyday applications. At one end, resistance to abrasion makes softer types of rubber ideal for the treads of vehicle tires and conveyor belts. At the other, hard rubber may be used for pump housings and piping where abrasion could be problematic. Rubber's flexibility is applicable to hoses, tires, and rollers, and its elasticity translates into shock absorbers and machinery mountings designed to reduce vibration. Because it is relatively impermeable to gases, rubber is used to manufacture air hoses, balloons, balls, and cushions; and its resistance to water and to the action of most fluid chemicals is utilized in everything from rainwear and wet suits to flexible tubing and tank lining. Electrical resistance allows soft rubber to be used in protective gloves, shoes, and blankets, and hard rubber to be used in various parts in electrical instruments. Rubber's coefficient of friction, which is high on dry surfaces and low on wet surfaces, leads to its use both for power-transmission belting and for water-lubricated bearings in deep-well pumps.

Tires

The feedstock for tire manufacturing may include up to 30 different kinds of rubber, plus process oils, carbon black, pigments, antioxidants, accelerators, and other additives. This is mixed in giant blenders called Banbury machines that operate under tremendous heat and pressure to form a hot, black, gummy compound. This compound, in addition to cord fabrics and bead wire, is shaped and cured in a curing press at $>300^{\circ}\text{F}$ for 12 to 25 minutes depending on size. According to Goodyear Tire and Rubber Company, a P195/75R14 all-season passenger tire, the most popular size, weighs about 21 lb and is composed of the following approximate amounts of these materials:

- 4 lb of eight types of natural rubber
- 5 lb of eight types of carbon black
- 1 lb of steel cord for belts
- 1 lb of polyester and nylon
- 1 lb of steel bead wire
- 3 lb of forty kinds of chemicals, waxes, oils, pigments, etc.
- 6 lb of five types of synthetic rubber

Typical percentages of synthetic rubber and natural rubber in various types of tires, respectively, are 55% and 45% in passenger tires, 50% and 50% in light-truck tires, 65% and 35% in racing tires, and 20% and 80% in off-highway (giant/earthmover) tires.

Rubber Production

Modern natural rubber production can be traced back to 1876 when the British explorer Sir Henry Wickham smuggled seeds of *H. brasiliensis* out of Brazil, successfully germinated them in the hot-houses of the Royal Botanical Gardens in London, and established plantations in Ceylon (now Sri Lanka). Subsequently, the British developed commercial rubber plantations within a narrow equatorial

belt in the eastern hemisphere. Natural rubber production in India, Ceylon, the Malay Peninsula and Archipelago (now Malaysia), and the Dutch East Indies (now Indonesia) peaked prior to World War II, when supply was halted. The resulting shortage encouraged the development and use of synthetic rubber, which had previously been restricted to specialty use because of the high price. In particular, the U.S. government launched a \$700 million program in the 1940s to establish synthetic-rubber production plants that succeeded in, among other things, bringing the price of synthetic rubber down to that of natural rubber. Since that time, synthetic rubber production has increased rapidly, becoming the dominant form of rubber currently manufactured.

Synthetic rubber was developed in Germany during the 1930s in order to make up for a deficiency of supply of natural rubber and for natural rubber's functional defects. The United States was cut off from virtually all sources of natural rubber in the Pacific during World War II. To meet the nation's needs for this vital material, the government built synthetic-rubber production plants and the rubber industry operated them. Synthetic rubber production jumped from 8,000 t in 1941 to 820,000 t in 1945. After the war, the government sold the plants to private industry.

World rubber consumption is approximately 20 Mt, more than three quarters of which is synthetic. The vehicle sector (tires together with components) uses about 70%–75% of all rubber. The tire industry is estimated to grow at a slightly slower pace than other rubber industries. Globally, most rubber products are consumed in North America, Western Europe, and Japan. The growth rate, however, is faster in China and other countries in the Asia-Pacific area.

Synthetic rubber comprises about 60% of the total volumes. Approximately 44% of synthetic rubber and 77% of natural rubber are consumed by the tire industry (see Table 2). Of synthetic rubber types, styrene-butadiene rubber is used the most. Ethylene propylene diene, however, has a faster growth rate. The fastest growing demand is experienced by thermoplastic elastomers, which are materials with properties falling between those of traditional rubbers and thermoplastics.

GOVERNMENT, ENVIRONMENT, AND HEALTH

Rubber and the products used to manufacture it have come under intense scrutiny by regulatory authorities because of concerns about potential environmental and health effects. The increasing use of precipitated and other forms of silica in rubber brings up the usual concerns about silicosis. Zinc compounds, considered harmful to aquatic environments, could be released in the effluent generated during the manufacturing process, through wear (especially tires), by extraction from rubber products in contact with water such as pipe seals or faucet washers, or after disposal in landfills. The problem is that elimination would require a change in rubber vulcanization technology and the substitutes (lead, cadmium, and mercury) are unacceptable.

There are increasing government-imposed restrictions on the use of volatile organic compounds (VOCs) in the rubber industry and in other industries that make use of a large quantity of solvents. For example, a European Union (EU) Directive on solvent emissions adopted in March 1999 aims to reduce VOC emissions throughout Europe by 1.5 Mtpy. The main use of VOCs is for rubber-to-metal bonding, including metal cleaning and solvent-based adhesives. These are being replaced, however, by aqueous adhesives that may include silane-coupling agents for specific assemblies.

Another problematic ingredient is the distillate of aromatic extracts (DAE) that are used as extenders and softeners in rubber compounding. These oils contain relatively high levels of poly-

Table 2. North American tire sales

Company	Sales, million \$
Goodyear Tire & Rubber Co.	6,500
Michelin North America Inc.	5,800
Bridgestone-Firestone Inc.	4,000
Cooper Tire & Rubber Co.	1,700
Continental Tire North America Inc.	1,600
Yokohama Tire Corp.	500
Toyo Tire (USA) Corp.	400
Kumho Tire USA	350
Hankook Tire America Corp.	250
Pirelli Tire North American	235
Carlisle Companies Inc.	225
China Manufacturers Alliance	185
GTY Tire	180
Ohtsu/Falken	160
Cheng Shin/Maxxis International	140
Titan Wheel International Inc.	135
Sumitomo Tire	130
Hulera Tornel S.A.	125
Denman Tire Corp.	75
Specialty Tires of America Inc.	65

cyclic aromatic hydrocarbons (PAHs), and some are classified as a Category 2 carcinogen by the EU Dangerous Substances Directive. These must be labeled R45, "may cause cancer." Manufacturers (especially of tires) are under increasing pressure to eliminate DAE from their products.

TRENDS AND OPPORTUNITIES

World rubber consumption is forecast to reach more than 21 Mt by 2006, with tire production reaching 1.3 billion units based on strong gains in the global vehicle industry combined with replacement needs within a steadily rising global motor vehicle inventory. Traditionally, growth in rubber consumption has been driven by the automobile industry, with production concentrated in industrialized regions such as North America, Western Europe, and Japan. These regions should experience modest growth, however, as manufacturing expands in Asia and to a lesser extent in Africa, the Middle East, Eastern Europe, and Latin America. Automobile output in Asia reached almost 22 million units in 2003 or some 36% of worldwide production. The top five automobile-manufacturing countries in Asia—Japan, China, South Korea, India, and Thailand—account for 90% of total region production capacity with future growth expected to be largely centered in China, Thailand, and Vietnam.

The need to improve fuel consumption rates may encourage the use of precipitated silica in OEM tires. Replacement tires, however, do not have to comply with Corporate Average Fuel Economy (CAFE) standards and the like, a fact that may dampen the increased use of precipitated silica in aftermarket tires. Historically, many aftermarket tires were retreads, but because modern tires are so light and thin-bodied, retreading has decreased greatly in the passenger-tire market. At the same time, tire rubber demand will benefit from the continuing popularity of performance tires and sport utility vehicles in many developed countries, raising the amount of rubber incorporated into new tires and vehicles. Performance tires also have shorter service lives relative to all-season radials, thus stimulating replacement demand.

According to the Freedonia Group, the nontire rubber market will grow to become the dominant market for rubber by about 2006. This growth will be driven by increased demand for mid-range elastomers (e.g., ethylene-propylene, nitrile, and polychloroprene) in numerous types of industrial rubber products such as hoses, belts, gaskets, and weatherstripping.

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Filters and Process Aids

Sharad Mathur and SA. Ravishankar

Process aids enable the desired results from a process to be achieved. The filtration process, for example, uses filters to remove dissolved and particulate matter from suspension to purify, clarify, and clean liquids. Absorbents are a convenient way to handle liquids and to clean up liquid wastes or spills. Rheological modifiers change the flow behavior of formulations such as paints, cosmetics, and inks. Lubricants allow for mold detachment that results in smooth surface finish. Binders are process aids that improve mechanical integrity of beads to enable better flow, for example. Finally, proppants are beads that help create and keep open the cracks caused in oil and natural gas bearing rocks to allow access to these raw materials from the surface.

The underlying phenomenon behind the action of the various process aids can be either chemical action or mechanical action or both. Mechanical action is derived from physical properties of the particles, such as size, size distribution, shape, surface area, and hardness, whereas chemical action is derived from surface chemical properties that are either native to the material or modified in a controlled manner. Filtration or absorptive processes are accomplished either mechanically, as in absorption and filtration, or chemically, as in adsorption. Rheology modifiers typically use both the chemical and mechanical forces.

Table 1 shows a number of processes, end-use applications, and minerals and rocks that are used as process aids.

This chapter focuses on the industrial minerals and rocks used as process aids for filtration, absorbents, rheology modification, and proppants. The selection of the minerals and markets reviewed was based solely on the total volume of material used or the value of the market and material. The materials include diatomite, perlite, sand, gravel, glauconite; specialty clays such as kaolinite, montmorillonite, and attapulgite; and their modified forms such as activated montmorillonite or surface-treated montmorillonite and kaolinite. Throughout this chapter the term *specialty clays* is used to describe clays used in such value-added markets.

RAW MATERIALS

On a volume basis, the most common industrial minerals and rocks—sand and gravel, along with diatomite—are used as filters and absorbents. High-quality sand finds more value when used as proppants. High value-added applications such as pet litter absorbents and edible and inedible oils filtration and clarification use specialty clays.

Table 1. End-use applications, processes, and the minerals and rocks that are used as process aids

Process	End-Use Application	Process Aid
Filtration	Liquid food products	Perlite
		Diatomite
	Water treatment	Perlite
		Diatomite
		Glauconite
	Petroleum and chemicals	Perlite
Absorption	Pharmaceuticals and drugs	Diatomite
		Perlite
		Diatomite
	Pet litter	Perlite, diatomite, attapulgite
	Oils and grease spills	Attapulgite
	Pesticides and fertilizers	Attapulgite
Rheology modification	Plastics	Montmorillonite, kaolin
	Paints	Attapulgite, kaolin
	Paper coatings	Bentonite
	Inks	Kaolin
Pressurization (proppants)	Petroleum and natural gas	Sand, kaolin, bauxite
Binding		Attapulgite
Lubrication		Attapulgite

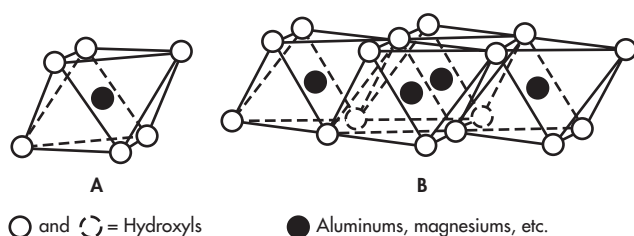
MINERALOGY

The common mineralogical trait of almost all industrial minerals used as process aids is that they belong to the silicate group. Silicates have an inherent chemical stability, unique molecular structures, and surface activity that can be used as is or modified for a given application. These characteristics enable the silicates to be used as process aids. Silica (SiO_2), the common chemical constituent, exists by itself in nature as an inert crystalline form as quartz or in an amorphous form such as diatomite. The fundamental building block of both forms is the SiO_4 tetrahedra. By combining with other chemical groups and rearranging the SiO_4 tetrahedra, a multitude of silicates, including specialty clays, are obtained in nature with varying physical and chemical properties.

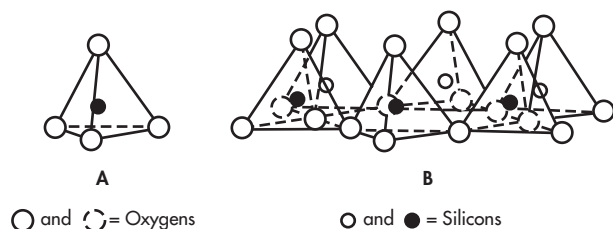
Table 2. Classification of the major specialty clays used as process aids

Clay Group/Principal Mineral	Synonymous Term	Theoretical Chemical Formula
Smectite (three-layer structure)		
Montmorillonite	Bentonite (fuller's earth)	$(\text{OH})_4\text{M}^{+0.66}\text{Si}_8(\text{Al}_{3.3}\bullet[\text{Mg}_{3.3}\text{ to Na}_{0.66}])\text{O}_{20} + \text{H}_2\text{O}$
Calcium montmorillonite	Nonswelling bentonite	Same formula as montmorillonite where M^+ is generally Ca^{2+}
Sodium montmorillonite	Swelling bentonite	Same formula as montmorillonite where M^+ is generally Na^+
Lithium	Hectorite	$(\text{OH})_4\text{Si}_8(\text{Mg}_{5.34}\bullet[\text{Li}_{0.66}\text{ to Na}_{0.66}])\text{O}_{20}$
Hormite (chain structure)		
Palygorskite	Attapulgite (fuller's earth)	$(\text{OH}_2)_4(\text{OH})_2\text{Mg}_5\text{Si}_8\text{O}_{20}\bullet 4\text{H}_2\text{O}$
Sepiolite		$\text{H}_6\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_{10}\bullet 6\text{H}_2\text{O}$
Kaolin (two-layer structure)		
Kaolinite	Kaolin	$\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8$

Adapted from Clarke 1985.



Source: Van Kouteren 1994.

Figure 1. Geometric representation of octahedron showing (A) a single octahedral unit and (B) the sheet structure of the octahedral units

Source: Van Kouteren 1994.

Figure 2. Geometric representation of silica tetrahedron showing (A) a single silica tetrahedron and (B) the sheet structure of the silica tetrahedrons arranged in a hexagonal network

Diatomite and Perlite

Although the mineralogy and origin of diatomite and perlite are very different, they have a physical trait in common that yields excellent filtration properties: both have cell structures that form microscopic voids, which aid in filtering by allowing the passage of fluids while retaining the solid particulate matter.

Diatomite is a chalk-like, soft, friable, earthy, very fine-grained, siliceous sedimentary rock, usually light in color. Diatomaceous silica is the preferred name for the principal mineral component. It is the fossilized skeletal remains of the diatom—a unicellular, microscopic aquatic plant related to algae (Kadey 1983). The silica of the fossilized diatom skeleton closely resembles opal or hydrous silica and has the chemical formulation $\text{SiO}_2 \cdot n\text{H}_2\text{O}$.

Naturally occurring perlite, on the other hand, is a dense, amorphous, hydrated (2% to 6% combined water) volcanic glass, generally of rhyolitic composition. It has a dual nomenclature in the industry because of its commercial applications. It is known by the same name as both the naturally occurring rock and, after processing and thermal expansion, as the lightweight aggregate (Kadey 1983).

Specialty Clays

Compared to other minerals used as process aids, the clay minerals are much more mineralogically complex. As a general definition, clays are naturally occurring, earthy, fine-grained hydrous silicates (Patterson and Murray 1983). Collectively, they are classified as phyllosilicates, a group of silicate minerals characterized by silica-oxygen tetrahedra linked together in two-dimensional sheets (Thrush 1968). Their uses in value-added applications may require extensive beneficiation to improve purity and control physical characteristics. Montmorillonite and attapulgite are known by their mineral name for the raw material as well as the final product. Montmorillonite is the principal mineral constituent of bentonite, and the two terms are used synonymously in the industry. Kaolinite, on the other hand, is known by the ore-body name kaolin for the end-use product.

The phyllosilicate group of clays consists of several minerals, each having different geologic occurrence, mineralogy, technology to beneficiate and engineer to its final form, and uses. The three major clay mineral groups, which account for the majority of the volume of clays used as process aids, are the smectite, hormite, and halloysite clay groups. Table 2 lists these clay groups, commonly used names, and mineralogical compositions. Although the mineralogy is complex, it is easier to think of these minerals as containing crystal structures that can be broken down into two simple building blocks: tetrahedra and octahedra. These building blocks form sheets or layers by joining at the corners (tetrahedra) or at the edges (octahedra) (Moll and Goss 1987), as shown in Figures 1 and 2.

Given these basic building blocks, the distinguishing structural difference between the different types of specialty clays is the arrangement of these blocks to generate layered and chain types of silicates.

Smectite Group

Two members of the smectite group, montmorillonite and hectorite, are used as process aids. Smectite minerals have a three-layer structure. Two outer layers of silica tetrahedra are attached to a central octahedral layer of hydrous metal oxide (usually aluminum, sodium, magnesium, calcium, or lithium). The layers are combined

in such a way that the oxygen atoms at the tips of the tetrahedra of each silica layer are shared with the octahedral metal oxide/hydroxide layer. A small proportion of the metal cations in the central octahedral layer is replaced by cations of lower valence but similar size. This leads to an electrical charge imbalance that is corrected by the presence of cations held outside and between each of the three-layer units. The electrical charge deficiency of the three-layer units and the presence of the exchangeable cations (commonly sodium or calcium) impart the characteristic expansion properties to the smectite group of clays (Clarke 1985).

Palygorskite and Sepiolite (Hormite) Group

Palygorskite (attapulgite), which is used primarily as an absorbent, is based on the hormite group. Sepiolite, a related mineral, is also used to a limited extent. Hormites are markedly different in terms of their structural characteristics in that they form chain-type rather than layered structures, which result in a fibrous morphology (Clarke 1985). Unlike the smectite minerals, which have sheets that extend laterally, the sheets in hormite minerals extend only a short distance and then flip up or flip down in a continuous pattern to yield a three-dimensional structure that includes long tubes instead of layers. Because of this structure, hormite minerals do not swell as do smectite minerals. Crystal lattice substitutions, or exchange capacity, however, do occur at the broken bonds on the edges of the crystal (Moll and Goss 1987).

Kaolin Group

Kaolin is the principal industrial mineral used as a process aid based on this group. This group consists of minerals that form a two-layer structure. The two layers comprise tetrahedral and octahedral sheets. The tetrahedra contain silicon and oxygen and the octahedra contain aluminum, oxygen, and hydroxyl, arranged in sheets (Figures 1 and 2). The apices of the tetrahedra join with the octahedra to form the two-layer structure with water molecules between the two layers. These sheets generally are neutral, except on the edges where broken bonds create unbalanced charges. These sites are areas where cation exchange can occur (Moll and Goss 1987).

Sand and Gravel

In the strictest sense, these two materials are defined by size rather than by composition or mineralogical makeup. Sand and gravel consist of separate grains or particles of detrital rock with a particular size range of $1/16$ to 2 mm in diameter. For filtration and proppant applications, however, sand consists mainly of pure, rounded quartz (SiO_2) grains (Davis and Tepordei 1985), and gravel typically consists of rock fragments.

Glaucanite

Glaucanite is a hydrous iron potassium silicate containing varying amounts of aluminum, calcium, magnesium, sodium, and numerous trace elements such as beryllium, cobalt, chromium, nickel, molybdenum, vanadium, titanium, and uranium. It has the chemical formula $3X_2(\text{Fe}^{+3}, \text{Fe}^{+2}, \text{Y})_6(\text{Si}_4\text{O}_{10})(\text{OH})_4 \cdot n\text{H}_2\text{O}$, where X is K^+ , Na^+ , or Ca^{+2} , and Y is Al or Mg. Its exchangeable sites are on the outside of the silica–alumina–iron framework, and the exchange reaction generally does not affect the glaucanite structure. Both cations and anions are exchangeable, but little information is available on the latter (Spoljaric 1994).

Minor Minerals

Other minerals used as process aids include vermiculite, talc, ball clay, bauxite, crushed limestone, gypsum, ilmenite, and garnet. Vermiculite, talc, and ball clay are also in the phyllosilicate group.

As a consequence, these minerals, especially vermiculite, are commonly used in certain absorbent applications. Such heavy minerals as garnet and ilmenite (and sometimes anthracite coal) are often used as filter media in wastewater treatment plants. Calcium carbonate (especially as lime) and gypsum are two nonsilicate minerals that find limited applications as filters, absorbents, and rheology modifiers. Bauxite is used as the raw material to produce superior-performing proppants to sand.

CHEMICAL AND PHYSICAL PROPERTIES

Silica or silicon dioxide, the main constituent of process aids, is responsible for their chemical stability. Physical characteristics such as high amount of porosity resulting from micropores allow for efficient filtration and absorbent materials. Good mineral filters and absorbents thus are chemically stable and have high porosity that allows liquids to either flow through or be retained in the structure. In addition to immobilizing the water, high aspect ratios of specialty clay particles such as needle-like (attapulgite) or plates (montmorillonite) play a critical role in modifying rheology of suspensions and pastes. Chemical modification of montmorillonites to result in an organoclay or acid-activated form enables application as rheology modifiers and sorbents, respectively. Round-grain deposits of high-purity sand are used to maximize the permeability and strength for proppant application. Thus it is not surprising that the minerals used as process aids in a given application have a number of similar chemical and physical properties. Table 3 shows chemical analyses of the major materials used as process aids.

Diatomite and Perlite

Minerals used as filtration aids typically are lightweight, structurally rigid, chemically stable, and chemically inert, and they form high-porosity filter cakes to maintain free flow of the liquid. Both diatomite and perlite have such characteristics. The major differences between these minerals, however, are in density and flow rate. Perlite is typically less dense or weighs less per unit of volume and thus yields additional filtering capacity per unit weight (Van Kouteren 1994).

Diatomite

The diatom structure, which provides high surface area, low-bulk density (floating on water at least until saturated), high absorptive capacity, and relatively low abrasion, consists of openings or pores at regular intervals, which in turn result in a very open lattice (Kadey 1983). The pore structure can account for about 50% of the volume of a diatom, which is typically only a few micrometers in thickness and 50 to 150 nm in diameter (Miles 1990).

Perlite

Perlite is known for its unique internal cellular structure, which forms on heating and subsequent expansion. The integrity of the cellular structure is dependent on the source rock. Hard perlites, which have coarse cell walls, are relatively dense and thus are typically used as aggregate. Soft perlites, which have finer cell walls and are less dense, are typically used as filtration aids (Kadey 1983).

Specialty Clays

The layer and chain structures, combined with cation-exchange characteristics, are responsible for specialty clays' unique chemical and physical properties. Clays are platy, are extremely fine grained, have flexible crystals with large surface areas, are naturally reactive, and have a house-of-cards structure (Moll 1986). During heating and the subsequent release of water, the clay's structure maintains its integrity. Structural integrity is responsible for the

Table 3. Typical chemical composition of the major industrial minerals and rocks used as process aids

Mineral Type (Oxides), %	Sand*	Diatomite†	Perlite‡	Attapulgitese§	Montmorillonite**	Kaolinite††	Glauconites
SiO ₂	99.45	89.7	72.1	54.0	50.2	44–46	46.9–52.9
Al ₂ O ₃	0.05	3.7	13.5	8.6	16.2	36–39	5.8–15.2
H ₂ O	ND††	ND	3.0	21.4	22.7	14	4.3–7.2
Loss on ignition	0.07§§	3.7	ND	ND	ND	ND	ND
Fe ₂ O ₃	0.02	1.1	0.8	3.1	4.1	0.3–1.0	9.3–24.1
TiO ₂	0.01	0.1	0.1	0.2	0.2	0.3–2.0	0–1.8
CaO	0.04	0.3	0.9	2.0	2.2	0.5	2.1
MgO	0.02	0.5	0.5	10.1	4.1	0.5	2.3–4.6
Na ₂ O and K ₂ O	ND	0.7	9.0	0.4	0.3	0.8	Traces–1.9
							5.1–9.3
P ₂ O ₅	ND	0.2	ND	ND	ND	ND	1.0–6.3
Other	0.34	ND	0.1	0.2	ND	ND	10.52
Total	100	100	100	100	100	100	100

* LaSalle, Illinois (Murphy and Henderson 1983).

† Lompoc, California (Kadey 1983).

‡ No Agua, New Mexico (Kadey 1983).

§ Attapulgis, Georgia (Patterson and Murray 1983).

** Polkville, Mississippi (Patterson and Murray 1983).

†† Macon, Georgia (Patterson and Murray 1983).

‡‡ ND = not determined.

§§ Fusion loss.

clay's low bulk density, high liquid-holding capacity, and high absorptivity (Moll and Goss 1987).

Glauconite

Glauconite grains range in size from 1 mm (coarse sand) to the sub-micron and develop different shapes. The largest percentage by weight is 0.49 to 0.125 mm in size. Grains are usually smooth and round. Like other layer minerals, glauconite has the capacity to absorb ions from solution. Ion exchange is important in chemical separations, water softening, and the properties of soil for both agriculture and engineering (Spoljaric 1994).

Sand and Gravel

The important chemical and physical characteristics of sand and gravel used as filters are chemical inertness and proper particle shape and size. As filter media, the removal of particulate matter is a function of both media size and filter bed depth. Optimal packing of sand grains, which are supported by the gravel, occurs in filtration applications when a high proportion of the sand particles are rounded and tend toward a generally spherical or equidimensional shape (AWWA 2002). When used as proppants, the sand has tighter requirements for its physical characteristics.

DISTRIBUTION OF MAJOR DEPOSITS

United States

The United States contains major deposits of all the industrial minerals and rocks used as filters and absorbents. In fact, the diatomite, kaolin, attapulgite, and sand deposits are world class in terms of size and purity. These deposits, however, occur in select areas of the country. Diatomite and perlite deposits are in the West, the specialty clay deposits are in the South, and sand and gravel deposits occur in all regions. The biggest disadvantage in regard to deposit location and market demand is that diatomite and perlite are mined

in the West and the demand is concentrated in the Midwest and the East.

Diatomite and Perlite

All of the commercial deposits of diatomite and perlite occur in the western United States. Diatomite is currently mined in California, Oregon, Washington, and Nevada. California and Nevada are the principal producing states; they accounted for 79% of U.S. production in 2002 (Dolley 2004).

New Mexico accounts for the majority of perlite mined in the United States, with the remaining portions mined in Arizona, California, Colorado, Idaho, and Nevada. Given that expanded perlite has a very low bulk density and that the majority of perlite is consumed in the East, crushed perlite ore is typically transported to expander plants, which are located close to major end-use markets (Meisinger 1988).

Specialty Clays

Commercial deposits of nonswelling or calcium montmorillonites are, for the most part, in Texas, Mississippi, and Alabama, which account for the majority of calcium montmorillonite. The swelling or sodium montmorillonite deposits are primarily in Wyoming, South Dakota, and Montana. Florida and Georgia account for all the attapulgite production. Sepiolite primarily occurs in Nevada. Hectorite is mined in California and Nevada. Georgia accounts for a majority of high-class deposits of kaolin.

Glauconite

The most important glauconitic greensands are developed in the Mid-Atlantic Coastal Plain. Glauconite is found as an accessory mineral in many coastal plain sediments of New Jersey, Delaware, and Maryland, but highly glauconitic greensand is best developed in Upper Cretaceous and Lower Tertiary formations.

Table 4. Key properties for diatomite and perlite used as filters

		Density, kg/m ³		Relative Flow Rate [*]	Ignition Loss, %	Medium Pore Size, μm
		Wet	Dry			
Diatomite						
Flux calcined	White	330	220	700–2,300	0.2	15.0
Calcined	Pink	375	140	100–430	0.5	3.5
Natural	Gray	260	105	<100	2.5	2.0
Perlite	White	300	120	170–930	3.0	Unknown

Source: Van Kouteren 1994.

* Water permeability flow ratio (basis: Grefco's Dicalite 215 as 100).

Sand and Gravel

The occurrence of sand and gravel deposits is pervasive throughout the United States. From a strictly geologic view, the quantity of sand and gravel is essentially inexhaustible (Dunn 1983). Although this is true for gravel used in filtration, it is not true for sand. The sand used in filtration and proppant applications has rigid specifications as to the purity, size, and shape of the individual grains. As a consequence, the major deposits that naturally yield such material are limited to locations in northern Illinois and central Texas (Van Kouteren 1994).

Other Parts of the World

A review of the U.S. Bureau of Mines mineral production statistics indicates that no one country dominates in producing materials used as filters and absorbents. A number of countries, however, are major producers of these raw materials.

Diatomite and Perlite

The production of filter-grade diatomite in the rest of the world is concentrated mainly in such European countries as France, Spain, and Germany. Korea, Romania, and the former U.S.S.R. are all large producers, but they are believed to have very limited, if any, production of filter grades. For perlite, nearly 80% of the production outside the United States is concentrated in Hungary, Greece, Turkey, and the former U.S.S.R. Perlite production has increased significantly in Greece at the expense of western states in the United States. Several developmental projects are under way in China and other Asian countries (Barker, Santini, and Alatorre 2003).

Specialty Clays

Production of specialty clays occurs mainly in Brazil, Canada, and Mexico. Europe and the Pacific Rim are also major producing areas, with Germany, Greece, Italy, Japan, Malaysia, and Turkey accounting for most of the production.

Glaucanite

Glaucanitic greensands are developed on all continents and have been geologically mapped in many countries. At some locations, glaucanite is the most abundant constituent of the formation. In most cases, however, it is present in relatively small amounts or as a minor component of the sediment (Spoljaric 1994).

Sand and Gravel

Given that the geologic occurrence of sand and gravel deposits is pervasive, sand suitable for filtration applications exists in many countries. The location and production of sand from these deposits are closely correlated to the location of population and industrialized areas (Bolen 1988).

TECHNOLOGY

Processing and Specifications

Diatomite and Perlite

The most important processing aspect for these materials is maintaining the integrity of the diatom cell walls and the expanded perlite cellular structure. After processing, these materials are subjected to filtration tests that measure flow rate through a filter cake under controlled conditions and the clarity of the resulting filtrate (Kadey 1983). Because of the difference in physical structures of perlite and diatomite, their performance varies from one grade to another. Table 4 lists the performance and specifications for these materials.

Diatomite. The degree of processing is highly dependent on the desired physical and chemical properties needed by the end-use industry. Depending on the desired filtration flow rates, diatomite is sold in three different forms: natural, calcined, and flux calcined. The natural products have the higher densities, smaller median pore sizes, and lower flow rates. Calcination of natural products yields less dense, larger median particle sizes, and, consequently, higher flow rates (Van Kouteren 1994).

Diatomite cannot be subjected to intense crushing or grinding; thus, it is crushed in spiked rolls and hammer mills, passed through air cyclones, and then fed to air separators to yield various sizes (Miles 1990). Material at this stage is classified as natural diatomite. For faster flow rates, the natural material is heated in rotary calciners to burn away both organic residues and the combined water that is part of the opaline structure. As a result, the diatom structure shrinks and hardens, and many of the diatom fragments are sintered into agglomerates (Kadey 1983). This heating process yields calcined products, which are usually for medium flow rate grades and typically are pink because of the oxidation of iron during the heating.

Filtration applications that cannot tolerate the presence of iron oxide or applications that require faster flow rates use flux-calcined diatomite products (Anon. 1987). These products are formed by adding a flux, usually soda ash or sodium chloride, before the sintering or calcination stage. The flux allows iron oxides to enter a glassy phase in which it is colorless and produces greater agglomeration of the diatom fragments. Variations in the kiln temperature, the amount and composition of the flux, and the heating time in the kiln enable suppliers to create products with differing filtration rates (Miles 1990).

Perlite. Perlite is used in its expanded form in filtration applications. The application for which it is intended plays a major role in the particle size range into which the material must be crushed and sized before expansion. Crude perlite ore is crushed with jaw crushers and impact milling and then sent to vibratory screening and air classification to separate the milled material into basic

Table 5. Key properties for select specialty clays used as absorbents

Grade	Color	Bulk Density, kg/m ³	Surface Area, m ² /g	Free Moisture, (110°C), %	Base Exchange Capacity ^a	pH
Attapulgite						
RVM	Gray	545	125	7	20	8.0
LVM	Tan	545	125	2	20	8.0
Other [†]	Cream	275	120	1	na [‡]	8.5
Montmorillonite						
Acid activated	na	640	250	16	na	3.2 [§]

Source: Van Kouteren 1994.

^a Milliequivalents/100 g.

[†] Powdered grade.

[‡] na = not available.

[§] 25 g of product in 75 mL deionized H₂O.

grades. The size range of the expanded perlite dictates the size of the furnace feed (Kadey 1983).

During heating, perlite particles reach a softening range, coincident with the volatilization of combined water at about 800°C. As a result, the particles can expand or pop in a manner similar to popcorn with the creation of countless tiny bubbles. The lightweight cellular aggregate that forms is 20 times or more the original volume of perlite. During the heating process, a good balance between the softening of the glass and the volatilization of the combined water must be maintained. If not, excess combined water will cause some perlites to explode with the subsequent production of fines. In contrast, insufficient water or an overly viscous glass will result in partially expanded, higher density perlite (Kadey 1983).

On expansion, the perlite is then milled and classified to a specified size and density. The perlite bubble aggregates must be broken into curved glass platelets and bubble junctions. Filter aids require the right proportion of these with a minimum of unmilled cells. Residual unmilled cells, or floaters, are undesirable in filter applications (Kadey 1983).

Specialty Clays

The processing of specialty clays for use in absorbent applications is fairly similar for attapulgite, hectorite, and montmorillonite. Because clay ore may contain up to 60% water, the main objective for processing is to remove water and to reduce the material to the appropriate size. Before the crude clay is dried, it must first be passed through shredders to reduce it to fist-sized pieces for feed to a dryer (Moll 1986).

Proper drying techniques are essential for developing and maintaining the open structure in montmorillonite and attapulgite. Between 100° and 200°C, water in the interlayer region of montmorillonite or in the tubes of attapulgite begins to evaporate. At higher temperatures, certain tightly bound water molecules in attapulgite begin to evaporate. Between 500° and 800°C, the hydroxyl ions begin to combine to form water, which leaves the structure (Moll and Goss 1987).

Once the clay is dried, the material is typically crushed in corrugated roller or hammer mills and passed over large shaking screens. Oversize material goes back to the crushers, and undersized material goes to the next set of smaller sized screens to make products of increasingly smaller granule sizes. These smaller products are typically destined for the pet litter and floor absorbents markets (Moll 1986).

Kaolin is processed either in a dry state (air-float grades) or in a slurry state (water-washed grades). The water-washed grades are

extensively beneficiated and thus contain less impurity, have higher degree of whiteness, are less abrasive, and have tight control on particle size distribution. Hydrous kaolin can be heated to eliminate the hydroxyls from the structure and thus resulting in calcined grades.

Absorbents. The key properties for clays used as floor absorbents are proper granule size, low bulk density, the ability of the product to absorb liquids readily and rapidly, and durability so that the granules do not break down in normal shipment and use (see Table 5). Floor absorbents, mainly used for oil and grease, are sold in sizes ranging from 4.00 to 0.43 mm. The other key properties typically are a bulk density of about 625 kg/m³ and the ability to absorb about 65% to 100% of their weight in water or oil (Moll 1986).

In cat litter, the pH and the granule size are the important factors that affect the clay's performance. Low-pH products are more effective in controlling the fermentation of urea in cat urine. The size of clay granules is important so as to avoid dustiness in use and to avoid tracking by the cat. A common size range for cat litter products is often 4.75 to 0.60 mm (Van Kouteren 1994).

Carriers. Specialty clays used in pesticide, fertilizer, and other carrier applications often require further drying. Products that do not undergo additional heating, called regular volatile material (RVM), are typically softer and dispersible in water. Low volatile material (LVM), however, undergoes additional heating to result in a moisture content of less than 3% compared to 7% in RVM products (Ross 1983). These products tend to be harder and far less dispersible in water because of the tightening of the interlocking crystals of the clay caused by further heating (Moll and Goss 1987).

Another key property is surface acidity, also known as Lewis acidity. The surface acidity of the clay granules can degrade some chemicals absorbed into the granule. To prevent the degradation, formulators must measure the strength of the Lewis acid sites to determine how much deactivation is required. High surface acidity clays, measured by the Hammett acidity function unit (pK_a), are deactivated with alcohols or glycols to neutralize the acid sites (Moll and Goss 1987). Table 6 gives examples of the important end uses for carrier minerals.

Filtering and Clarifying. Acid-activated montmorillonite clays used for filtering and clarifying or bleaching vegetable and petroleum oils are an important part of the market. Although the tonnage of acid-activated clay is relatively small, it represents one of the highest value products.

Treating calcium montmorillonite clay with HCl or H₂SO₄ yields a modified clay product with significantly greater surface

area and acidity. The acid-activated clay offers enhanced absorptive and catalytic properties. These products, commonly called bleaching clays or bleaching earths, are not to be confused with fuller's earth, which is processed only by drying and grinding. Acid-activated clays are processed by predrying the clay to remove excess moisture. The material is then mixed with either HCl or H₂SO₄ to form a clay–water slurry that is then transferred to a reaction vessel. Once inside the vessel, it is heated to near boiling by steam or other means until the desired degree of activation has been achieved (Taylor and Jenkins 1986).

Generally, physical factors such as particle size and porosity along with surface acidity determine the suitability of a particular activated clay to perform in a particular environment. Small particles and larger pores are usually preferred when large molecules are involved (e.g., vegetable oils) and diffusivity limits transport of a molecule to an active site. Another consideration, more chemical than physical, is the strength of the acidity associated with the sorbent/catalyst. In some cases, excessive functionality may be detrimental. For example, strong acid sites can catalyze undesired reactions (e.g., disproportionation of toluene to benzene and xylene; Dombrowski and Henderson 1997).

Rheology Modification. Naturally occurring clay minerals such as hectorite and bentonite (sodium montmorillonite with some nonclay impurities) are hydrophilic in nature. When dispersed in water, the clay particles swell and separate into individual clay platelets. Because of platelet interaction, a three-dimensional “house of cards” structure is developed. This colloidal structure provides thickening properties. In oil or solvent systems, however, the natural clays do not disperse and do not provide rheological properties. To thicken oil and solvent systems, the hydrophilic clays are modified with various types of hydrophobic quaternary ammonium compounds. To make an organoclay, the smectite clay is reacted with a quaternary ammonium compound. The quaternary amine ion (Cl[−]) exchanges with the sodium cations on the surface of the clay. The resultant product is an organoclay, where the organic component is firmly bonded to the clay surface. During this reaction, the salt produced is washed out. Supplied as powders, the organoclays are in the form of agglomerated platelet stacks. A combination of wetting and mechanical energy is needed to deagglomerate these platelet stacks. Adding a polar group containing materials like low-molecular alcohols, water, or propylene carbonate help force the clay platelets further apart, resulting in a completely dispersed rheological structure (Braun and Rosen 2000).

In recent years, organoclay-type products have been improved to increase the ease of dispersability of these products. The new types of organoclays offer a more open structure compared to the conventional organoclays. The open structure helps dispersability of the product under low shear and short processing times and eliminates the milling stage of the ink manufacture. In most cases, the overall throughput is improved by reducing the production cost (Braun and Rosen 2000).

Glaucanite. Processing at Sewell, New Jersey, involves first screening crude, mine-run green sand. Approximately two thirds of the crude is recovered as −1.0+0.25 mm feed for the production of manganese greensand for use as a water filtration medium. Washing with water and chemical treatments with an intervening freshwater rinse cycle follows the screening to build a manganese dioxide coating on the glaucanite. This coating is the active agent in removal of iron, manganese, and hydrogen sulfide from well water. The coated glaucanite is dried and packed in 0.03-m³ bags or 1-t supersacks, palletized, and stretch-wrapped for shipment (Spoljaric 1994).

Table 6. End uses for industrial minerals and rocks used as filters and absorbents

Absorbents	Industrial
Hazardous wastes	Alginates
Oil and grease	Catalytic reactions (hydrogenation)
Pet litter	Cellulose liquors
Water	Electroplating
Waxes and varnishes	Dry cleaning
	Metalworking industries (coolants, cutting oils, etc.)
	Nonedible oils and greases
	Nylon and rayon liquids
	Soaps and glycerine
	Synthetic resins
	Varnishes and lacquers
Carriers	Metallurgy
Fertilizers	Cyanidation
Pesticides	Metal extraction (Be, W, others)
Chemicals	Recovery of metal values
Acids (sulfuric, phosphoric, organic)	Uranium processing
Dyestuffs and intermediates	
Inorganic-general	
Organic-general	
Solvents	
Sulfur	
Titanium pigments	
Desiccants	Petroleum
Documents	Contact filtration (clay removal)
Electronic packaging	Dewaxing
Equipment storage	Greases and lubricants
Food packaging	Hydraulic fluid
	Jet fuel
	Oil well pressurizing
	Petrochemical
	Still residues
	Used oils (crank case, transformers)
	Waxes
Drugs and Pharmaceuticals	Waste Disposal
Antibiotics	Paper mill effluents
Cosmetics	Sewage
Enzymes, serums, vitamins, etc.	Radioactive (underground injections)
Pharmaceuticals	Laundry waste waters
	Industrial wastes, general
Food Products	Waters
Beverages (beer, wine, whisky)	Industrial
Corn products (sugar, glucose, oil)	Military (potable, engine condensate)
Fruit products (apple, grape, citrus)	Municipal
Miscellaneous (casein, dairy products)	Super-clarified (electronics, beverages)
Oils and fats (vegetable, animal)	Swimming pools
Packing house products	
Sugars (cane, beet, plantation, etc.)	
Yeast	

Sand and Gravel

The mining and processing of sand and gravel vary considerably with the type of deposit and the physical and chemical requirements of the desired product. Gravels are typically quarried or dredged and processed by screening. Sand is typically hydraulically mined because of the friable nature of the deposits (Van Kouteren 1994). The sand slurry is purified in cyclones where clays and other impurities are removed. The material is then drained and placed into fluid-bed dryers. After drying, vibratory screens, gyratory screens, mechanical or air classifiers are used to yield various sizes and size distributions (Davis and Tepordei 1985).

The American Water Works Association (AWWA) has prepared standard specifications for sand and gravel to cover such water filtration applications as surface water, sewage disposal, industrial waste, and swimming pools. The main specifications include freedom from organic matter, silt, minerals that fracture or deteriorate,

and acid-soluble components, and minimum specific gravity requirements (Severinghaus 1983). Filter gravel should contain a high proportion of particles that are rounded and tend toward generally spherical or equidimensional shape. For sand, the grains must be rounded or angular, very durable, and have a uniformity coefficient of 1.7 or less. The required size of sand and gravel is a factor of the viscosity of the filtrate, the type of contaminant, and the flow rate desired. Sand size typically ranges from 0.35 to 0.65 mm and gravel ranges from 2 to more than 60 mm (AWWA 2002).

Proppants have the same requirements of sand as in filtration except that high purity and integrity is required to deliver crush resistance to high pressures present in the oil and gas wells up to 2,400 m deep.

TESTING

As is common with most industrial minerals, the testing procedures by which processed minerals and aggregates are evaluated and standardized are designed to quantify an attribute required in the performance of a product (Kadey 1983).

Filtration

The two important characteristics that filter aids must produce are clarity and flow rate. A filter aid grade, then, must be subjected to a filtration test under controlled conditions. The test will measure how efficient the filter aid is in obtaining the required clarity at a reasonable flow rate.

Diatomite and perlite suppliers provide such bench-scale pressure or vacuum filtration tests as the bomb filter, Buchner funnel, and Walton filter. These tests help to determine the best balance of variables to obtain required clarity, maximum throughput, and minimum filter aid dosage. Before laboratory filtration tests, materials are tested for such physical properties as particle- and pore-size distribution, turbidity, and surface area. Wet and dry bulk densities are also important because diatomite and perlite are purchased on a weight basis and used on a volume basis (Severinghaus 1983).

The use of sand and gravel in the filtration of surface and wastewaters requires tests for acid solubility, sand and gravel shape, specific gravity, and particle size to ensure proper quality. AWWA, the American National Standards Institute (ANSI), and the American Society for Testing and Materials (ASTM) have established standard tests for these properties. For details on the testing procedures, contact either AWWA or ASTM (AWWA 2002).

Absorbents

For absorbents, the important characteristics to measure include clay's ability to absorb liquids easily and quickly, to have a high liquid-holding capacity, to have granules that do not break down during shipment, and to have relatively low bulk densities. Standard tests and techniques to measure a granule's maximum absorption and resistance to attrition are outlined by federal specifications. In addition, agricultural carriers undergo a liquid-holding capacity test. The Rhone-Poulenc method MP-12 is a test that measures the amount of liquid the granules can absorb without sticking together (Moll 1986).

Particle-size distribution, surface and titratable acidity, concentration of minor components, moisture level, and degree of leaching are all properties that make one acid-activated clay different from another, and these nuances are major considerations in selection of the right grade (Dombrowski and Henderson 1997). In filtering and clarifying applications, the final color of the bleached oil is the critical property. Test methods for evaluating montmorillonite and other types of fuller's earth for bleaching edible oils are outlined in the American Oil Chemists' Society (AOCS) Official

Method Cc 8b-52 and AOCS Official Method Cc 8a-52 (Patterson and Murray 1983). These specifications contain instructions on bench-type tests, including stirring time, heating rates and temperatures, approved equipment, quantities of clay and raw oil required, and other items (Patterson and Murray 1983).

Rheology Modifiers

The selection of the rheological additive is dependent on the application as well as the composition of the formulation ingredients such as solvents, binders, extenders and pigments, and the nature of their interactions. The viscosity profile in Figure 3 illustrates the relationship between shear rate and other important properties of two different paint formulations. Settling, sag, and leveling occur at low to ultralow shear rates. Package appearance and stirred consistency are determined by rheological behavior at medium shear rates. Application usually occurs at high shear rates (Elementis 2002).

Viscometers with well-defined geometry such as capillary, cone and plate, coaxial cylinders, falling balls/needles/rods, or cup is used for testing rheology. A great range of such equipment was designed over the past several years. These range from equipment with well-defined geometries capable of providing shear stress data at well-defined shear rates to equipment without such capability. The former type is highly useful for measurement of Newtonian fluids as well as non-Newtonian types; the latter types are equally useful to the practical rheologist and for quality control. There are many situations where it is possible to obtain a reproducible set of numerical data that correlates with some critical aspect of product formulation, behavior, or control (Braun and Rosen 2000).

Proppants

The critical properties for sand, or bauxite- and kaolin-based beads, to be used as proppants are as follows:

- Size—coarser size is better to improve permeability but needs to be optimized to ensure that transportation is not prohibited.
- Shape—equidimensional shape is better to enable improved porosity and thus permeability and withstand load. Thus only Ottawa and Jordan sand are deemed fit for use as proppants.
- Concentration in the suspension—higher concentration results in improved permeability.
- Strength—higher strength allows for use in deeper wells.
- Density—for given concentration in the fracture, there is proportionate decrease in propped fracture width for a denser proppant.

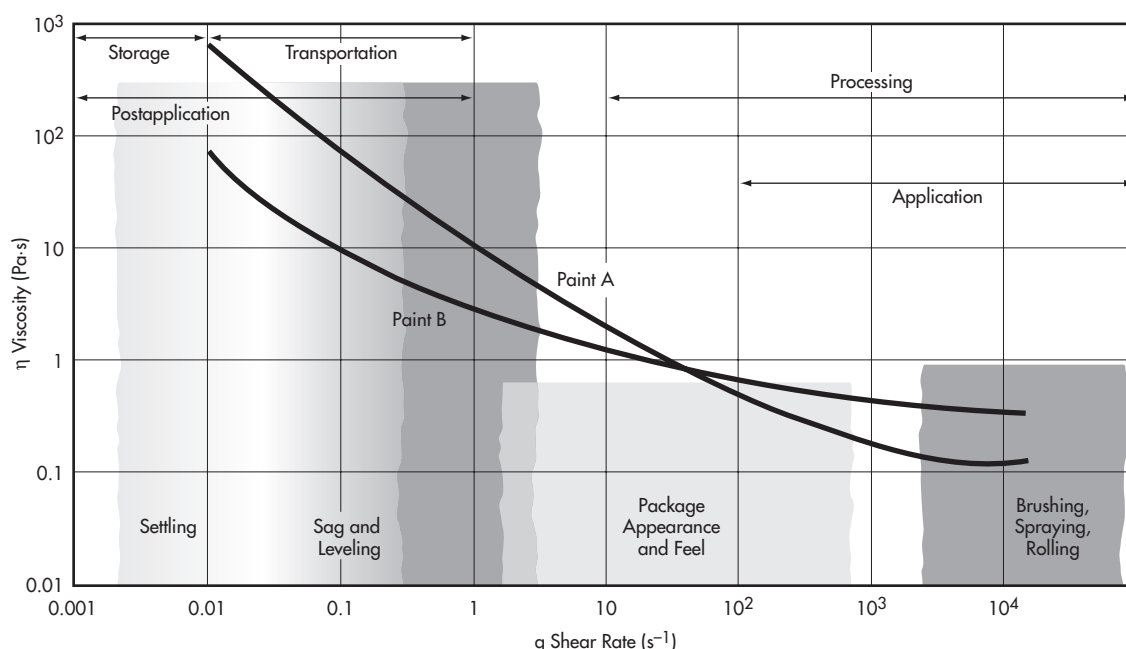
USES

Industrial minerals and rocks are used in many process-related applications, as shown in Tables 1 and 6. On a tonnage basis, however, the majority of these minerals, including sand, diatomite, perlite, attapulgite, and montmorillonite, are used in such end uses as municipal waters, food products, chemicals, pet litter, oil and grease, and carriers.

Filtration

Filtration is commonly referred to as the separation of solid particulate matter from the solvent media via use of a porous medium. Minerals comprise only a small part of the total market for materials used in the filtration of liquids. Such materials as membranes, cartridges, fabrics, and centrifuges account for the majority of the materials (Rees 1990).

The main mechanisms of filtration that use minerals are depth filtration and cake filtration. In depth filtration, solids are trapped



Source: Elementis 2002.

Figure 3. Relationship between shear rate and other important properties of two different paint formulations

within the medium using such granular media as sand. In cake filtration, solids are separated from the liquid by forcing the liquid to flow through a porous medium, such as diatomite or perlite, and depositing the solids to form a filter cake (Thrush 1968).

Depth Filtration

The major applications that utilize depth filtration are municipal water facilities that process surface water and sewage. These consumers use sand, anthracite, and, occasionally, gravel to remove impurities from water and other liquids. Gravel, however, is generally used—primarily in water treatment facilities—as a support media for the filtration sand (Van Kouteren 1994).

In depth filtration, the filter media is the portion of the filter bed that removes particulate matter from the water. The removal of particulate matter is typically a function of both media size and filter bed depth, and removal generally improves with greater depth or smaller media size or both. Selecting filter bed depth and media size is typically a function of the raw water conditions, plant pretreatment facilities, and designer preference. Therefore, the bed depths, particle sizes, materials, and the number of mediums vary widely plant to plant (AWWA 2002).

Most sand filters, or single-medium filters, are horizontal beds of carefully graded grains beginning with coarse particles to form the bed and becoming progressively finer toward the top layer (Severinghaus 1983). For improved overall performance, dual- or multimedia filters have been used instead of single-medium filters in many water treatment applications, and in some cases high specific gravity filter media, usually garnet or ilmenite, are used to remove more suspended solids at higher filtration rates (AWWA 2002).

Cake Filtration

Cake filtration uses a filter aid that controls the flow and amount of solids removed from the liquid. Filter aids form a porous layer

known as the filter cake on the septum, which may be cloth, screen, porous stone, or metal. The filter cake on the septum traps solids from suspension and prevents them from blocking the septum.

Good filter aids require a suitable particle size and shape to achieve optimum cake permeability, particle retention on surface versus depth, minimum flow resistance, good cake release, and relatively low cost. Because cake filtration is a mechanical process, the structure of the particles must be such that they will not pack too closely. For example, diatomite's skeletal structure and irregular-shaped particles interlock to leave 85% to 95% voids. These voids form billions of microscopically fine interstices in which suspended particles can be trapped (Anon. 1991) and are responsible for filtration flow rate and the final filtrate clarity.

The selection of the proper grade of filter aid in cake filtration depends on the size of the suspended particles to be removed. As the particle size and thus the flow rate increase, the ability of the filter aid to remove small particles of suspended matter decreases. Conversely, as filter aid particle size and flow rate decrease, the ability of the filter aid to remove small particles of suspended matter increases (Kadey 1983).

The two major types of filters used to remove solids from food products, chemicals, petroleum, and drugs and pharmaceuticals are pressure filters and rotary filters. The most common types of pressure filters include horizontal tanks with rotating leaves, sluicing filters, tube or candle filters, horizontal plate filters, vertical tank or vertical leaf filters, and the filter press. Pressure filters are used for many different types of applications; for thick, difficult-to-filter liquids or when solids content is high, however, vacuum rotary filters are typically used.

Pressure Filtration. Filtration in a pressure filter is a two-stage operation. First, a thin protective layer of filter aid called the "precoat" is built up on the filter septum by recirculating a filter aid slurry. This slurry is either diatomite or perlite and the liquid. The mixture continues to circulate until the liquid becomes clear, which

is when a precoat bed about 2 mm thick has been established and filtration is ready to begin (Anon. 1985).

The next step is called the body feed because, as the liquid is pumped through the filter, small amounts of filter aid are constantly fed into the liquid. As filtering progresses, the filter aid mixed with the suspended solids from the unfiltered liquid is deposited on the precoat. Thus, a new filtering surface is continuously formed (Anon. 1985).

Body feed rate is increased or decreased depending on the turbidity of the unfiltered liquid. As filtration proceeds, the volume of the cake increases until the solids trapped in the bed cause the flow to drop to an unacceptable level or the pressure to increase to an unacceptable level. At the end of the cycle, the filter is opened, cake is removed from the septum, and a fresh precoat is established for another cycle (Anon. 1985).

Rotary Vacuum Precoat Filters. As mentioned previously, these filters are generally used only where a large percentage of suspended solids is to be removed. A rotary vacuum precoat filter consists of a horizontal drum, of which 30% to 50% is submerged in a filter bowl containing the unfiltered liquid. This drum is covered with a septum capable of retaining a filter aid. Vacuum is applied to the surface of the drum by means of internal piping (Anon. 1985).

In operation, a precoat of diatomite or perlite up to 150 mm thick is built up on the drum by revolving the drum under vacuum in a filter aid slurry. After the precoat is built up to the desired thickness, unfiltered liquid is introduced into the filter bowl. As the drum rotates, a blade running across the face of the drum above the liquid level continually advances toward the drum. This peels off the solids plus a very small amount of precoat, thereby presenting a new precoat surface for the next submergence. This continues until the knife is within 6 to 10 mm of the drum, at which time the drum is cleaned and precoated again (Anon. 1985).

Absorbents

Consumer

Specialty clays in the pet litter market have proved to be very effective in absorbing liquid pet waste and related odors. They can absorb large quantities of liquid cat waste and retard the formation of ammonia, which is created when urea from cat urine ferments (Harris and Eckert 1989).

Industrial

Any user of oil and grease or machinery requiring oil and grease may ultimately require specialty clays to absorb and control spills. Slippery films of oil and grease and puddles of water and other chemicals often create dangerous conditions on the floors of machinery repair shops, factories, service stations, and numerous large and small industrial facilities (Harris and Eckert 1989). Specialty clays can absorb up to their own weight in oil, grease, water, and a variety of other chemicals. The clays also are safe, absorb rapidly, and can be cleaned up with a broom or shovel (Moll 1986).

Carriers

Specialty clays used as mineral carriers have a wide variety of applications in the field of agricultural chemicals. Most pesticides, including herbicides, fungicides, and insecticides, are highly toxic and typically require only a kilogram per hectare (Moll 1986). The primary function of these carriers is therefore to dilute high-potency chemicals to a spreadable field concentration so that they can be applied to a location where the pest can be destroyed but

damage to desirable plants, wildlife, and the environment is minimized (Swayer 1983).

The two main types of mineral carriers are absorbent and non-absorbent. The absorbent carriers, which account for the majority of demand, provide a highly porous structure that accounts for their high absorptivity and low density. The nonabsorbent types provide only surface area to carry the chemicals and typically have high bulk densities, which limits the amount of chemicals they can carry. Montmorillonite, attapulgite, and diatomite are the absorbent carriers. Minerals such as ball clay, calcium carbonate, quartz sand, and talc are considered nonabsorbent (Moll and Goss 1987).

Clays are also used as anticaking additives in dry fertilizer mixes. The anticaking function of the clay works by coating fertilizer particles and absorbing solvents or water that may be present. This reduces the formation of crystals that often bind particles and cause caking problems (Harris and Eckert 1989).

Filtering and Clarifying

Acid-activated montmorillonite clays and attapulgite clays (also called bleaching clays or fuller's earth) are used to filter and clarify such liquids as edible and in edible oils, petroleum products, and beverages. Although filtration is a part of the process, selective adsorption plays a major role in clarifying these products. Bleaching or clarifying these products is necessary to remove organic pigments from plant oils, sulfur compounds from mineral oils, and contaminants from fuel and lubrication oils (Anon. 1968).

The two main methods used for commercial bleaching are contact and percolation. The contact process is commonly used in refining edible oils and consists of mixing clay (0.5% to 3.0%) with the crude oil and heating the slurry to about 80° to 120°C for about 15 min. The slurry of clay and oil is then filter-pressed to remove the clay (Anon. 1968).

The percolation method, which is also a filtration process, is generally used to clarify lubricating oils. Granular clay is placed in a column and oil is then trickled through the clay by way of gravity. To obtain maximum efficiency, the viscosity of the oil is lowered by heating or dilution. This allows the oil to penetrate the minute pores of the clay. At the end of the cycle, the clay is washed with naphtha, steamed, and burned in a rotary kiln to regenerate the adsorbent, which then can be reused (Anon. 1968).

Other Markets

The most significant other absorbent market for specialty clays is desiccants and catalysts. Clay desiccants are used to adsorb moisture from the air enclosed in such packaged products as military equipment and electronic components. This helps prevent corrosion of the product and retards the formation of mildew. The desiccants are calcium montmorillonite clays that are oven dried, crushed, and packaged in bags or canisters. These products are most effective in conditions of moderate relative humidity (15% to 40%) and are generally preferred because of their ability to adsorb more than 20% of their equivalent weight in water without any apparent change in size, shape, or texture. Furthermore, they are also available at a relatively low cost (Harris and Eckert 1989).

Acid-activated montmorillonite clays are unique in that these possess not only high solid acid properties but also regular pore openings of about 20 Å. This latter feature is not found on zeolites or molecular sieve catalysts. This combination permits acid-activated montmorillonite to be used in various catalyst applications such as manufacture of silicone oils used in sealants. Acid-activated montmorillonite is also used as a catalyst in esterification, dehydration, and alkylation processes (Dombrowski and Henderson 1997).

Rheology Modifiers

Specialty clay additives are added to formulations primarily for rheological control. Dispensing viscosity and flow properties can be customized by using one of these clay additives in a formulation. These products provide unique rheology without the ropiness or tackiness often encountered with gums or other thickeners. Associated functions of these clay additives are emulsion stabilization and solids suspension. These clay additives can also be used as carriers for therapeutic or medicinal compounds. A variety of clay additives provide virtually all water-based and solvent-based consumer products with unique rheological properties and superior stability.

Applications in personal care, cosmetics, and pharmaceuticals are numerous, for example, facial masks, color cosmetics, moisturizing lotions, medicated creams, hair conditioners, and sunscreens. The unique rheological properties provided by these clay additives are ideal for products that are applied topically. Applications in household, industrial, and institutional cleaners are also numerous. The specialty clay products can also be used to create formulations that adhere to surfaces with a minimum amount of dripping or sag. These products can be used in a wide pH range and are compatible with bleaches. Common applications in these areas include hard surface cleaners, toilet bowl cleaners, bleach cleaners, oven cleaners, metal polishes, and laundry products (Braun and Rosen 2000).

Organoclays, prepared by exchange of sodium ions of the montmorillonite with the organic compounds, are used in oil-based paints, in high-temperature grease, in oil-based drilling muds, and in inks (Braun and Rosen 2000).

Proppants

Hydraulic fracturing is a technique used to allow oil and natural gas to move more freely from the rock pores where they are trapped to a producing well that can bring them to the surface. The fracturing is accomplished by pumping a highly viscous fluid containing sand particles into the well bore. The extent of the fracture is controlled by the characteristics of the geologic formation, its depth, the fluid type, and pumping pressure. When the fracture reaches the shale above (or below) the geologic formation being fractured, it will stop; shale does not fracture easily. A hydraulically created fracture will always take the path of least resistance, which means staying within the formation that fractures most easily. Hydraulic fractures typically extend 250 to 750 ft from the wellbore. The fracture initiates from the wellbore and extends out in two wings in opposite directions. Therefore, the total distance of the fracture from tip to tip is 500 to 1,500 ft, with the wellbore located in the middle.

To carry sand horizontally for 250 to 750 ft, a viscous fluid is used to keep the proppant in suspension during its journey through the fracture. After the operator has completed the fracture job, the viscous fracturing fluid needs to be removed from the reservoir so that the oil or gas molecules can move easily through the fracture. After all, the operator doesn't want a thick fluid similar to instant pudding in the sandstone or coal reservoir; it would just block the pathways to the wellbore. With this in mind, fracture fluids are designed to "break down" after the job has been completed. The break-down technology has improved dramatically over the years. For example, when a predetermined amount of time passes after the fluid has been pumped, the viscous fluid begins to thin. Typically, the fluid will break down until it has the relative consistency of water, so it can easily pass through the propped fracture into the wellbore for production to the surface. The only substance intended to remain downhole is the sand proppant. The fluid used to carry the proppant is pumped into the well but then is recovered once the job is complete. The process of creating these fractures sounds complex, but, in reality, it relies on the laws of nature and takes

only a few hours. The actual time spent pumping fluid into the well depends on the formation, the fluid type, and the depth, but it can be as little as 30 min. The fluids themselves are the product of extensive research to develop the right combination of ingredients to efficiently create fractures, prop them open, then return the carrier fluid to the surface to open the way for oil or gas to flow. The appropriate fluid depends on the formation being fractured.

Hydraulic fracturing is a safe, effective, and valuable tool for increasing the recovery of oil or gas. Many oil and gas formations cannot be economically produced without fracturing. By creating a "highway" with a fracture, the hydrocarbon molecules are more inclined to "travel" to the wellbore, increasing production and helping oil and gas producers meet growing demands for energy (IOGCC 1999).

INDUSTRY STRUCTURE

As with most other mineral-based industries, the industry structure determines the competitive environment in which the seminal process aids are sold. The four major factors that determine the industry structure are

1. The concentration of the supply and the demand side of the business
2. The barriers to entry
3. The availability of substitutes or not-in-kind products that can compete on a cost performance basis
4. Deposit quality and technology with the existing suppliers

These major factors play a significant role in the profitability of suppliers of minerals and rocks to this industry.

Industry Concentration

Supply

Because of the limited number of high-quality deposits, a few suppliers control the supply of the minerals.

Diatomite and Perlite. The perlite industry in the United States is changing, and competition is increasing. U.S. production in 2003 was 512 kt, a fourth consecutive year of decreasing production from the record 711 kt in 1999. The economic downturn resulting in decreased consumption and the availability of cheaper imported perlite to the eastern and Gulf Coast states from Greece were the major reasons for the shortfall in production. In 2003, crude ore production in the United States came from 10 mines operated by eight companies in seven western states. Processed ore was expanded at 63 plants in 30 states, and 9% of processed perlite was sold as filter aids (Barker, Santini, and Alatorre 2003).

The United States is the world's largest producer and consumer of diatomite, which is primarily used for filtration. Diatomite production in the United States in 2003 was estimated to be 624 kt. Production came from seven companies with 12 processing facilities in four states, and 63% of finished product was used as filtration aids and 13% was used as absorbents. Diatomite filter aids have been used in about 200 locations throughout the United States to treat potable water. Celite, Eagle-Picher, and Oil-Dri are major producers of diatomite (Dolley 2004).

Specialty Clays. Specialty clay production in the United States is highly concentrated. The major producers of attapulgite are Oil-Dri (Zemex), Milwhite, Engelhard, and ITC (Kline & Company 2002). IMV Nevada is a supplier of sepiolite, a mineral similar to attapulgite and used in similar applications as attapulgite. American Colloid, BPM Minerals, and Black Hills Bentonite have similar market share of sorbent granular products based on bentonite (Landis 2004). Süd-Chemie, Laporte Inorganics, Engelhard, Mizusawa Industrial Chemicals, and Wembley Activated Clay are

major producers of activated bentonite (Dombrowski and Henderson 1997). R.T. Vanderbilt, Elementis, Sud Chemie, and Southern Clay Products are the major suppliers of bentonite used as rheological modifiers (Kline & Company 2002). For kaolin, the major producers are Engelhard, Imerys, J.M. Huber, and Thiele Kaolin.

Silica Sand. Although the supply of high-purity silica sand is also concentrated, it is much less so than diatomite, perlite, and the specialty clays. The top 7 to 10 companies that supply high-purity sand to the filtration industry are estimated to account for about 50% of the total sales. The major suppliers of these materials are Unimin, U.S. Silica, and Vulcan Materials (Van Kouteren 1994). Unimin, U.S. Silica, Oglebay Norton, Badger Mining Corporation, and Fairmount Minerals are the sand suppliers for the proppant application.

Glauconite. Glauconite production is concentrated in the coastal plain of New Jersey, where greensand is extracted from Cretaceous and Tertiary sediments. Inversand Co., a division of Hungerford & Terry, Inc., produces processed greensand, also called manganese greensand, in the United States.

Demand

On the demand side, the filtration industry is generally more concentrated than the absorbent industry.

Filtration. The demand side of the filtration market is highly concentrated. Beer brewing is considered the largest end-use application and on this basis the market can be considered to be highly concentrated. Five consumers account for about 80% to 85% of total diatomite and perlite use in such food product markets as soft drinks, juices, sugars, and beer. The concentration of consumers in the chemical, petroleum, and drugs and pharmaceutical industries is also high. Less concentrated filtration markets include industrial varnishes and lacquers, industrial water filtration, and dry cleaning. Another exception is the waste and surface water filtration market. The demand for sand and gravel in filtration is mainly from municipal water treatment plants, which exist in nearly every county in the United States.

There are two avenues of distribution for manganese greensand: dealers and original equipment manufacturers (OEMs). Dealers are primarily small- to medium-size water treatment companies that resell tanks, chemicals, and so forth, and provide service for domestic and other small water systems. OEMs design and manufacture equipment for large-scale municipal and industrial installations as well as smaller commercial and domestic systems, and service these water treatment facilities. They receive a small price incentive for making large, single orders and promoting the product. Many dealers are located in the midwestern United States. Large dealers in Europe distribute greensand from ports of entry in Sweden and Italy. Inversand Co. has also shipped greensand to Indonesia, South Korea, Trinidad, Chile, and Thailand in the past few years. A large manganese greensand water treatment system, possibly the largest ever, has been built in Saudi Arabia.

Absorbents. The demand side of the absorbent market is relatively unconcentrated. The pet litter and oil and grease markets consist of hundreds of brokers or wholesalers who purchase and distribute the clay products to thousands of retail stores. The carrier market is the only major end-use market for absorbent applications that is fairly concentrated: about 10 firms account for more than 50% of the demand for clays in this industry. The pet litter market could be considered highly concentrated with companies like Ralston Purina (Nestle) and Clorox controlling most of the major brands.

Rheology Modifiers. These modifiers are used in numerous applications in the personal care, cosmetics, household, and industrial markets.

Proppants. Three well services companies—Halliburton, M-I Drilling Fluids, Schlumberger, Ltd., and BJ Services—account for more than 90% of the global demand for proppants. The well services companies typically purchase the proppants and resell them to well owners as part of their well-fracturing service.

Barriers to Entry

Industry competition is also affected by the threat of new entrants. New entrants to an industry bring new capacity and the desire to gain market share; they also often add new resources, which can result in lower profitability. The threat of entry into an industry in part depends on the barriers to entry combined with expected reaction from existing competitors.

The major entry barriers for the materials used as filters, absorbents, rheology modifiers, and proppants are related to the availability and location of economical deposits and significant capital investment. The limited availability of high-grade deposits of diatomite, sand, and specialty clay materials is the most significant barrier to entry in this industry. New entrants into the specialty clay markets are probably further deterred by the need to have access to distribution channels for the pet litter and oil and grease markets. In addition, brand or brand name recognition is especially important in the pet litter market.

Not-in-Kind Materials

The availability of not-in-kind or substitute materials that are competitive on a cost-performance basis plays an important role in industry structure. Substitutes limit the potential returns of an industry by placing a ceiling on the prices that firms charge. A number of good organic and inorganic substitutes for filter and absorbent applications are being used in the market today. Such materials as synthetic fabrics, ground corncobs, paper-based product, cellulose products (wood based), and ground alfalfa play a role in the absorbent markets. A discussion of these materials and others, their markets, and performance is in the Economic Factors and Government Regulations section of this chapter. Rheology modifiers are being challenged by synthetic polymeric products such as carboxymethylcellulose (CMC), for example. In the proppants area, the need to dig to deeper levels for natural gas is shifting the material requirement and the market share from sand to higher performance ceramic proppants.

ECONOMIC FACTORS AND GOVERNMENT REGULATIONS

Costs

The major cost factor for mining, processing, and transporting industrial minerals and rocks used as filters and absorbents is typically the energy costs associated with drying and calcining. Mining costs are relatively low because material is mined in open pits and generally does not require blasting. Processing costs are high, however, because of the moisture content of these deposits, which is often in the 30% to 60% range (Miles 1990). The significant increase in the natural gas pricing (about three times from 1997 to 2004) with little or no gain in product pricing has strained the profitability of the industrial minerals.

The cost, on a tonnage basis, to transport filtration and absorbent raw materials to the market is typically higher than with other industrial minerals and rocks because of their low bulk densities. As a result, transportation costs are a significant portion of the total cost of the delivered product. This is especially true for diatomite and perlite because production is in the West and the major markets are east of the Mississippi River. Thus, because imports from Greece to the East Coast are cheaper, these imports are increasing. Furthermore, perlite must be shipped in a crude form to the major markets and then processed or expanded.

Table 7. Breakdown of demand for major industrial minerals used in filtration and absorbents markets (2003 USGS data), Mt

Mineral	Filtration	Absorbent, Pet Waste	Absorbent, Others
Bentonite (calcium and sodium)	127,000*	987,000	W†
Fuller's earth (montmorillonite and attapulgite)	66,200	2,400,000	353,000
Diatomite	425,290	65,890‡	
Perlite	59,600	NA§	NA

* Data for 2002.

† W = Withheld to protect company proprietary information.

‡ Includes both pet waste and other absorbents.

§ NA = Not applicable.

Another cost factor, although not directly related to mining, processing, and transporting products to the market, is disposal costs. Consumers of industrial minerals and rocks are facing increasing disposal costs for spent filter cakes and absorbent materials. The cost to transport the spent materials to an acceptable landfill, combined with the costs and liabilities of disposing the materials, is rapidly increasing. Also, clay absorbents cannot be incinerated because most incinerators do not run hot enough to disintegrate them. Thus nonclay absorbent usage is on the increase. A good example is oil spills on water. Clay absorbents will absorb the oil but quickly sink, carrying the pollution from the top of the water to the bottom. This market is now dominated by synthetics—which are treated to absorb only oil and not water—that float for gathering and then incineration.

Markets

Table 7 shows the breakdown of demand for the major industrial minerals used in the filtration and absorbent markets.

Sand and gravel used in the filtration application are typically the lowest priced materials whereas acid-activated clays are the most expensive. Attapulgite pricing can range up to \$400/t for some specialty applications, including cosmetics (T. Harris, personal communication). The acid-activated clays have the highest average price; however, the total demand for these clays is relatively minor (Van Kouteren 1994).

Filtration

The filter aid market is the single largest application for diatomite, accounting for 73% of total diatomite consumption in a given year (Kline & Company 2002). High-purity quartz sand, diatomite, and perlite accounted for the majority of the volume used in such major uses as wastewater, food products, and chemical industries. The wastewater markets account for the most tonnage because of the large volumes of municipal and industrial water and waste that require treatment. These applications use sand and gravel, along with anthracite and, in some cases, such high specific gravity minerals as garnet and ilmenite.

Absorbents

The cat litter and oil-specific filtration media markets generate \$1 billion each at the retail level; spill clean-up absorbents is estimated to be a yearly market approaching \$120 million (International Absorbents Inc. 2004). This includes both industrial minerals and not-in-kind products. Roskill (1997) estimated that the total world market for bentonite and allied clays in absorbent uses is between 4.3 and 4.5 Mt with modest annual growth. Bentonite's gain in the pet litter market since the mid-1980s has resulted from (1) clumping of its granules versus those of hornite clays, making it easier to remove soiled litter; (2) reduction in dispersal or "tracking" because

of its high density; (3) stronger and longer lasting granules; and (4) the presence of free silica in the form of cristobalite (considered harmless from a safety viewpoint) in sepiolite grades.

Although the volume of clays used in filtering and clarifying oils is only 4% of the total volume, these acid-activated clays account for nearly 15% of the total value.

Rheology Modifiers

The total demand for minerals used as rheology modifiers (including organoclays) in paint and health and personal care products was about 16 kt, valued at about \$81 million, in 2001 (Kline & Company 2002).

Proppants

The 2001 sales of sand in the proppant market are estimated to be \$150 million.

Substitute Materials

Until recently, the threat to minerals from substitute materials or alternative technologies was somewhat limited. Recent environmental and health regulations, however, combined with improvements in such alternative technologies as membrane or ultrafiltration, have and will continue to have an adverse impact on the demand for minerals.

Filtration

Competitive materials and alternative technologies are currently decreasing demand for diatomite and perlite. Perlite, a competitive material to diatomite in filter cake applications where clarity is not so critical, has gained market share in recent years. The rivalry between the use of diatomite and perlite has intensified because of regulations on crystalline silica as well as the growing volume of low-priced perlite imports. Some perlite suppliers have increased their marketing efforts to exploit the fact that perlite's crystalline silica content is much less than that of diatomite. As a result, perlite has made gains in such food product markets as juices (Rees 1990; Van Kouteren 1994).

Ultrafiltration technology or cross-flow membrane filtration uses pressure gradients, chemical and electrical potentials, and synthetic membranes to separate macromolecular and colloidal solutes or particles (Clark 1985). In recent years, this technology has gained market share in the food products, biomedicine, and biotechnology markets. The gain is due in part to the increasing disposal costs of spent diatomite and perlite filter cake. In addition, the cost to use this technology has decreased because of advances in membrane and equipment performance and durability (Rees 1990).

Unusually high levels of dissolved iron in water are commonly caused by low pH. This problem can be corrected with a neutralizing calcite filter, a water softener, raising the pH to a

minimum of 6.7, or oxidation with chlorine bleach followed by filtration. Manganese can be removed from water by reverse osmosis and by oxidation with chlorine bleach followed by filtration. Small concentrations of manganese can be removed with a water softener. Hydrogen sulfide in concentrations greater than 6 ppm is treated with constant chlorination followed by filtration/dechlorination (Spoljaric 1994).

Absorbents

Substitute materials for absorbent minerals include such organic materials as paper, sawdust, ground alfalfa, corn cobs, and citrus fruit grinds. Their major advantage over specialty clays is little or no dust with these not-in-kind products. But, although these materials are typically less expensive, they are not as effective as specialty clays. On the other hand, such synthetic materials as molecular sieves, silica gel, precipitated silica, and nonwoven polyethylene fabrics are very effective but are too expensive. In more limited cases, such mineral products as vermiculite, gypsum, lime, sand, and zeolites are used in specific applications where low cost or performance is desired. Other substitutes include diatomite and perlite, especially in the western United States, because of the transportation cost advantage that they have over clays (Harris and Eckert 1989). Waste fiber products from International Absorbents look and feel like clay, are healthier than clay, and are flushable and price competitive. The agriculture granular market is stagnant for the clays because new biotechnology products have taken some market share and because of U. S. Environmental Protection Agency (EPA) cancellation action against some granular clay products.

Polyethylene fabric has had the largest impact on the demand for mineral absorbents. These nonwoven fabrics have a natural affinity for petroleum-based products, and so they can absorb up to 20 times their weight of oil and grease. The use of these materials has grown because of the classification of spent clay as a hazardous material and the subsequent disposal costs associated with these clays. The big advantage of these nonwoven fabrics is that they can be incinerated with less than 1% ash remaining (Harris and Eckert 1989).

Rheology Modifiers

Minerals used as rheology modifiers receive competition from naturally occurring or synthetic polymeric additives.

Proppants

The demand for high-quality proppants at depths exceeding those that can be adequately served by sand has resulted in sand being increasingly replaced by ceramic proppants based on mixtures of kaolin and bauxite or bauxite alone.

ENVIRONMENTAL AND HEALTH REGULATIONS

Governmental regulations concerning crystalline silica have had an adverse effect on the demand for diatomite. This trend began in 1988 when the International Agency for Research on Cancer (IARC) classified crystalline silica as a probable carcinogen. The classification triggered regulation of crystalline silica at a threshold concentration of 0.1% in materials under the Occupational Health and Safety Administration's Hazard Communication Standard (Miles 1990).

Diatomite and other minerals suppliers responded to this in a number of different ways, including worker and user training programs, product labeling, and dust reduction programs. The diatomite industry also created the International Diatomite Producers Association (IDPA) to study and issue reports on health, safety, and environmental issues related to the use of diatomite. Other mineral and

chemical producers formed a Chemstar Crystal Line Silica Panel. This panel, formed in 1989 and sponsored by the Chemical Manufacturers Association (CMA), works with government agencies to avoid random banning of minerals suspected of being hazardous.

Another governmental regulation that has reduced demand for minerals and rocks used as filters and absorbents was the 1991 EPA ban on disposing of wastes containing oil in landfills. This ruling caused some consumers of clays for oil and grease absorbents to switch to other products. The switch was mainly because organic products could be incinerated instead of being placed in landfills. Clay suppliers are currently fighting to have new tests approved for measuring the leaching or leaking of absorbed oil from clay products. Under the current regulations, a toxicity test renders the clays hazardous, but if proposed liquid release tests are accepted, the absorbent minerals may prove to be less hazardous.

The area of southern New Jersey where glauconitic greensand is being produced is heavily populated. It is likely, therefore, that any new mining permits or changes to current land use zoning to accommodate expansion of the greensand mines will be difficult to obtain. In 1988, however, Inversand Co. had reserves estimated to be sufficient for at least 20 to 25 years of production.

Inversand Co. is required to comply with a number of environmental regulations and to operate a wastewater treatment plant under the jurisdiction of the New Jersey Department of Environmental Protection (New Jersey Pollutant Discharge Elimination System, or NJPDS). The company must have permits for both surface water discharge and groundwater discharge. Its operations are inspected periodically by the Mine Safety and Health Administration (MSHA), which checks workers for exposure to crystalline silica dust and enforces regulations regarding safety practices.

PROBLEMS AND FUTURE TRENDS

Although health and environmental regulations will continue to lessen demand for industrial minerals and rocks, they will not cause the demise of the use of these materials. Overall, the minerals and rocks used as filters and absorbents do their job very effectively and economically. The regulations may increase the cost, but in most cases the increased cost will not immediately result in the substitution of alternative materials or technology. Therefore, despite the regulations, the use of minerals and rocks as filters and absorbents will continue to be cost-effective.

Market Developments

Environmental issues will continue to affect the demand for industrial minerals and rocks. In many areas of the United States, the closure of landfills has been increasing the total cost to dump material. The total cost includes fees for material disposal and the added cost to transport the material to a more distant landfill. In addition, landfill users can incur additional liability if a site requires future cleanup because of another user's disposal practices (Miles 1990).

The EPA ruling that spent clay oil and grease absorbents are classified as hazardous wastes also will continue to reduce the demand in this application. Another area that has caused problems in the past is the disposal of spent clays from edible oil filtration. The problem is that the spent clay product is highly flammable and special precautions must be taken when dumping the material. Although procedures have been developed to safely dispose of used material, some landfills still do not accept such material (Harris and Eckert 1989).

The end result of increasing disposal costs for spent filter cake and clay absorbents will be increased substitution or new technology to circumvent these problems. For example, diatomite and perlite will continue to lose market share to ultrafiltration or membrane

technology. Another example of consumers switching to a different technology because of increasing spent clay disposal cost is in the petroleum refining industry. Refineries are increasing their hydrogenation capabilities, which is another way of cleaning or purifying petroleum products without incurring the additional cost and liability associated with disposing the spent clay (Harris and Eckert 1991).

The crystalline silica issue will continue to be a problem for the industry. The initial negative impact of the regulation appears to have peaked in 1991. Consumers have either taken protective actions and continued to use diatomite or they have switched to another material. The 0.1% target, however, may not be final and could actually be changed. If it is lowered, more problems await both suppliers and users of any mineral product containing crystalline silica.

On the other hand, increased environmental regulations will also have a positive impact on the demand for these materials. Because of more stringent regulations on wastewater, companies will be required to clean their effluents, and filtration will be one of the methods.

Specialty clays used as pet litter is another area that will show good growth. The cat population in the United States is expected to continue to increase as the population ages. Cats are, in many ways, ideal companions, especially for the elderly and apartment dwellers, because they care for themselves, require no outdoor exercise, and consume little food.

In light of declining demand for greensand, efforts have been made recently to develop new uses. Glauconite's catalytic properties have been investigated in some detail in the United States, the former U.S.S.R., Japan, Germany, and France (Hartough and Kosak 1947; Kvirikashvili 1962, 1964). Acylating reactions, dehydration of cyclohexane to benzene, and condensation of aldehydes have been carried out with glauconite-based catalysts. The relationship between catalytic activity and cation-exchange capacity (CEC) has encouraged efforts to enhance the former by increasing the latter through heat treatment and chemical methods. Because CEC increases with the amount of mixed-layer component present, these efforts also have focused on replacing more of the potassium in the glauconite structure with hydroxyl ions. Heating of glauconite in a reducing atmosphere leads to the formation of metaglauconite, the sorptive properties of which are being studied.

An entirely different approach is the destructive dissolution of glauconite and recovery of at least three marketable products: high-purity silica, potash, and iron oxides. This process was first proposed in the mid-1920s. Efforts are under way to prove its economic feasibility with the help of up-to-date chemical engineering practices.

Some extensive greensand deposits are situated near population centers. As a result, glauconite's capacity to absorb hazardous waste fluids is being investigated, and an increasing demand for this mineral in solving pressing pollution problems can therefore be anticipated. Food shortages in several parts of the world may also bring about renewed interest in glauconite as an inexpensive fertilizer.

Outlook

The outlook for filtration and absorbent materials will vary considerably by end use. For the most part, however, many of the markets are mature and the growth is expected to follow the overall economy. Average annual growth of filtration and absorbent materials in the 2000s will range from mostly flat to 2% a year (T. Harris, personal communication). Most end use applications for diatomite are mature with relatively static projections for future growth. Although

pet litter demand tends to grow with the population, the loss of markets to substitute materials and alternate technologies because of environmental and health problems could worsen and thus lower the average annual growth rate. Consumption of organoclays in consumer and industrial markets is forecast to grow at a compounded annual growth rate of less than 1% a year. This low rate is almost entirely caused by flat sales to the paint sector (T. Harris, personal communication).

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Fine Ceramic Products

Denis A. Brosnan and John P. Sanders

INTRODUCTION

Fine ceramics such as ceramic dishes, toilets, tile, and related products (Figure 1 A–D) are part of our everyday lives. Clay minerals are used in the composition of all these products, which are processed at high temperatures to cause limited melting or fusion. This produces a glass or vitrified phase that creates a permanent bond within the articles and gives them their permanence and utility.

Ceramic products are composed of nonmetallic and inorganic constituents. In other words, ceramics are composed of oxides, and traditional ceramics have constituents that commonly occur in the earth's crust. This means that traditional ceramics contain oxides of aluminum, silicon, magnesium, calcium, iron, and alkali metals (sodium and potassium), along with trace quantities of other elements.

Fine ceramics are essentially made from fine particles, with particle sizes less than about 150 μm and typically less than 75 μm . After heating (also known as firing), such ceramics have a fine texture—meaning that the solid material consists of crystals and amorphous phases with dispersed areas of pores of small diameter.

By contrast, some traditional ceramics are made from large or coarse particles ranging in size up to about 6,000 μm . These include products such as clay bricks, clay roofing tile, refractory bricks, and clay pipe. Although coarse particulate ceramics are fired in kilns or furnaces to achieve permanence, they generally exhibit lower strength than fine ceramic products. Another important distinction is that many coarse particulate ceramics may contain iron oxide in their composition in the range of 2% to 8% by weight, producing colors in the fired products ranging from pink to red to blue (or black).

Technologists apply the name *whitewares* to fine ceramic products, and the term simply reflects the fact that most of the products are white (or near white) in color. *Ware* is the technical name for a ceramic object that is sold in commerce. Whitewares include many different classes of functional products (Table 1). Whitewares are distinguished or classified in commerce according to technical subgroups based on use. The classifications are also correlated with the amount of void space in the fired ceramic, which is called its porosity. In the historical development of traditional ceramics, porosity was measured indirectly as water absorption (i.e., the weight of water the ceramic would absorb on immersion compared to the dry weight of the ceramic object), expressed as a percentage of the dry weight.

The general relationship in whitewares is that low porosity is associated with high mechanical strength, high resistance to chipping (or breakage), and excellent durability. Adjusting the composition or mineral constitution and increasing the amount or degree of vitrification in firing are means to achieve low porosity in whiteware manufacturing.

With respect to composition, mixtures of clay, flint (ground silica), and feldspar minerals achieve high strengths in clay-based whitewares. These products are called *triaxial* whitewares because of the three components in their composition. Further improvements in strength are obtained when aluminum oxide (alumina) or other minerals such as zircon are added to the composition.

Vitrification is achieved in kilns as the ceramic composition melts when temperatures achieve red heat (i.e., rise above about 950°C). As temperature increases further in the kiln, more melted phase is formed, and this glass is distributed by capillary forces throughout the ceramic. When temperatures increase above 1,000°C, a new mineral, mullite, appears. Simultaneously, the ceramic ware shrinks, effectively increasing density and reducing porosity. Residual pores tend to “grow” or increase in size during the highest temperature period of firing. After cooling in the kiln, the fired product has mechanical properties that reflect the degree of vitrification and densification achieved in the firing process.

The degree of vitrification is the percentage of melting of the original constituents that has occurred in manufacturing. In whiteware ceramics, the amount of melting may exceed 40% to 60%. In glass products, the extent of melted phase approaches 100%. In manufacturing of white wares, measurements of firing shrinkage and porosity (water absorption) reflect the extent of vitrification during firing (i.e., the quality of the fired product).

Whiteware products may be glazed to increase their utility and improve their appearance. A *glaze* is a glass coating formed by melting or fusing an applied particulate mass over all or part of the ceramic ware's surface. Glazes provide a smooth surface that can easily be cleaned, and they also prevent water from being absorbed by the product, promoting sanitation and improving performance. Glazes can also be colored using pigments or oxides, which enhance the appearance of the finished product.

One advantage of glazing over a white surface is that it is relatively easy to achieve light colors without color bleeding through from the substrate ceramic. This is a distinct advantage of whiteware products over red clay (red body) ceramics. With red clay



Figure 1. (A) Fine china cup and saucer (Lenox, United States); (B) cup with unique black porcelain saucer (Rosenthal, Germany); (C) toilet in a bathroom with porcelain wall and floor tile; and (D) kitchen application of tile products

ceramics, it is frequently necessary to apply double layers of glaze (a white underglazed, or engobe layer covered by a colored outer layer) to achieve a desired light color.

RAW MATERIALS AND REACTIONS ON FIRING

General Information

A variety of raw materials are used in the production of whiteware ceramics. These raw materials or minerals can be broken down into three categories: clay (kaolin and ball clay), flux, and fillers (or nonplastics). Each material has a specific function, but in general, the clay is the component that provides plasticity or cohesion for forming and the flux promotes vitrification. The filler is inert, but it also may serve to modify the glass viscosity during vitrification, which effectively extends the usable range of firing temperatures for the composition.

Clay, which is composed of kaolinite, is a hydrous sheet silicate produced by the weathering of feldspathic rock, is the component of primary importance in traditional ceramic compositions. Characterized by plasticity when mixed with water, clays exhibit an extremely small particle size in an unagglomerated state. Figure 2 gives a typical particle-size distribution. The small particle size and the plate-like morphology of the particles result in a large surface area. The particle surfaces, then, tend to have an affinity for water. The clay's affinity for water gives rise to a monolayer of water around the particle. The water layer promotes cohesion and allows the particles to slip relative to one another during forming.

Because kaolins are the product of weathering of the parent feldspathic rock, they can exist as either primary (residual) deposits or secondary (sedimentary) deposits. Primary deposits are formed by geological processes in situ, and they typically have the coarsest particle size and highest impurity level among clay sources. Secondary deposits of clay involved transportation of minerals by

water, with eventual deposition in the location where they are now mined. Secondary deposits typically exhibit smaller particle sizes and lower impurity levels when compared to primary deposits.

As a product of weathering, clays are capable of a wide range of atomic substitution in the silicate structure, which gives rise to the large variety of clay minerals. Clays also contain nonclay impurities or accessory minerals.

The major accessory mineral found with clay deposits is crystalline silica (quartz). Sulfides, sulfates, carbonates, and hydroxides can also be present. Clays also contain organic impurities. The organic impurity can play a role in the plasticity of the body, and it can be a rate-limiting factor in fast-firing applications, because carbon must be removed by oxidation in firing. A variety of processing and refining steps can remove impurities before the clay is incorporated in whiteware compositions, but the cost of these treatments may be prohibitive. Clays are available in lump or prill, powdered (air-floated), and slurry forms.

There are three main groups of clay minerals used in whitewares—kaolin, illite, and smectite. Kaolin clays are the most common group, and they have the approximate composition of $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$. White clays of this type are composed of the clay mineral kaolinite. Kaolinite is also the major clay mineral in ball clay—a highly plastic and cohesive sedimentary clay. Depending on the origin or geologic history, kaolins are used in several forming processes (product shaping), ranging from pressing for kaolins from Georgia (secondary kaolins with extremely small particle sizes) to casting for the coarser kaolins.

Kaolin

Table 2 gives selected chemical analyses of kaolins. Because fired color is a concern with kaolins, the iron content (reported as Fe_2O_3) and titanium (reported as TiO_2) content are very important. As the iron content increases, the fired color develops a red shade. Increasing titanium content imparts a buff or tan color. For products where extreme whiteness is desired, clay with a minimum level of these impurities must be selected.

Kaolinite undergoes chemical reactions during firing. The first and most important reaction is dehydroxylation. During this reaction, the crystalline water (or hydroxyl units) is evolved from the clay mineral above 500°C . Evidence of dehydroxylation is given in Figure 3, which is a simultaneous thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis with evolved gas analysis of a commercial kaolin. After dehydroxylation, the clay mineral is in a disordered form that exists as a residual material called metakaolin.

A second reaction, at about $1,000^\circ\text{C}$, is apparent in Figure 3, and it is associated with mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) formation. This reaction is characterized by a large exothermic peak indicating the reaction. During the reaction, a portion of the clay mineral reorganizes or recrystallizes to form mullite. Mullite formed during the initial heating is called primary mullite. Mullite is considered advantageous because it has a needlelike crystal habit, and it mechanically reinforces the glassy matrix of the whiteware ceramic.

On heating above about 950°C , some of the residual material from the clay dehydroxylation forms amorphous material as melted phase or glass. Impurities and other minerals contribute to the overall quantity of vitrified material during firing. On cooling, additional mullite (called secondary mullite) can crystallize from the glass present. The process of forming secondary mullite involves expansion reactions, and it may help prevent excessive shrinkage or slumpage of the ware at the elevated temperatures in the kiln.

Table 1. Classification of unglazed ceramic whiteware products

Class	Description	Distinguishing Factor for this Class
Earthenware	Clay-based ceramic ware of medium porosity.	Water absorption of 4%–20%. Earthenware is typically off-white to red because of its iron content.
Stoneware	Ceramics made from a single clay or clay blend with other minerals (including silica) fired to produce harder and more durable products.	Water absorption of 0%–5%. Stoneware is typically off-white to gray because of its iron content and the presence of nonclay minerals.
Vitreous china	Very low porosity and highly vitrified products. Product classes include: Hotel china Bone china Frit china Vitreous plumbing fixtures Cookware	All product classes typically exhibit water absorption of less than 0.5% except for cookware, which may exhibit up to 5% absorption. The low water absorption creates high strength and negligible water transmission in use.
Porcelain	The lowest porosity and highest strength of traditional ceramic products. Product classes include: Hard porcelain Vitreous porcelain Electrical porcelain Dental porcelain	The products may be compositions of flint (quartz), clay, and feldspar (vitrification enhancer), and they may contain additional minerals to increase their strength (such as aluminum oxide).
Electrical porcelain	Compositions are adjusted depending on the intended application. Product classes include: Steatite ceramics Electrical ceramics	Steatite ceramics contain the mineral talc to enhance the product performance in high-frequency electrical applications. Electrical ceramics are usually porcelains of high aluminum oxide content (such as spark plug insulators).
Technical whiteware ceramics	This general classification includes many low-absorption ceramics for structural and chemical applications.	Compositions are altered to include aluminum oxide, zircon, and other minerals to obtain specific properties.

Ball Clays and Other Clay Minerals

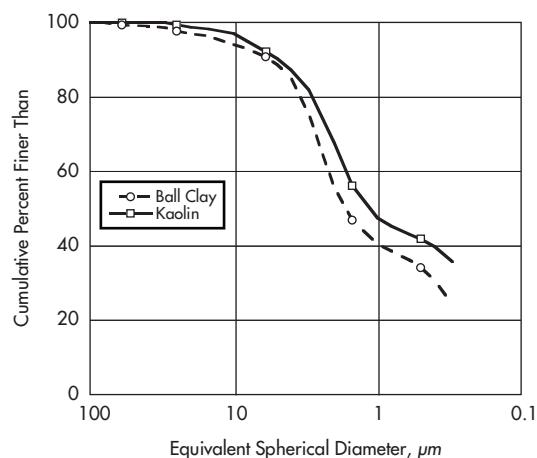
In addition to kaolin, there are other commercially important clay minerals. Ball clays are commonly used in whitewares where higher plasticity is required. Ball clays typically fire to buff or tan because of their iron or titanium dioxide content. Table 3 gives selected ball clay chemistries.

Smectite is another class of clay minerals. Often referred to as *montmorillonites* $[(Al,Mg)Si_4O_{10}(OH)_2]$, smectites are characterized by small particle size and a very high level of plasticity. As the chemical formula implies, montmorillonites are subject to a high degree of atomic substitution. Montmorillonite, in the form of bentonite, is used in limited quantities to improve plasticity in whiteware compositions. Their fine particle sizes cause montmorillonites to produce high drying shrinkage, and their presence can make drying more difficult. They fire to darker colors than kaolins or ball clays because of their impurity levels.

Another clay mineral used in whitewares is illite, which is sometimes known as *hydrous mica*. Illites have a variable composition because of the wide variety of atomic substitutions that can take place. Illites are desirable for fast-fired tile formulations because they exhibit lower weight loss and shrinkage on firing than most other clay minerals. Table 3 gives examples of illite and montmorillonite chemistries.

Fluxes Used in Whitewares

Fluxes promote the formation of a glassy bond during vitrification. Fluxes provide alkali (Na_2O and K_2O) or alkaline earth (CaO or MgO) elements to the composition, promoting glass formation and reducing glass viscosity during firing. This serves to enhance vitrification. The level of fluxing components must be optimized to achieve the desired fired property in the selected firing range. Feldspars and nepheline syenite are the usual fluxes, but recycled glass powders and other waste materials are gaining popularity for cost reasons. Materials such as spodumene $[(Li,Al)SiO_3]$, calcined bone ash $[(Ca(PO_4)_2]$, limestone ($CaCO_3$), dolomitic limestone

**Figure 2. Typical clay particle-size distribution****Table 2. Examples of kaolin chemistry, wt %**

Oxide	Georgia Kaolin (United States)	Florida Kaolin (United States)
SiO ₂ (silicon dioxide)	44.4	45.7
Al ₂ O ₃ (aluminum oxide)	39.6	37.4
Fe ₂ O ₃ (ferrous oxide)	0.4	0.8
TiO ₂ (titanium dioxide)	1.7	0.4
P ₂ O ₅ (phosphorous pentoxide)	trace	0.3
CaO (calcium oxide)	trace	0.2
MgO (magnesium oxide)	trace	0.1
Na ₂ O (sodium oxide)	0.1	0.06
K ₂ O (potassium oxide)	0.1	0.3
Loss on ignition (LOI)	13.7	13.9

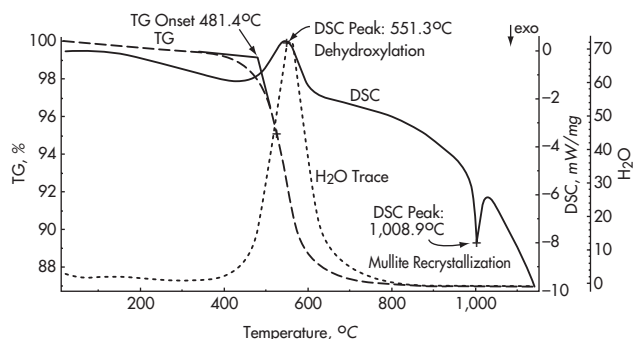


Figure 3. TG and DSC analysis of kaolin in air

Table 3. Selected clay chemistries, wt %

Oxide	Ball Clay A	Ball Clay B	Montmorillonite	Illite
SiO ₂	61.2	55.2	64.3	49.3
Al ₂ O ₃	24.3	27.9	20.7	24.3
Fe ₂ O ₃	1.4	1.2	3.5	7.3
TiO ₂	1.0	1.1	0.1	0.6
CaO	0.3	0.3	0.5	0.4
MgO	0.4	0.4	2.26	2.5
Na ₂ O	0.2	0.3	trace	trace
K ₂ O	1.3	1.0	2.9	7.8
LOI	9.9	12.6	5.2	8.0

[(Ca,Mg)CO₃], wollastonite (CaSiO₃), and talc [Mg₃Si₄O₁₀(OH)₂] are also used as fluxes.

Several types of feldspar are used in white wares, including soda feldspar (albite, NaAlSi₃O₈), potash feldspar (microcline or orthoclase, KAlSi₃O₈), and lime feldspar (anorthite, CaAl₂Si₂O₈). Feldspar does not exist as pure albite or pure anorthite, but it is found as mixtures of these major types. It is possible to buy a soda feldspar, for example, but this simply means that albite is the predominant mineral. Particle sizes can range from granular to powders, and the selection of particle size depends on the application. Feldspar usually contains quartz as an impurity. Table 4 gives some examples of feldspar chemistries.

Another flux used in white wares is nepheline syenite, a material that is higher in alkali and alumina and lower in silica than feldspar. Nepheline syenite is a naturally occurring mixture of nepheline (K₂Na₆Al₈Si₉O₃₄) with microcline and albite feldspars. It is relatively expensive, but it provides greater fluxing power (effectiveness) and a wider firing range than feldspars in porcelain compositions. Additionally, it does not usually have significant quartz contamination, although it may contain a trace of mica.

Fillers for Whitewares

The nonplastic or filler portion of the whiteware composition consists of flint (ground quartz), and it may include alumina (Al₂O₃), pyrophyllite [Al₂Si₄O₁₀(OH)₂], or sericite depending on desired function of the filler. Ground quartz used in whiteware compositions is frequently called *potter's flint*.

In the case of quartz, the silica particles are partially melted at high temperatures (above red heat) and enter the glassy phase formed by the fluxing components. One result is the increase of the viscosity of the glassy phase, thereby allowing for a relatively wide

Table 4. Examples of feldspar chemistry, wt %

Oxide	North Carolina Feldspar	Potash Feldspar	Nepheline Syenite
SiO ₂	68.3	67.6	60.7
Al ₂ O ₃	18.8	18.0	23.3
Fe ₂ O ₃	0.1	0.1	0.1
CaO	1.4	0.8	0.7
MgO	trace	trace	0.1
Na ₂ O	6.8	3.0	9.8
K ₂ O	4.1	10.4	4.6
LOI	0.1	0.2	0.7

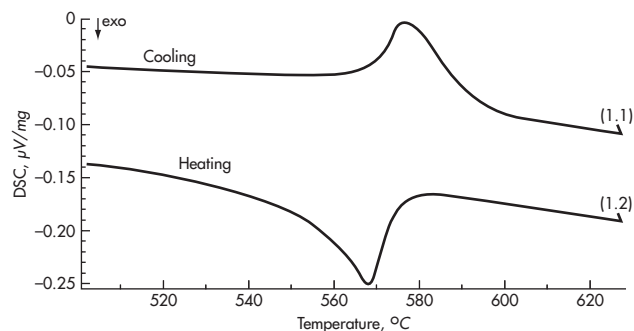


Figure 4. Quartz inversion by DSC

firing range characteristic of porcelain compositions. The residual or unmelted quartz serves as a "skeleton," which prevents the product from slumping under its own weight at elevated temperatures.

Quartz undergoes a reversible phase change during firing, requiring special care during cooling of the fired ware in the kiln. On heating, quartz inverts from the α quartz polymorph to the β quartz polymorph at 573°C with an accompanying expansion. The reverse reaction takes place on cooling for any residual quartz grains. Figure 4 shows an example, illustrating the heat associated with the quartz inversion on heating and cooling.

On heating, the phase change consumes heat (is endothermic), but on cooling, the reaction releases heat (is exothermic). A potential problem arises from the 2% volume expansion on heating and an equal contraction on cooling. Excessive cooling rates in the kiln can result in a defect known as *dunting* (cracking), where the volume contraction during the quartz inversion is the cause of crack formation and extension.

When alumina is added to a whiteware composition, increased mullite formation increases the strength of the fired ceramic. Alumina porcelains are commonly used when very high strength is required. When alumina is substituted for quartz as the filler, *dunting* becomes less of a concern, compared to compositions containing a high content of flint.

In steatite compositions, talc is used as a source of magnesium. Talc is also used in the production of cordierite ceramics, which have a very low thermal expansion and are used as substrates in catalytic reactor products.

Glazes

Raw materials used for glazes include clay, finely ground silica, and fluxes. High alkali and alkaline earth contents and low silica contents are desired in glazes to achieve good flow (coverage)

during firing. Changing the alumina content, for example, makes glazes with a gloss finish exhibit a matte finish instead. In some cases, lithium silicates (such as spodumene) are added to glazes to modify their thermal expansion characteristics to achieve better thermal expansion match (equivalence or fit) between the glaze and the ceramic body.

Because the use of lead as a flux has been curtailed, borates and zinc oxide are employed in small quantities as fluxes. Zinc oxide also promotes color development in the fired glaze. A common source of borates is borax (sodium tetraborate decahydrate). The levels of both zinc oxide and borates must be limited to avoid glaze defects.

Glazes are now commonly prepared from frits (premelted glass compositions). Frits have the advantage of requiring low energy to melt, and they involve less batching and material handling effort. Frits simply require milling and mixing with the remaining glaze components to prepare the glaze suspension prior to application. Frits are used to achieve a particular effect for which they were specifically prepared.

Clays are used in glazes as suspending agents in preparing the glaze slurry. It is possible to purchase premixed combinations of frit and clay (known as *compostos*). These formulations simply require a water admixture to form a suspension, and coloring agents are added to achieve visual effects.

Transition metal oxides such as hematite (Fe_2O_3) or cobalt oxide (CoO) can be added directly to formulations to impart color. These oxides are dissolved by the glassy phase during firing. Recently, ceramic pigments based on zircon have become popular because of their stability and coloring power in glaze formulation. These colorants are zirconium silicate crystals with additions of transition metal oxides to achieve a coloring effect. Pink colors are based on chemically *doped* alumina.

Zircon (ZrSiO_4) is used as an opacifier for white glazes and engobes (thick coatings). On cooling of the molten glaze, the zircon that has been dissolved in the melt precipitates and forms discrete crystals in the glassy matrix. These crystals block the transmission of light and scatter light entering the glaze, effectively masking the substrate.

FORMING METHODS FOR WHITEWARE PRODUCTS

Whiteware products are shaped (formed) by the conventional processes of plastic forming (turning, jiggering, extrusion, or combinations thereof); slip casting; or compaction (wet or dry pressing). In a few products, dry isostatic compaction may be followed by turning in lathe-like machines to achieve a formed shape. Drying, firing, and quality inspection follow these processes. Glazes may be applied before firing (in single-fire processes) or after firing (in double-fire processes); the latter product is then fired a second time to melt the applied glaze to the surface.

The object of forming is to achieve near-perfect particle packing in the formed mass. This means that entrained air has been reduced to the extent practically possible. In addition, constituents of the mixture are uniformly dispersed in the mass before the forming process is used. The wetting of materials, as required by the forming process, is achieved in special mixers, and it is frequently aided by the “aging” of wetted raw material mixtures. There is considerable art and science in preparing raw materials for the forming process to achieve optimum properties in the formed ware.

Plastic Forming

As the name implies, plastic forming involves deformation of a plastic mass of raw materials into a desired shape before the product is dried and fired. By definition, plasticity (in ceramics) is the property allowing the mix to be deformed without breaking or cracking. Plas-

ticity originates from the clay constituent of the mix, and it may be increased through mineral additions and polymeric additives.

The simplest plastic forming process is hand forming, as is practiced by potters. In high-volume manufacturing, jigs are used to force the plastic mass into a consistent shape. In many cases, the plastic forming process forces the mass into a mold cavity under pressure, in a process called *plastic pressing*. If the mold is permeable, air may be used to assist in ejecting the formed product from the mold after pressing, in a process called *ram pressing*.

The most common plastic-forming process is extrusion, where the plastic mass is forced through an orifice (die), which forms two of the three dimensions of the desired product. Extrusion is carried out in piston-type or auger-type devices. In higher volume manufacturing, the auger extrusion device may be preferred because of high production output. The “column” of the composition is then cut with wires to form the third dimension of the formed product. Some products, such as electrical insulators, may be formed by extrusion into plastic “blanks,” and the blank is subsequently pressed or turned in lathe-like processes to accomplish additional forming of surface features. To avoid slumpage of the wet clay mass after forming, some degree of drying may be required between extrusion and the subsequent turning operation.

Formed ware is always purposefully greater in dimension than the fired product because of shrinkage in drying and shrinkage in firing. The drying and firing shrinkage can exceed 5% to 8% linear shrinkage in plastic formed products. For this reason, the formed dimension is always adjusted so that the net dimension after firing is the required product size.

Slip Casting

In slip casting, a suspension of ceramic particles is poured (cast) into a permeable or absorptive mold to draw a layer of particles to the surface of the mold, forming the product. Slip casting can be used to make both solid and hollow objects. Drain casting is the process of timing the casting process until the desired wall thickness of cast product has formed, and then draining the mold, preserving a void or cavity in the cast object.

After the casting process or draining is completed, the cast object is left in the mold until the mass has been dewatered sufficiently to allow handling of the formed object without deforming it. Then, the mold is opened and the cast object is withdrawn. The object is placed on a tray or other fixture and conveyed into a conditioning room before drying.

The slip casting process is preceded by the production of a batch of the required proportions of minerals. This batch is mixed with water and chemicals in special mixers called *blungers*. The mixed material is stored in tanks that are agitated to prevent settling of the constituents of the suspension. The suspension is typically called the *slurry*.

The slurry contains chemicals that cause deflocculation or separation of the fine mix constituents. Some chemicals assist in wetting of the particulate matter and stabilization of the slurries. The solids content of the slurry is carefully controlled by meeting goals for the specific gravity of the slurry, and the viscosity of the slurry is monitored. Controlling the solids content of the slurry and its viscosity keeps the casting rate (rate of buildup of solid on the mold surface) consistent, allowing the use of discrete schedules for draining molds.

The usual mold material in slip casting is plaster of paris. Such molds must be handled carefully to avoid breakage or wear, and consistent mold moisture content before reuse is important. Polymer molds have been introduced in pressure casting operations where applied pressure over the mold increases the casting rate.

Dry Pressing or Dust Pressing

Powdered mineral mixtures can be formed by compaction in molds using large presses. The process is called *dry pressing* or *dust pressing*, and it is used extensively in producing ceramic tile and certain electrical ceramics. The process begins with the preparation of the powdered material using a granulation process. Granulation is required so that the dry or near-dry powders will flow into mold cavities, achieving even fill before compaction. In high-volume manufacturing, spray drying is used to form granules 1 mm or less in diameter, and these granules, or pellets, are stored before use in pressing. In lower volume manufacturing, mix-pelletizing may be used to produce granules. Granules can have a small percentage addition of moisture, binders, or plasticizers added before their use in the pressing operation.

Modern presses employ isostatic molds that allow for even pressure application to the surfaces of the part during compaction. The rate of compaction is important to allow de-airing during the press cycle, and the total pressure applied in compaction largely determines the as-pressed or “green” strength of the pressed ware.

DRYING AND FIRING OF WHITEWARES

Drying

Drying is conducted in continuous convection dryers containing zones to control evaporation rate. The initial drying may be accomplished in predryers in which the rate of evaporation is held as low (using low temperature and high relative humidity) as needed to avoid high shrinkage rates and associated cracking. In the first dryer zone, temperatures are kept just below the boiling point of water to avoid steam spallation in the product. In the final dryer zone, the temperature can reach 150° to 200°C.

Radio frequency and microwave dryers speed up the processing of high-valued whiteware ceramics. Such dryers allow for greatly reduced drying time, and they are amenable to larger objects like electrical insulators. Convection dryers remain popular because most ceramic plants have excess waste heat available from the cooling section of their kilns.

Firing

Firing ceramics involves heating the dried ceramic to high temperature at a defined heating rate, holding (soaking) for a discrete time, and cooling back to room temperature under a defined cooling schedule. Firing is accomplished in batch kilns or continuous kilns. Batch kilns hold a defined quantity of product and go through a complete firing schedule before unloading of the fired product. In continuous kilns, the product is continuously charged to one end of the kiln, and it moves through the kiln at a uniform rate before discharge. Continuous kilns include tunnel kilns (where the product is set on kiln cars) and roller hearth kilns (where the product sits on and is propelled by ceramic rollers).

PHYSICAL PROPERTIES OF WHITEWARES

Key Physical Properties

The product requirements determine the physical properties of fired whiteware ceramics, and the properties can vary widely depending on the specific formulation, additives, forming method, and firing. Table 5 lists key physical properties by product.

Water adsorption, or porosity, is a critical physical property for all types of whiteware ceramics. Low values of porosity indicate a high degree of vitrification. Some product standards specify that a product must be impervious, which is defined as exhibiting a water adsorption of less than 0.5%. Many products are glazed on any surface that will be exposed to water during use to improve their resistance to water adsorption.

Methods for determining water adsorption and porosity for whiteware ceramics are described in ASTM C373 or in ISO 10545-3. In these methods, the ware is exposed to saturation for a specific period of time to determine the quantity of water that the ware can adsorb. Saturation can be achieved through boiling or vacuum, depending on the method.

Mechanical Properties

The mechanical strength of a whiteware product is important for many types of applications. For sanitary ware, the product must be able to resist the stresses applied during normal use; for tile, the product must be able to withstand the compressive load applied to the floor. Strength tests can be used to measure compressive strength or tensile strength, depending on the application. The most common type of test for the mechanical strength of whitewares is a simple bending or flexure test. Bending tests such as a modulus of rupture test measure the tensile strength of the ceramic in flexure. As with all ceramics, whitewares tend to fail more readily under a tensile stress than under a compressive stress because of their brittle nature.

The flexure test method is given in ASTM C648, ASTM C674 or ISO 10545-4. In these tests, a load is applied that flexes the ware, and this load is applied until failure occurs. For many intricately shaped products such as toilets or other sanitary ware, it is difficult to measure strength on the finished product because of the irregular geometry. For these products, samples can be cut to measure mechanical properties. Table 6 gives typical mechanical properties of whiteware products.

Another aspect of mechanical strength is impact resistance. For tableware, the product must have sufficient impact resistance to withstand dropped utensils or to resist impact stress in handling. Impact resistance not only is a function of the mechanical properties of the fired ware but also has to do with the physical design of the product. ASTM C368 gives methods for measuring impact resistance for tableware. A pendulum arrangement can determine the magnitude of impact that will initiate failure and the amount of energy required to produce complete failure. A similar method, described in ISO 10545-5, exists for ceramic tile.

For products subjected to wear in flooring applications, resistance to abrasion is a key concern. For glazed ceramics, the abrasion resistance test measures the resistance of the glaze and not that of the underlying ceramic ware. Tableware must be able to resist degradation by abrasive cleaning agents.

ASTM C1027 and ISO 10545-7 describe the measurement of abrasion resistance of ceramic tile. In these methods, an abrasive load is agitated on the glazed surface of the tile for a set number of cycles. The surface is inspected at specific intervals. Observers note the number of cycles that the product passes through before the surface is degraded and that observation determines the category of abrasion resistance.

For unglazed surfaces, the procedure for measuring abrasion resistance is slightly different. In these methods, a large wheel is rotated over the ceramic surface. The wheel can be made of abrasive material or abrasive grit can be introduced to the rotating wheel just above the surface of the ceramic. The loss of mass after a defined number of rotations is used to determine the abrasion resistance. ASTM C1243 and ISO 10545-6 give examples of this type of measurement.

Chemical Resistance

Chemical resistance is especially important for products that are in contact with food or exposed to harsh cleaning agents. Staining resistance is important for similar reasons. Properly formulated and

Table 5. Key physical properties

Product Type	Physical Properties
Tile	Water adsorption (porosity), strength, abrasion resistance, chemical resistance, dimensional tolerance, surface finish and color
Sanitary ware	Water adsorption (porosity), strength, resistance to staining and color
Tableware	Impact resistance, abrasion resistance, chemical and staining resistance, resistance to metal marking, resistance to lead and cadmium release, and color
Electrical porcelain	Mechanical strength, water adsorption (porosity), and electrical resistance

Table 6. Typical mechanical properties of whiteware ceramics

Property	Earthenware	Hard Porcelain	Bone China	Hotel China	Normal Electrical Porcelain	Hard Electrical Porcelain
Water absorption, %	6–8	0.0–0.5	0.0–1.0	0.1–0.3	0.0	0.0
Bulk density, g/cm ³	2.20	2.40	2.70	2.60	2.40	2.77
Compressive strength, MPa	na	400	na*	na	700	700
Modulus of rupture, MPa	55–72	39–69	97–111	82–96	105	175
Modulus of elasticity, GPa	55	69–79	96	82	na	na
Thermal expansion coefficient, per °C, 20°–500°C	7.3–8.3	na	8.4	7.3–8.3	5.7	6.7
Thermal expansion coefficient, per °C, 20°–1,000°C	na	3.5–4.5	na	na	na	na

Adapted from Wood 1991.

* na = not available.

fired glaze compositions should be very resistant to household chemical attacks and easy to clean. Some unglazed surfaces such as mechanically polished porcelain tile can exhibit poor staining resistance because closed pores near the surface can be exposed by the polishing process.

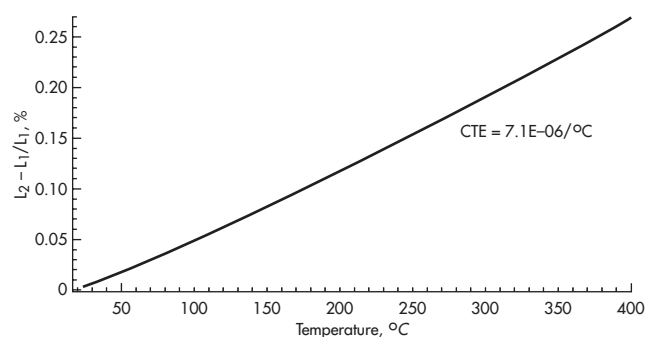
Most chemical and staining resistance tests involve exposure to the chemical or staining agent followed by a specified cleaning procedure. After the cleaning procedure, the surface is inspected under specified viewing conditions, and the results are qualitatively determined. Staining resistance indicates how easy the surface will be to clean after use. ASTM C650 and ISO 10545-13 give examples of methods for measuring chemical resistance, and ASTM C1378 and ISO 10545-14 give examples of staining resistance methods.

The resistance of tableware to “metal marking” is related to staining resistance. In this case, the glaze must resist staining when cutlery is passed across the surface. Resistance to metal marking is a function of both the condition of the glaze surface and the composition of the glaze. Typically, glossy surfaces are more resistant than matte surfaces.

The leaching of metals from tableware is also related to chemical resistance. Test methods have been developed specifically for cadmium and lead release from ceramic products. One concern is that acidic components of food or beverages may leach small quantities of these species from the glaze. Test methods such as ASTM C738 detail an accelerated leaching test for glazed ceramic surfaces that can be used to determine the potential risk of metal exposure from a particular glazed surface. The leaching takes place in an acetic acid medium, and atomic adsorption spectroscopy measures the quantity of metal leached from the surface.

Thermal Shock

Resistance to thermal shock is important for products such as sanitary ware, which may be subjected to rapid switching between cold and hot water. ASTM C484 reports a method for measuring thermal shock resistance. In this method, the ware is soaked in water at 16°C and then immediately moved to an oven operated at 145°C for up to 10 cycles.

**Figure 5. Thermal expansion of fired whiteware body and glaze**

Thermal Expansion

In most cases, it is desirable to measure the thermal expansion of the ware. This is often done in product development to match the thermal expansion of the glaze and the body. The coefficient of thermal expansion (CTE) is measured according to the following equation:

$$CTE = \frac{\left(\frac{L_2 - L_1}{L_1} \right)}{T_2 - T_1}$$

where L_1 is the length at temperature T_1 , and L_2 is the length at temperature T_2 . Thermal expansion can be useful for architects or engineers determining where to place expansion joints in large ceramic tile installations. The dimensions of the CTE are in./in./°F or simply /°F (and similarly cm/cm/°C or /°C).

Thermal expansion is measured using a dilatometer, which employs a ceramic pushrod to follow the dimensional change of a sample as it is being heated. ASTM C372 gives test methods for measuring thermal expansion with a dilatometer, and Figure 5 shows an example measurement of the CTE on a glaze sample.

Color and Gloss

Color and gloss are routinely measured on whiteware products. The first step in measuring color is to quantitatively describe color. The phenomenon perceived as color derives from the interaction between visible light and matter. This interaction can include adsorption, reflection, refraction, diffraction, scattering, and fluorescence. Adding to this interaction is the fact that color perception is strongly influenced by the illumination source.

The science of describing color received a great deal of attention in the last century. Of the several color measurement systems, the most common is based on the International Commission on Illumination (CIE) $L^*a^*b^*$ color system. These measurements describe a three-dimensional color space where the L^* value describes the whiteness or lightness of the article, the a^* value describes a red to green axis, and the b^* value defines a yellow to blue axis.

Two types of instruments for measuring color are available. These instruments have a selection of standardized illumination sources and illumination angles. Colorimeters are the simplest color-measuring instruments, and they use a set of filters to approximate the color space measurements and relate them to the standard observer curves published by CIE. Spectrophotometers are more advanced color measurement tools that measure reflectance and transmission data versus wavelength in small steps to describe the color.

Several standards, such as ASTM C609 and ISO 10545-16, exist to quantify small color differences between glazed surfaces. The color difference, ΔE , is defined as the magnitude of the difference between the vectors describing the color of each sample, as is shown in the following equation:

$$\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$$

The measurement of gloss is related to color perception. One common method for quantifying the perception of gloss is the method for measuring specular gloss described in ASTM C584. In essence, high-gloss surfaces result in very little scattering of the incident light. More scattering occurs as the amount of surface texture increases. Opacity measurements can also be made on translucent glazed products.

Electrical Properties

ASTM D116 summarizes the method to determine the electrical properties of whiteware ceramics. This method describes measurement of dielectric strength, electrical resistivity, and other properties of ceramics intended for electrical insulating applications.

GLAZES FOR WHITEWARES

Glazes are thin glass coatings applied to the whiteware surface. Glazes can be decorative layers or they may serve a purpose such as making the surface impervious so that it resists water penetration and staining. Glazes can be used to increase the electrical resistance or the mechanical strength of a particular product. Glazes are generally applied as suspensions (slips) of ceramic particles in water, but dry applications of particles are available. Functionally, the glaze formulation must readily bond to the ceramic surface and provide even surface coverage during melting in the firing cycle. The glaze should also have a similar thermal expansion to the body to avoid defects on cooling in the kiln.

A variety of constituents are used in glaze formulations; these can include materials used in the body formulations (clay, feldspar, and silica), and other components such as coloring agents, zinc oxide, carbonates of barium and strontium, and borates are usually present.

Silica (SiO_2) is the primary constituent of the glass formulation; it provides the network structure of the glass. The silica is derived from quartz (flint), clay, feldspar, or any other silicates in the formulation. Borates are unique in that they serve as network formers and they typically decrease the melting temperature. Excessive levels of borates can result in durability problems with the glaze. Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) is the primary source of borates, but other minerals such as colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$) are also available. The boron content of a glaze is generally reported on a chemical analysis as boric oxide (B_2O_3). Lead (as PbO) was an integral part of any glaze formulation in the past. Adding lead to the glaze allowed a lower firing temperature and improved glaze coverage in firing. Leaded glazes produce a superior fired finish, but, because of health concerns, manufacturers severely curtailed lead usage, using instead zinc oxide and borates in glaze formulations. Zinc oxide acts as a flux, and it enhances the effect of other fluxes.

The silicate structure is modified by alkalis and alkaline earth components, which act as fluxes (reduce the melting temperature). These components “disrupt” the silicate structure, reducing the viscosity of the melt. The more alkalis and alkaline earth elements in the glaze, the lower the melting point, but care must be taken because excessive levels of these elements can result in durability or devitrification problems.

Alkalis and alkaline earths are introduced into the glaze from silicates such as feldspar, but they can also be contributed by soda ash or other carbonates and hydroxides. Care must be taken when dealing with soluble carbonates or hydroxides because they alter the rheology of the glaze. Also, high levels of alkalis and alkaline earth components increase the thermal expansion of the glaze. As the thermal expansion of the glaze increases, the likelihood of defects in the fired product increases.

Oxides such as alumina (Al_2O_3) are known as “modifiers” and help improve the chemical durability of glasses. Alumina can also be added to glazes to produce matte or satin finishes. Similarly, when zirconia is added to glazes, usually in the form of zircon (ZrSiO_4), it acts as an opacifier by precipitating zirconia crystals. Opacifiers based on titanium oxide and tin oxide may be required in combination with certain pigments.

Glaze Application

Glazes are applied in liquid or paste form, requiring that the ceramic components be in aqueous suspension. Glazes can be milled to achieve the proper particle size or, if the components are fine enough, can be simply mixed with water in a high-intensity mixer to disperse the suspension.

Frits are commonly used in glaze formulations. Frits allow the use of soluble components such as B_2O_3 , which would be difficult to incorporate in raw mineral form. Frits offer an energy savings because they are premelted and require less batching when preparing the glaze application.

Glaze formulations that require particle size reduction are ball milled to create homogeneous suspensions. As with slips for spray drying, the residue, solids content, and viscosity are monitored during milling of glaze suspensions. The residue is simply the amount of material retained on a selected screen, usually 200 or 325 mesh, after a sample of the glaze has been washed over the screen. The higher the amount of material retained on the screen, the coarser the glaze. Specific gravity can be measured with a pycnometer, and viscosity can be measured with either Zahn or Ford cups, the latter of which measure the time required for a sample of the suspension to drain through a specific diameter orifice.

The specific gravity (or viscosity) can vary widely with glaze slurries used for spraying and with thick pastes used for screen

applications. Binders or suspending agents are commonly added to glazes to achieve desired effects. Organic binders such as carboxy methyl cellulose (CMC) are commonly used, or a lternately bentonite or hectorite clay minerals are added to thic ken the glaze and improve green strength. Suspending agents such as kao lin, bentonite, or colloidal silica can be used to prevent settling in the glaze before application.

The oldest method of glaze application is dipping the ware into a bath of the glaze composition. This leaves a uniform coating of the glaze on the surface of the ware and facilitates application to intricate shapes. Handling the glazed ware, especially large or heavy pieces, can be problematic. Brushing is another simple technique to achieve uniform coatings of glaze.

A modern glaze line is a collection of modular glazing equipment that is assembled to achieve particular effects. The simplest operation is the bell or waterfall. In this system, a continuous flow of glaze is allowed to flow across a curved metal surface. The glaze, as a continuous "waterfall," is applied as the ware passes under. This application method is chosen to apply uniform coatings of engobes or glazes on wall tile.

Spray booths are also used to apply uniform glaze coatings. For some very intricate shapes, the glaze may be sprayed on by atomizing the glaze in a moving air stream. The glaze adheres to the surface of the ware when the droplets impact the surface. This application requires a skilled operator to achieve a uniform coating.

Excess glaze from these systems is collected and recycled in the glaze system. Usually screening is used to remove contamination from the glaze. Brushes or fettling systems remove excess glaze from the edges of tile. In some systems, brushes partially remove the applied glaze after an application, to achieve a particular visual effect.

For many applications, uniform coatings are not desired. Either patterns or random effects may be desired. Spray guns are used to apply mists of glaze called *fumes*. The guns can be stationary or move as the product, usually a tile, passes underneath. Timers are also used to turn the gun on and off to achieve a random effect. Patterns are applied with silk screens. A paste or thickened glaze composition is placed on the back of the screen, and when a tile passes under the screen, a squeegee moves across the screen, pushing the glaze through the screen and thereby applying the pattern to the tile.

Modern systems producing highly decorated tile use banks of screens that can apply multiple patterns to a single tile. Other systems apply a particular pattern intermittently to give a randomized decoration to the tile. In addition to flat screens, roller systems are popular. These roller systems can be operated asynchronously, which randomizes the decoration.

When a granular texture is desired, dry glazes or crushed frits can be applied to the tile. In these systems, a liquid glaze is first applied to the surface of the ware, and the dry glaze is then distributed on the surface. The liquid glaze helps the granular glaze adhere to the surface. This application technique can be used to apply abrasive to the surface of the ware to improve the slip resistance of the fired surface.

Hand painting and decals are used to apply a final decoration. This is especially true for fine china, where a ceramic decal may be applied to the fired glaze followed by a final firing to bond the pigments in the decal to the glazed surface. Decals made from ceramic pigments are available from a variety of sources.

Firing of Glazed Ware

During the maturing of the glaze in the kiln, a number of processes take place, including decompositions, solid-state reactions, vitrification, fusion, and crystallization. Although these processes tend to

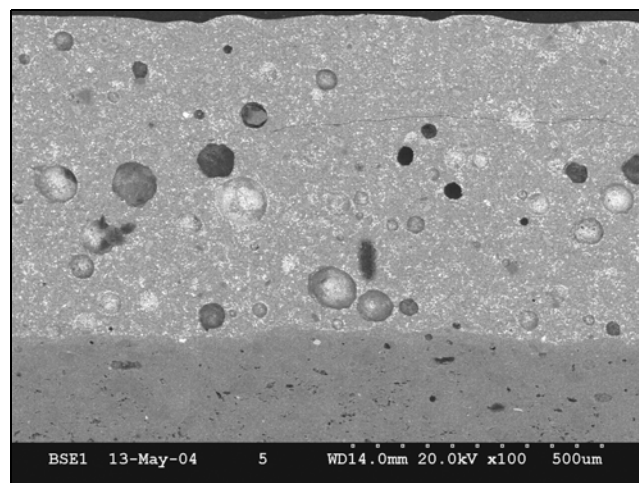


Figure 6. Backscatter scanning electron microscopy (SEM) image of gas bubbles in a sanitary ware glaze

take place in the order listed, in fast firing this may not be the case. For example, decompositions may still be taking place as a glassy phase is developing, in effect retarding the rate of decompositions. Decompositions include the oxidation of organic binders, dehydroxylation of clays used as suspending agents, and decomposition of hydroxides, carbonates, or sulfates. These decompositions yield porous, high-surface-area components that react readily with other glaze constituents.

Before the formation of a glassy phase, some solid constituents react to form new compounds. These can generally be characterized as acid/base reactions. The acidic species is silica and the basic species are either alkalis or alkaline earth constituents. New compounds such as CaSiO_3 can be formed from CaO and SiO_2 at relatively low temperatures. The extent of the formation of new compounds is limited by the low mobility (low diffusion rate) of oxides in the solid state.

During vitrification, a glassy phase forms. The formation of this phase is a kinetic process, meaning that both temperature and time are important variables. This temperature/time relationship is called *heat work*. As the heat work increases, the quantity of glassy phase increases. This glassy phase tends to wet the ceramic particles. The phase continues to grow by dissolving residual ceramic particles. The liquid phase pulls the unmelted particles together, resulting in shrinkage and reduced water adsorption. Additionally, the presence of the glassy phase improves the mobility of the various oxides in the glaze during firing. This improved mobility helps homogenize the glass composition and enhances the rate of glass formation.

As the quantity of glassy phase increases because of the heat work, the viscosity of the glaze decreases and eventually the glaze becomes molten. The surface tension of the glaze allows it to wet the surface of the ware, which promotes adherence of the glaze to the ceramic surface. Once the glass is molten, degassing must occur to achieve a defect-free surface. Gases can be the result of incomplete decompositions in either the glaze constituents or the underlying body. Components of the ceramic body formulation, such as talc and carbonates, can contribute to gas evolution since they begin to decompose only after the glaze has begun to vitrify. Gas trapped between glaze particles or adsorbed on surfaces can contribute to bubble formation. Figure 6 shows an example of bubbles in a fired glaze.

On cooling, some species are not soluble in the glaze composition and precipitate crystals in the melt. The most common crystallization process that takes place is the precipitation of zircon crystals, which opacify the glaze. Precipitated opacifier crystals are visible under magnification as bright spots in the sanitary ware glaze. Crystallization of either alumina or other aluminates on cooling produces matte or satin glaze finishes. Other unintentional crystallizations, referred to as devitrification, can occur. These are mainly caused by a high level of alkalis or alkaline earth constituents in the glaze.

To impart color, pigments are added to the glaze composition. The array of pigments and their potential interactions are extensive. There are three methods of imparting color to a glaze:

1. For body colors in porcelains, finely ground transition metal oxides such as CoO (cobalt oxide), Cr₂O₃ (chromium oxide), and Fe₂O₃ are added to the glaze formulation. These metals dissolve into the glaze during firing. This method is not frequently used because of problems obtaining sufficient color intensity.
2. A second method for coloring glazes is to specially formulate the glaze, allowing colored crystals to precipitate from the melt on cooling.
3. Adding insoluble colorants to the glaze is the most common method for coloring glazes. The most frequently used pigments are doped zircon compounds, although a wide variety of synthetic spinels and other oxides are available. The doped zircon compounds are the most stable over a wide temperature range. Some examples of these colorants include (Zr,Pr)SiO₄ (yellow), (Zr,Fe)SiO₄ (pink or coral), and (Zr,V)SiO₄ (blue). These crystals are capable of small substitutions of transition metals into the Zr⁴⁺ sites in the crystal structure to achieve the desired colors.

Defects in Glazes

Several types of defects are observed in glazed ceramic ware. The defects are related to gas evolution from the ceramic ware or from the glaze constituents, thermal expansion mismatch, or the lack of adhesion of the glaze to the ceramic substrate.

Bubbles or pinholes in the glaze are the most common defect. They are more frequently observed in leadless glazes, because these glazes do not flow as well as the older leaded glazes. The gases can originate from decompositions taking place in the glaze components, from decompositions taking place in the body, or from the air trapped between particles in the glaze. To avoid these gas entrapments, thin applications are used to shorten the path that the bubbles have to travel to be expelled. More heat work or more fluid glazes at the firing temperature help in bubble removal. Alternatively, materials that decompose once the glaze is molten should be removed from the glaze or body composition. Examples of materials to avoid if gas evolution is a problem are lime stone and talc. Another approach is to prefire the ceramic ware before glazing. Double firing of wall tile is relatively common. An uneven surface texture can indicate that better firing or a more fluid glaze is needed.

Thermal expansion mismatch between the glaze and the body can result in crazing or peeling, depending on the type of mismatch. Commonly the glaze has a higher thermal expansion than the ceramic ware. In this event, the glaze shrinks faster than the ware on cooling, resulting in tensile stresses in the glaze. The tensile stresses can literally "pull" the glaze apart. Crazing is a pattern of cracks that radiate outward from the center of the ware. The tendency to craze can be corrected by using thinner glaze applications, which reduce stress accumulation, or by reducing the thermal

expansion of a glaze. Removing some of the alkali content of the glaze can reduce thermal expansion. In some cases, lithium is used to replace some sodium (or potassium) in the formulation to reduce thermal expansion.

Excessive dimensional change during the quartz inversion on cooling the ware can also result in crazing. Reducing the quartz content or reducing the particle size of the quartz can help minimize the crazing that results from dunting.

When the glaze has a lower thermal expansion than the ware, compressive stresses result. Excessive compressive stresses produce a defect known as peeling or shivering, where defects are a section of glaze that separates from the edge of the ware. The stresses can be corrected by using a thicker glaze application and increasing the thermal expansion of the glaze. Increased alkali content of the glaze typically increases the thermal expansion.

Adhesion defects known as crawling or tearing can result from several sources. These defects appear as irregular areas with poor glaze coverage. Drying problems with the glaze are a common source of adhesion defects. When the glaze has excessive shrinkage resulting from a very fine particle size or high clay content, the coating can tear. An organic binder can be added to improve the green strength of the glaze to reduce tearing. A minimum application thickness, clay content, and grinding will help reduce the tendency to tear. When there are multiple glaze applications, drying problems can result if adequate drying does not take place between the application layers. Surface contamination can interfere with the adhesion of the glaze to the surface and result in crawling. Green or bisque ware should be handled as little as possible to avoid contamination by dust or oils, for example. Finally, excessive levels of opacifier in the glaze can result in poor wetting of the ceramic ware by the glaze.

Foreign matter in the glaze can result in defects. Inadequately ground frit or granular contamination can result in surface irregularities. Metal contamination can result in discoloration. The source of the foreign matter should be identified and removed from the system. It is also possible for problems with the ceramic ware to show through the glaze. Large pyrite or marcasite (FeS₂) agglomerates in the clay can erupt through the glaze surface during firing. Typically, the source of the contamination can be identified by sectioning at the defect and examining the limited area of the defect (body or glaze) by microscopy. Chemical analysis of the contamination may also help identify the source of the defect.

ECONOMIC TRENDS IN NORTH AMERICA

Globalization and consumer preferences are causing rapid changes in the fine ceramics economic sector in North America. Globalization is placing pressure on manufacturing costs, and the volume of imported products is growing rapidly. This is, in part, based on new consumption patterns, with large quantities of products purchased through wholesale and retail outlets that are part of national chain stores. The purchasing policies of chain stores focus on price. For toilet bowls, nonclay refractory, and ceramic tile, the selling price is relatively high compared to the unit weight of the product, making importation economically feasible. By contrast, import penetration for lower valued products like clay brick is limited to land shipment from Mexico or Canada in North America (Table 7).

Changes in consumer preference have affected sales for some whiteware sectors, including fine china. As an example, previous generations preferred fine china for wedding gifts, but many people today prefer other consumer products.

Quality improvements in imported white ware products and product innovation have been factors in increased import growth. In sanitary ware, "one-piece" toilets and innovative glazes that reduce

Table 7. Estimated production and import statistics for North America for 2004

	Brick	Flat Glass	Toilet Bowls	Nonclay Refractory	Ceramic Tile
Annual domestic production increase, %	8.0	1.4	0.2	0	10–20
Current import percentage	<0.25	8	8	18	50+
Growth in market share by imports, %/year	≤1.4	–0.3	0 until 1998	2.2	2.7

home maintenance and provide a measure of protection from mold and bacteria are available with some imported products. These products provide added value for the consumer and the potential for additional profits for builders.

With sales of white ware products linked to slow population growth and housing starts in developed countries, the prospects for rapid market expansion appear to be limited. Growth in import percentages is likely.

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Container Glass

Robert C. Freas

INTRODUCTION

Container glass, a mature product category that traces its roots back through more than 200 years, is distinguished from other glass industry sectors by both manufacturing method and end-use market. The container glass industry has undergone numerous technical changes in the past 30 years. For many years, glass containers were the primary packaging for beverages and most food products. Today, glass has been replaced in many of those markets with other competitive materials such as plastic, aluminum, and in some cases, polymer-lined cardboard containers. Yet in many applications and markets, glass holds its own, and in fact, the container glass industry has experienced a minor resurgence in recent years. Increases in container glass production and value have been very modest, averaging only 0.2% compounded annual growth over the last 5 years (Tincher 2004).

The container glass industry is of great importance to many industrial minerals producers. Glass manufacturing, including containers, consumes millions of metric tons of mineral raw materials annually, and may use up to 15 or 20 different mineral materials, depending on the specific glass batch requirement for the product being manufactured. The major mineral components consumed in container glass manufacturing are silica sand, soda ash (Na_2O), and limestone, although other minerals are also critical to the glass-forming process.

GLASS PRODUCTION

Glass containers are highly engineered products from both a structural and an aesthetic perspective. The design of the container includes multiple points of stress, which can be points of weakness and/or failure if there is an error in either the glass batch composition or the manufacturing process. On the aesthetic side, glass can be made in many colors and hues, but in most instances, it must be uniform throughout with no signs of bubbles or inclusions, which are frequently referred to as “seeds.”

In the glass-manufacturing process, raw materials are combined, or batched, before entering a throated furnace where they are melted together. Clark-Monks (1996) notes that this is the critical point, because the understanding and control of interdependent factors—starting with time/temperature relationships, consistent melting and forming properties, and consistency of raw materials—are the keys to furnace balance and quality control. The melting process follows a “critical current path” that represents the lowest temperature

and shortest time the molten glass will experience within the furnace and becomes the point at which the glass quality is defined. As noted in the discussion later on raw material, consistency in both the chemistry of each raw material and its particle-size distribution plays a critical role in the uniformity and consistency of the molten batch and the quality of the container produced.

The glass batch begins to melt at 600° to 900°C, and as melting continues, carbon dioxide (CO_2) and other gases are released, forming bubbles in the molten glass. The temperature of the batch continues to increase until it reaches approximately 1,300° to 1,400°C, although the temperature may vary depending on the type of furnace. Currently, about 25% of glass furnaces in the United States are newer-generation oxy-fuel systems (Tincher 2004) that are more thermally efficient in reaching and maintaining higher temperatures. This is important because the molten glass is refined at these higher temperatures. It is here that the last bubbles are driven off and the melt is in motion, becoming homogenized, which is critical to the uniformity of each container produced and to the elimination of slag or scum forming on or in the glass.

Once the glass has been refined, the temperature of the batch is cooled to 1,100°C to achieve the proper viscosity for glass forming. As the more viscous glass exits the throat of the melter, it flows to one of several forming machines. Here, a specific volume of glass, or “gob,” is metered from the melt. The gob is the molten glass required to form one container. Each gob drops into a mold where air is injected to form the “parison,” or preliminary shaped blank of molten glass. While still glowing hot, the glass is flipped and air is injected again to finish forming the container. The newly formed container is cooled to maintain its integrity, but it is not yet fully cooled nor structurally stable. Once formed, the glass moves to the annealing ovens where it is reheated slowly and then cooled at a specific rate to allow the stresses in the glass to stabilize (i.e., be relieved), thus preventing premature or excess breakage.

MANUFACTURING COMPANIES AND LOCATIONS

In the past two decades, the container glass industry has undergone extensive rationalization in the United States and throughout the world. Ball, Kerr, Diamond, and Thatcher—once household names as U.S. glass producers—no longer exist. Consolidation within the North American glass industry has left three primary container glass manufacturers in the United States—Owens-Illinois, Saint Gobain, and Anchor Glass Container—along with a limited number

Table 1. Container glass plants in the United States

Container Glass Plants	
Anchor Glass	Saint Gobain
Elmira, NY	Burlington, WI
Henryetta, OK	Carteret, NJ
Jacksonville, FL	Dolton, IL
Lawrenceburg, IN	Dunkirk, IN
Salem, NJ	El Monte, CA
Shakopee, MN	Henderson, NC
Warner Robins, GA	Lincoln, IL
Winchester, IN	Madera, CA
Owens-Illinois	Milford, MA
Atlanta, GA	Pevely, MO
Auburn, NY	Port Allegany, PA
Charlotte, MI	Ruston, LA
Chicago Heights, IL	Sapulpa, OK
Clarion, PA	Seattle, WA
Crenshaw, PA	Waxahachie, TX
Danville, VA	Wilson, NC
Lapel, IN	Arkansas Glass
Los Angeles, CA	Jonesboro, AR
Muskogee, OK	Carr Lowery Glass
Oakland, CA	Baltimore, MD
Portland, OR	Demptos Glass
Streator, IL	Louisville, KY
Toano, VA	Napa, CA
Tracy, CA	Flat River Glass
Waco, TX	Flat River, MO
Winston-Salem, NC	Gallo Glass
Zanesville, OH	Modesto, CA
Wheat Ridge, CO	Longhorn Glass
	Houston, TX
Specialty-Glass Producers	
Anchor Hocking	Leona Industries
Lancaster, OH	Bridgeton, NJ
Monaca, PA	Libby Glass
Corning Glass	Toledo, OH
Harrodsburg, KY	Industry, CA
Durand Glass	Spectrum Glass
Bridgeport, NJ	Woodville, WA
Gentile Glass	Saint Gobain
Star City, WV	Covington, GA
Indiana Glass	Wheaton Glass
Dunkirk, IN	Millville, NJ
Sapulpa, OK	

of small single-plant or specialty-glass manufacturers. The only new producer is Longhorn Glass in Houston, Texas, which is owned by Anheuser-Busch.

Anchor Glass Container, which operates eight glass plants, is the third largest producer of container glass in the United States. Over the years, Anchor acquired both Diamond Bathurst and Thatcher Glass before being acquired by Vitro (Mexico). Next, it was bought by Consumers Packaging of Canada before filing for bankruptcy. The company emerged from bankruptcy in 2001 as Anchor Glass Container Corporation and is now on solid financial

footing. Anchor Glass produces a diverse line of glass, including flint (clear), amber, and green containers for the food and beverage markets.

Owens-Illinois, formerly Owens Brockway after the acquisition of Brockway Glass in 1988, purchased the Canadian assets of Consumers Packaging, Inc., in 2001 and became the largest producer of glass containers in North America. Owens has 19 glass-production facilities in the United States, including the former Coors Glass plant in Colorado. The company is the only one of the three major U.S. glass producers to manufacture plastic containers; its Web site (www.owens-illinois.com) notes that they have 33 plastics plants in the United States and that plastics account for one third of corporate sales worldwide. Owens has been a leader in glass technology and recycling, reporting that 35% of its glass batch raw materials are from recycled glass. Outside of North America, the company's international container glass plants include facilities in several European and South American countries and China.

Saint Gobain, a French-owned company headquartered in Les Miroirs, France, is the second largest container-glass producer in the United States. In 1999, the company purchased Ball Glass (which had previously acquired Kerr Glass), along with the Foster Forbes Glass Division of American Can Company, and combined the two under the Saint Gobain name. Today the company operates 17 glass plants, producing a full array of container glass products. Saint Gobain's worldwide operations produce container glass, float glass, fiberglass, and ceramics (O'Driscoll 1977). The company's container-glass production facilities are located in the United States, Europe, and Brazil.

Other major non-U.S. producers of glass include Swedish-based Rexam PhC, one of the world's 10 largest packing producers (Kendall 1999). Rexam operates plants that produce glass, metal, and plastic containers. Rockware Glass Ltd. is the largest container glass producer in the United Kingdom, followed by TT Group PLC. Owens-Illinois, the world's largest producer of consumer packing, is one of the most dominant producers in Asia through its ACI Australian glass subsidiary and affiliated plants in Japan and China.

Although consolidation within the North American container glass industry has had an impact on industrial minerals producers, that is only part of the story. Many glass plants have closed in the United States, several of which were older, smaller, and less-efficient plants. Others represented excess capacity that could no longer be justified by the industry. At the same time, other plants were rebuilt, modernized, and expanded. Table 1 lists the locations of container glass plants in the United States.

CONTAINER GLASS MARKETS

For many years, the container glass industry experienced extensive competitive pressure from the aluminum can and plastics industries, particularly those that manufacture polyethylene terephthalate (PET) containers. Soft drinks and other beverages as well as numerous food and household products that were once packaged in glass are now marketed in plastic and/or aluminum. The key factors affecting the shift from glass to aluminum and plastic packaging are their light weight and ease of handling. The full impact on the container glass industry, which was at overcapacity both in North America and Europe, resulted in many plant closings during the 1980s. Plants continued to close through 2004, when Anchor announced the closing of its plant in Connellsville, Pennsylvania. The overcapacity also resulted in pricing pressure that ultimately led to consolidation in the industry.

For the last decade, U.S. container glass production has been fairly flat at 270 to 275 million units per year; the only segment

showing any real growth is the beer market. Kendall (1998) noted that glass shipments had increased nearly 25 % throughout the 1990s, and that apparent growth has continued into the early twenty-first century. Today, narrow-neck beer bottles account for nearly 60% of the container glass consumed. The growth in the beer bottle market has been offset largely by losses in other container glass markets as plastic continues to replace glass.

Although beer bottles have been the major bright spot for container glass producers, it is not without its challenges. Plastic beer bottles, which have been produced in Europe for more than 10 years, have now found limited acceptance in the United States. The key to producing plastic beer bottles is the co-extrusion of a barrier film that prevents the gas migration that causes the beer to become flat. Although several polymer systems have been used successfully, they are expensive and provide only limited shelf life for the beer. U.S. beer consumers have been reluctant to accept plastic beer bottles, so distribution has been limited to athletic stadiums and recreational beach locations where broken glass poses serious safety risks. Currently in the United States, it appears that plastic beer bottles will have a greater impact on the aluminum can market than on the container glass market.

Looking toward the future, the prospects for the container glass industry are positive. Rationalization is essentially complete, and most production facilities have been upgraded. More importantly, the trend from glass to plastic has slowed considerably now that the conversion of soft drink and milk packaging from glass to plastic is complete. Specialty ice tea and boutique beverages, along with the emergence of microbrewery beers, have had a positive impact on container glass consumption. That, combined with continuing growth in beer consumption, suggests that the market for glass containers has stabilized, and the market is actually growing at a modest 1.5% to 3.0% per year (Fredonia Group 1999).

RAW MATERIAL REQUIREMENTS

Each glass producer has its own formulation for the production of glass containers, and each includes high-purity silica sand as the primary batch raw material. Table 2 lists the general raw materials required for container glass, and Table 3 shows a typical composition for container glass as oxides. It is critical in the manufacture of container glass that all mineral raw materials be consistent in both chemical composition and particle-size distribution. Four excellent articles on raw materials for container glass are Lines (2004); Kephart, Pool and Ryder (1986); Lavender (1988); and Vogel (1985).

Silica (SiO_2) is the basic building block in glass formation. As the dominant oxide in glass, it provides much of the body bulk. Silica must have a minimum value of 99.0% SiO_2 ; some specifications may require a minimum of 99.5% SiO_2 . High-purity quartz sand is the primary source of silica in the glass batch. Several of the other batch raw materials, however, include small amounts of silica that must also be accounted for in the batch. Some glass formulations, particularly where high thermal shock or chemical resistance are critical to end use, require a very small amount of borosilicate that can be added with the silica sand.

Soda ash, the second most common ingredient in container glass, is the predominant glass modifier. As a modifier, Na_2O acts as a flux that allows the melting point of the batch to be approximately 200°C lower. An additional benefit is that the lower temperature extends refractory life.

Limestone contributes calcium oxide (CaO) to the batch, which modifies the glass, increasing its strength and resistance to abrasion. Much of the value of the limestone is realized during the annealing phase of glass production. Most limestone specifications require a

Table 2. Raw materials required for container glass

Raw Material	Percentage
Silica sand	60
Soda ash	19
Limestone	14–18
Alumina*	4–5
Sulfate	1

* Usually feldspar or nepheline syenite.

Table 3. Typical oxide composition for container glass

Oxide	Percentage
SiO_2	73
Na_2O	14
CaO	10
Al_2O_3	2
SO_4^*	1

* Sulfate from salt cake or gypsum.

minimum of 97% calcium carbonate (CaCO_3) and a maximum of 0.12% iron oxide (Fe_2O_3).

The specification for iron in limestone for standard container glass is 0.12% Fe_2O_3 ; however, there are several specialty-glass producers with a lower maximum iron specification of 0.04% Fe_2O_3 . These producers make very clear flint glass and/or crystal and cannot tolerate iron discoloration. Traditionally they use aragonite with low iron from the Bahamas, but this source was sold and aragonite production was curtailed sharply in late 2003.

Feldspar is the most common source of alumina (Al_2O_3) for glass production, although in many instances nepheline syenite is used instead. Alumina is an important glass modifier, and its inclusion in the batch increases durability of the glass and reduces its tendency to devitrify.

Several minerals are used as coloring agents or chromophors in container glass. Clear, or flint glass, may be tinted for reasons of both function and appearance. When tinting is required, the following elements commonly are used to produce specific colors:

- Green—chromium and iron
- Yellow—chromium, vanadium, and cadmium
- Blue—cobalt and iron
- Amber—iron
- Red—selenium

Other minerals may be used in container glass formulations to assist in developing other specific properties, particularly for specialty containers (e.g., containers that require an opacifier to be added). The chapter on Specialty Glass presents an excellent discussion on the use and application of these minor constituents.

As mentioned previously, the chemical and physical consistency of batch raw materials is vital to quality glass production. It is necessary to maintain homogeneity in molten glass and to sustain constant, uniform viscosity throughout the glass-forming process. Medalyer (1996) notes that the homogeneity of glass is affected by both the chemical uniformity of batch raw materials and their moisture levels. Because raw materials are blended on the basis of weight evaporation, moisture can affect the composition of glass during melting.

Cullet, or recycled glass, is an ingredient used in most glass batches. Bottle laws and environmental initiatives on recycled

content have mandated that more cullet be employed in batch raw materials. The amount of cullet being handled and blended varies significantly from one glass plant to another (Rosenthal 1996). But from a minerals standpoint, the greater the content of cullet, the lower the requirement for natural mineral raw materials.

SUMMARY AND CONCLUSION

Glass container production in the United States and throughout the world has declined as other types of packaging have replaced glass. Nevertheless, the industry has now stabilized and is growing at a very modest rate. As glass container producers look ahead, three major issues receive the most attention: container weight, increased melting and energy efficiencies, and ever-changing environmental laws and requirements.

As plastic competes with glass, and as bottles are recycled rather than refilled, container weight receives more attention. A container weighing less means reduced wall thickness and less glass by volume. As the wall thickness decreases, stresses within the glass container increase and durability and strength suffer. Minerals producers are concerned that decreasing container weight will result in a decrease in the volume of minerals that the producer requires.

Because energy is a major cost component of glass manufacturing, melter efficiency has been the focus of industry research for many years. Future goals of the industry leaders for 2020 are (1) reduction in production cost to 20% below 1995 levels, (2) reducing energy use by 50% below 1995 levels, and (3) reducing air and water emissions by 20% below base-year levels (Tincher 2004). These goals can be met with aggressive technological innovations such as the oxy-gas-fired submerged combustion melter; (Greenman 2004).

The manufacture of glass requires melting of a number of raw materials that, when thermally altered, emit various compounds in the atmosphere. Major emissions include CO₂, sulfur, and nitrous oxides with lesser amounts of hydrochloric acid, hydrofluoric acid, and carbon monoxide.

Norman and Shulver (1999) present a complete discussion of these emissions along with a discussion of other impacts on the glass industry. Emphasis on environmental quality has been ongoing in both the United States and Europe, with the U.S. Environmental Protection Agency (EPA) emphasizing the use of best available control technology (BACT). BACT will have associated costs that most likely will increase the focus on using recycled glass to reduce emissions from unmelted natural raw materials, but the full impact of this has yet to be determined.

In conclusion, the supply of industrial minerals materials to the producers of glass containers represents a very high-volume market. The container glass market is a mature market that is stable to slowly growing. As industrial minerals producers recognize container glass as a major market for their products, they must be ready to maintain consistently high-quality specification standards because these standards will probably increase over time. The move to lightweight containers and the increased use of cullet will reduce the volume of raw materials consumed, but the demand for higher-quality industrial minerals will exist for many years to come.

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Fiberglass

Kevin Schaal

INTRODUCTION

It is estimated that there are about 600 glass-melting furnaces operating in North America. These furnaces produce glass for a variety of products ranging from architectural and automotive glass, glass containers, and specialty glass to fiberglass. Of the 600 furnaces, approximately one-sixth produce fiberglass, including both insulation glass and textile glass.

Insulation and textile fiberglass are differentiated on the basis of their end use, the raw materials used and their specifications, and to a somewhat lesser degree by the manufacturing methods employed to produce these two products. This chapter discusses the manufacture of fiberglass, the raw materials required, and the end-use markets for both insulation-grade and textile-grade fiberglass.

GLASS-MAKING FURNACES

Glass furnaces are generally first categorized by the fuel sources used to heat them. Some furnaces are heated electrically, others are heated by the combustion of natural gas or propane, and in many cases, combustion and electric boost are used in combination. Combustion-heated furnaces are further categorized by the method used to recover heat from the exhaust gas stream, and by whether air or oxygen is used in burning the fuel.

The use of oxygen in place of combustion air is one of the more recent developments in the fiberglass industry and is becoming widely accepted and highly successful. When oxygen is used, an oxygen-generating plant is often constructed on site in the general vicinity of the glassmaking furnace. In cases where the glass furnace is smaller in size, tanker trucks make deliveries of oxygen.

When the furnace is heated with natural gas and combustion air, it is common to recover some of the waste heat from the exhaust gas with a recuperator or less often with a regenerator. Recuperators are heat exchangers in which the outgoing hot waste gases transfer some of their energy to cold air needed for combustion by transfer through metal or ceramic pipes. In a regenerator, the waste gases pass through a chamber in which refractories are stacked in such a way that the hot flue gases pass between them and the rebuy transfer some of the thermal energy to the refractories. After about 20 minutes, the flue gases are diverted through an alternative chamber while cold air is passed through the first chamber in the reverse direction, thus absorbing thermal energy. The air then passes as preheated combustion air to the burners.

When the furnace is heated with natural gas but oxygen is used in place of combustion air, the volume of exhaust gases is reduced by approximately 80%, making it uneconomical to install and operate a recuperator or a regenerator.

For electrically heated furnaces, current can be passed through the glass bath using submerged electrodes made from metallic molybdenum, because glass at elevated temperatures is electrically conductive. The electrode-holders are water cooled on the cold face of the furnace to prevent the molybdenum from overheating, as molybdenum oxidizes rapidly when temperatures exceed 600°C (1,112°F). Electrodes can be inserted into the furnace from the top, the bottom, or through the side walls. Electrodes are slowly consumed in the process of melting the glass, making it necessary to add replacement electrodes periodically. Electrodes come supplied with threaded ends so replacement electrodes are screwed into the end of the existing electrodes and pushed into the glass bath.

Operating glass furnaces produce from as little as several metric tons of glass per day to upwards of 227 tpd. The dimensions of the larger furnaces might be 18 m (60 ft) long by 6 m (20 ft) wide, with a glass depth of slightly more than 1 m (40 in.). Smaller all-electric furnaces might be 2 to 3 m (6.6 to 9.8 ft) in diameter and hold 0.6 m (24 in.) of glass. The life of a combustion-fired furnace can be as long as 7 or 8 years, whereas the life of an all-electric furnace, depending on design, can be as short as 6 months. One advantage to a small all-electric furnace is the short length of time required to re-brick a furnace. For some furnaces, the glassmaking operation can be resumed in as few as 24 hours.

Charging of mixed batch to the furnace is usually accomplished through the use of feed screws or augers that deposit the well-blended ingredients directly onto the surface of the molten glass. As the batch melts and moves downstream, the glass is often stirred or agitated by the use of bubblers pulsing air or oxygen into the glass from the bottom of the melter via metal bubbler tubes.

The glass exits the melter into a refining chamber or into distribution channels or a forehearth that directs the glass to the device used to convert it to fibers.

FIBERIZATION TECHNOLOGIES

Rotary Fiberization

Rotary fiberization uses a metal disc with multiple rows of holes precisely drilled around the circumference of the disc. Hot glass

enters the spinning disc and centrifugal force causes the hot liquid glass to exit the holes in the form of fine, discontinuous fibers required for insulation products. Additional attenuation is accomplished by putting the fibers in the path of a high-velocity stream of air or combustion gases. Next, liquid binders are applied, and the fibers are collected in a vacuum box in the form of a blanket. Binders are cured by passing the glass mat containing the uncured binder through an oven. The average diameter of fibers produced by the rotary process ranges from 2 to 6 μm , with the diameter distribution running from submicrometer to as high as 20 μm . The velocity of fibers exiting the rotating spinner is in the range of 150 m per sec (500 ft per sec) and the throughput of one spinner can be as high as 1,135 kg per hr (2,500 lb per hr).

Flame Attenuation

Flame attenuation fiberization is one of the oldest techniques used to make fiberglass insulation products. The flame attenuation process is sometimes referred to as the pot and marble process. In this process, glass marbles are melted in small-volume, cylindrical-shaped Inconel pots. The pot bottom contains concentric rings of holes from which a primary glass fiber, approximately 1 mm in diameter, are drawn. Secondary attenuation occurs when the primary fibers are carefully placed in front of a high-temperature, high-velocity burner. The flame breaks the filaments into long fibers with a narrow diameter distribution that then pass through the binder spray. Fibers less than 0.5 μm in diameter can be produced by this process. The drawbacks of the flame attenuation process are that it is very inefficient in terms of energy consumption and the production rate per pot hour is very low.

Continuous Process

Textile fibers produced by the continuous filament process are made by drawing molten glass through orifices in platinum-alloy bushings and then rapidly pulling them to reduce their diameters to the prescribed size. Each orifice ranges from 0.8 to 3 mm (0.03 to 0.12 in.) in diameter and bushings have been constructed with as many as 6,000 orifices producing at a rate of more than 210 kg per hr (460 lb per hr). A bushing is heated by the hot glass entering it from the glass distribution channel and by supplemental heat applied electrically. The individual filaments from each bushing orifice are gathered into one strand or bundle, which is then either chopped into discrete length pieces from 3 mm to 50 mm ($1/8$ in. to 2 in.) long by a mechanical chopper or wound into cakes by filament winders. These mechanical devices operate at speeds up to 120 m per sec (394 ft per sec) and result in fiber having diameters that range from 3 to 20 μm . Because glass filaments are highly abrasive when rubbed against one another, size coatings are applied to the individual filaments before the strand is gathered to minimize degradation of strength. An integral part of the bushing design is cooling fins or water-circulating cooling tubes that extract heat from the bundle of fibers as they exit the bushing orifices and before the size coatings are applied.

RAW MATERIALS USED IN THE MANUFACTURE OF FIBERGLASS

Overview

The major criteria for selecting raw materials for the manufacture of fiberglass are composition and particle size. With respect to composition, purity and consistency need to be closely evaluated. The fiberglass producer must be able to make a glass that is compatible with its fiberizing process and that has excellent consistency in the short term as well as over days and weeks. To accomplish the

necessary degree of consistency of the glass composition, it is necessary that the starting raw materials have an equivalent degree of consistency. With respect to purity, if a particular raw material is slightly less pure but has excellent consistency, the fiberglass producer will often be able to compensate for that impurity by adjusting the quantity of other batch ingredients used.

In terms of impurities, iron oxide receives a high level of attention. Iron oxide present in the glass in the reduced form as FeO plays a major role in how the glass is able to transmit radiant energy. In most fiber-producing processes, it is desirable to limit the amount of FeO, so this places a limit on the iron oxide content of the starting raw materials. The level of organic matter present in a glass raw material is also important. Organic matter acts as a reducing agent to the glass and reduces iron oxide from the oxidized state, Fe_2O_3 , to the reduced state, FeO, which has already been noted as undesirable from a heat transmission point of view.

Other impurities of concern that need to be minimized or eliminated are hazardous elements that are volatile, particularly during the batch melting process. Arsenic, mercury, selenium, and the like are included in that list. Additionally, refractory minerals that are hard to melt in the glass are undesirable. These minerals include anorthite, beryl, tourmaline, garnet, corundum, ilmenite, rutile, and zircon.

In considering the specifications for the particle-size distribution of glass batch raw materials, the fiberglass manufacturer needs to have materials that exhibit good flow properties so that feeding materials into and out of storage silos is done without material bridging over the silo discharge opening. Good flowability is also necessary so that the material can be weighed accurately as the glass batch is being prepared. It is also important that no single material segregates from the other materials in the batch during blending and conveying. Finally, the materials need to be small enough in size so that they melt in the allotted time and at the operating temperature of the glass-melting furnace, but yet not so small that excessive dust is generated in the batching and unloading operation.

For the raw materials that supply silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3) to the glass, there must be a limit to the amount of the coarsest particles present in the raw material. For these materials, the fiberglass manufacturer will want to limit the amount of material greater than about 425 μm (40 mesh) to not more than 2% by weight. For controlling dust in the batching process, the amount of material finer than 75 μm (200 mesh) is limited to not more than about 2%.

For other materials that are not as difficult to melt, such as the alkali, alkaline earth, and borate minerals, there is not as stringent a requirement on coarse particles. The particle-size distribution that imparts the best flow properties to these materials is more important, as is making sure that the particle-size distribution of the entire mixed batch is cohesive and not prone to having one or more materials segregate from the other materials.

RAW MATERIALS USED IN THE MANUFACTURE OF INSULATION FIBERGLASS

Silica Sources

Silica is present in the highest concentration of any oxide in the glass formula. As the backbone of the glass structure, it takes on great importance. Sands that are used to supply this oxide are therefore equally important. Sands used in the manufacture of insulation fiberglass are categorized into two classes: glass sands and feldspathic sands. Glass sands are very high in quartz content with some minor clay-bearing minerals present as contaminants. They have a SiO_2 content of 99% or higher, with SiO_2 being held between $\pm 0.4\%$ of

the nominal value. The Fe_2O_3 content can be as low as 0.025% and cannot vary by more than $\pm 0.02\%$ – 0.03% . Feldspathic sands, which are combinations of quartz and feldspar, consequently have SiO_2 contents that are less than those for glass sands and Al_2O_3 contents as high as 8% to 12%. Feldspathic sands are generally characterized by higher concentrations of iron oxide, and the chemical composition is less consistent overall. For feldspathic sands, the iron oxide content can be as high as 0.25%. Other oxides that accompany feldspathic sands are sodium oxide (Na_2O), potassium oxide (K_2O), or calcium oxide (CaO), depending on the type of feldspar present in the deposit. Na_2O can range from about 1.5% to 5%. K_2O can be present from about 2% to 4.5%, and CaO is generally present at levels of less than 1%.

The fiberglass manufacturer will set limits to the particle-size distribution of the silica source independent of whether it is glass sand or feldspathic sand. The primary requirement is to limit the quantity of coarse particles so that the sand completely melts in the glass furnace at the furnace melting temperature and in the length of time it spends in the furnace. The second requirement is to limit the fine particle-size fraction for dust control during the material unloading step. The limit on the coarse particles is generally no more than 1% to 2% as coarse as 425 μm (40 mesh), with only a trace allowed as coarse as 600 μm (30 mesh). The limit on the fine end of the particle-size distribution is no more than 1% to 2% finer than 75 μm (200 mesh). The trend for sand specifications with respect to particle size is to seek finer and finer sands.

Borates

The most commonly used borate minerals in the manufacture of insulation fiberglass is 5-mol borax. The composition of 5-mol borax is $\text{Na}_2\text{B}_4\text{O}_7 \times 5\text{H}_2\text{O}$. It is produced from tincal ore that is mined in the California desert, in central Turkey, or from solution mining operations in Searles Valley, California. Five-mol borax is the preferred source for adding boric oxide (B_2O_3) to the fiberglass composition because it is very highly refined, which gives it high purity and consistency. The B_2O_3 content of 5-mol borax is consistently 49% with Na_2O being 21.7%. It contains 5 molecules of chemically combined water that comprises 29.3% by weight.

Ulexite is also used as a source of B_2O_3 to fiberglass compositions. Ulexite is a sodium, calcium borate mineral, mined in Turkey, having the approximate composition of 37% B_2O_3 , 6% Na_2O , 17% CaO , and lesser amounts of SiO_2 , Al_2O_3 , and magnesium oxide (MgO). The major oxides, B_2O_3 , Na_2O , and CaO , are all controlled within $\pm 1\%$ of their nominal values. For the equivalent amount of B_2O_3 , 25% more ulexite must be used compared to 5-mol borax. Additionally, because ulexite is a less highly refined material, its chemical consistency is poorer than 5-mol borax. The amount of chemically combined water in ulexite is about 34%.

Because borate minerals are not particularly refractory in nature, there is less concern about ease of melting in the glassmaking furnace, so the limits set on the coarse particles are not as stringent. Particles as coarse as 1,400 μm (12 mesh) are commonly seen in both 5-mol borax and ulexite. Again, dust control is of concern, so the amount of particles finer than 75 μm (200 mesh) is ideally limited to a few percent.

Alkali

The alkali oxides, Na_2O , K_2O , and lithium oxide (Li_2O), are classified as modifier oxides in the glass structure. They are added to the glass formula because they serve as fluxes for melting the more resistant quartz grains. The primary alkali oxide used by fiberglass manufacturers is sodium oxide, but there are occasional needs for potassium or lithium oxides. Soda ash is almost universally used to

supply sodium oxide to the glass. Potassium carbonate is used to supply potassium oxide, and either lithium carbonate or spodumene is used to supply lithium oxide.

The chemical composition of soda ash is Na_2CO_3 . Most domestic soda ash is produced from trona ore deposits in the Green River, Wyoming, area with lesser amounts produced from solution mining operations in Searles Valley, California. Soda ash is highly refined and chemically consistent, so the ability of the fiberglass manufacturer to closely control the sodium oxide content of the glass is excellent. In melting, the carbon dioxide in soda ash is evolved as a gas and leaves sodium oxide to enter into the glass structure. Soda ash contains 58.4% Na_2O and 41.6% carbon dioxide (CO_2).

In some specialty fiberglass compositions, potassium carbonate or potash is used to supply K_2O to the glass. The chemical composition of potassium carbonate is K_2CO_3 . In melting, the carbon dioxide in potash is evolved as a gas and leaves potassium oxide to enter into the glass structure. Potassium carbonate contains 67.5% K_2O and 32.5% CO_2 . As is soda ash, potassium carbonate is a highly refined and very consistent material.

Potassium oxide is added to the glass because—when used in conjunction with sodium oxide—it provides a more complex glass structure, which is beneficial in preventing alkali ions from leaching from the glass surface when exposed to liquids.

Lithium oxide is touted as a melting aid in glass batch formulations and is seeing some application within the industry. When used, Li_2O is typically added to the glass in concentrations of 0.2% to 0.4% by weight with either lithium carbonate or spodumene used as the source of this oxide. The use of lithium oxide has been reported to increase the capacity of a given furnace by as much as 10%, or instead of pulling the glass furnace at the higher daily throughput, significant energy reductions have been realized. There is debate about whether lithium carbonate or spodumene is the more effective melting aid. Lithium carbonate contains 40% Li_2O , with the balance being CO_2 . Glass-grade spodumene contains 5% Li_2O , with the balance being made up of 75% SiO_2 , 18% Al_2O_3 , and less than 0.5% of Na_2O and K_2O .

As with the borate minerals, alkali-bearing minerals are not particularly refractory in nature. Concern with difficulty of melting in the glassmaking furnace is diminished, so the limits set on the coarse particles is not as stringent. Particles as coarse as 600 μm (30 mesh) are commonly seen in these materials. Dust control is again required, so the amount of particles finer than 75 μm (200 mesh) is ideally limited to several percent. Sizing the alkali materials to match the particle-size distribution of the other batch ingredients to avoid material segregation is another important consideration.

Alkaline Earth

Alkaline earth oxides are added to a glass formula to serve as stabilizers within the glass structure, imparting chemical durability to the glass. For insulation fiberglass, limestone or quicklime is used to provide CaO to the glass. Limestone, CaCO_3 , is converted to quicklime by burning the CO_2 out of the raw stone in a high-temperature calcining operation. Limestone generally needs to have a purity level of 97% or higher with a resultant CaO content of 54.5% that is generally consistent to within about $\pm 0.4\%$. Limestone may contain MgO up to about 1% and Fe_2O_3 as high as 0.5%; however, glassmakers generally prefer to limit the iron oxide to no more than about 0.1%. When these limestones are converted into quicklime by calcining, they contain 95% or more CaO , allowing for a 2% to 3% residual loss on ignition (LOI) from incomplete burning.

Dolomite or dolomitic quicklime is used to provide MgO to the glass. Again, the purity level needed for dolomite is 97% or

higher, which results in a CaO content of about 43.7% and an MgO content of about 31.4%. When these dolomites are converted into dolomitic quicklime, the CaO content is about 57% and is consistent within $\pm 0.8\%$, and the MgO content is about 40% and is consistent within $\pm 0.4\%$. The residual LOI from incomplete burning is 2% to 3%. These materials may have iron oxide contents as high as 0.5%, but glassmakers generally prefer iron oxide to be no more than 0.1%.

The glass composition determines the ratio of limestone to dolomite that will be required in the batch formulation. If the glass composition requires less than about 1% MgO, it is likely that only limestone will be used. If the glass composition requires more than about 1% magnesium oxide, a corresponding amount of dolomite will be required.

Limestones and dolomites comprised of material as coarse as 2,000 μm (10 mesh), but not more than about 10% finer than 150 μm (200 mesh), are specified by the fiberglass manufacturer. For quicklime and dolomitic quicklime, the raw material specifications are closely negotiated with the supplier. Calcining limestone and dolomite results in a softer, more friable, and finer material that tends to be dependent on the calcining process and the downstream materials handling system. These materials are frequently more difficult for the fiberglass manufacturer to handle, and at times, flow aids are added to improve their handling characteristics. Although the fiberglass manufacturer would prefer less of the fine fraction, the supplier is not always able to accommodate that need.

In some special circumstances, processed magnesium oxide is used in place of dolomites. In that case, the fiberglass manufacturer must ensure that the magnesium oxide is not so refractory or too coarse that it will not adequately melt under the time-temperature conditions of the melting furnace.

Alumina

Aluminum oxide falls into the class of stabilizer oxides, similar to the alkaline earths, and imparts chemical durability to the glass. Al_2O_3 is generally supplied to a fiberglass composition through the use of feldspar, nepheline syenite, or aplite. These materials are combinations of sodium, potassium, or calcium aluminosilicates. Albite is the sodium feldspar end member, and microcline and anorthite are the potassium and calcium feldspar end members, respectively. The approximate Al_2O_3 content of feldspar is 19% and is consistent to approximately $\pm 1.0\%$. Nepheline syenite is a quartz-free rock consisting mostly of nepheline and feldspar. It has approximately 23.5% Al_2O_3 and is consistent to approximately $\pm 0.4\%$. Aplite is light-colored igneous rock with the same mineral composition as granite but with a fine-grained texture. Aplite contains 21.5% Al_2O_3 and is consistent to approximately $\pm 0.7\%$. Aplite also contains trace amounts of titanium dioxide (TiO_2) and phosphorus pentoxide (P_2O_5). The iron oxide content of these materials ranges from about 0.05% to about 0.2%, with feldspar being the lowest and aplite being the highest.

The feldspathic sands described earlier are also used to provide Al_2O_3 to the glass. The particle-size requirement for these materials is essentially the same as that for sand.

Zinc Oxide

In specialty fiberglass compositions used to produce liquid filtration media that requires a very chemically resistant glass, granulated zinc oxide (ZnO) is added to the glass composition. The zinc oxide used for this purpose is generally 98% pure or greater.

Barium Carbonate

Barium oxide (BaO) is added to some specialty fiberglass compositions by the use of barium carbonate (BaCO_3) as a batch ingredient.

These glasses are used for making liquid filtration media where producing a chemically resistant glass is important. The barium carbonate used for this purpose is generally 95% to 98% pure. The primary contaminants found in barium carbonate are strontium carbonate and sodium carbonate, and they are present in concentrations of approximately 2% and 1%, respectively.

Fluorspar

Fluorspar is used as a flux in certain glass formulations. Typically, fluorspar will have a purity level of greater than 97% calcium fluoride (CaF_2) with a limit on the Fe_2O_3 content of less than 0.1%. Trace impurities like SiO_2 , Al_2O_3 , MgO , and CO_2 are found. Many glass companies have successfully removed fluorine (F_2) from the glass composition following regulatory decisions preventing its use. Fluorine is a particularly volatile element in the glass. It is not unusual for nearly 50% of the added fluorine to be lost as a result of evaporation or volatilization.

Sodium Sulfate

In many fiberglass compositions, a minor amount of sodium sulfate, commonly called salt cake, is added as a refining agent to aid in the removal of seeds and blisters. Salt cake has two other functions in the glass. When molten, it functions as a surfactant, wetting grains of sand to assist in their melting. It also functions as an oxidizing agent, acting to offset some of the reductants found as contaminants in glass batch raw materials. In some cases, barium sulfate might be substituted for sodium sulfate.

Cullet

Many insulation fiberglass batches use some percentage of recycled glass, called cullet. Most of the cullet available for use as a batch ingredient is from recycled bottles or recycled plate glass. ASTM D5359 describes the industry-accepted specification for cullet. Both bottle and plate cullet are soda-lime-silica glasses, so the oxides supplied from cullet need not be supplied from the other batch ingredients. The use of cullet in a fiberglass composition will lessen the requirement for sand, soda ash, and limes or limestones. The particle-size requirement from the ASTM specification is that cullet shall be smaller than 6 mm ($\frac{1}{4}$ in.) in size and can contain no more than 15% finer than 75 μm (200 mesh).

Synthetic Minerals

A recent development in the fiberglass industry is the availability of manufactured minerals in the family of calcium and calcium-magnesium silicates. These materials are manufactured by spray-drying fine silica sands, together with quicklime or dolomitic quicklime, to form the precursors of diopside ($\text{CaMgSi}_2\text{O}_6$) or wollastonite (CaSiO_3), respectively. These materials, when heated rapidly upon entry in to the glass furnace, convert completely to diopside or wollastonite because of the intimate contact of the mineral particles and the heat of the furnace. The reported advantage to these materials is that the melting reactions take place faster so that more glass can be produced per day for a given furnace or so that melting energy can be reduced. These materials are effective because, with their use, the quantity of coarser-grained sand is reduced, and the resultant ratio of flux to quartz particles is increased.

RAW MATERIALS USED IN THE MANUFACTURE OF TEXTILE FIBERGLASS

Overview

One fundamental difference between insulation fiberglass and textile fiberglass made by the continuous filament process is the glass composition. E-glass, the historical industry standard for textile

Table 1. E-glass definitions from ASTM D578-00

Chemical	E-Glass for General Applications, wt %	E-Glass Used in Aerospace and Printed Circuit Boards, wt %
B ₂ O ₃	0–10	5–10
CaO	16–25	16–25
Al ₂ O ₃	12–16	12–16
SiO ₂	52–56	52–56
MgO	0–5	0–5
Alkali*	0–2	0–2
TiO ₂	0–1.5	0–0.8
Fe ₂ O ₃	0.05–0.80	0.05–0.40
Fluoride	0–1.0	0–1.0

* For general applications, alkali is defined as Na₂O + K₂O + Li₂O. For aerospace and printed circuit boards, alkali is defined as only Na₂O + K₂O.

fiberglass, is limited in an alkali content to a maximum of 2%, as defined in ASTM D578-00). In this standard, ASTM makes a distinction between glass compositions used for general applications and those used in aerospace and printed circuit board applications. Table 1 shows the allowable glass compositional ranges for each of these categories.

The two most significant differences between the general use category and the aerospace and printed circuit board category are the allowable level of boric oxide and the inclusion of lithium oxide as one of the alkali oxide members. For general use applications, E-glass can now be free of boric oxide, and lithium oxide is included in the definition of total alkali. Owens Corning fiberglass's patented Advantex composition contains no boric oxide. For textile fiberglass sold into aerospace applications and for printed circuit boards, E-glass must contain between 5% and 10% B₂O₃ and the use of Li₂O is prohibited.

In addition to the low level of alkali oxides found in E-glasses, they have Al₂O₃ and CaO contents significantly higher than insulation fiberglass compositions. In E-glasses, Al₂O₃ typically ranges from 12% to 16%, and CaO can be as high as 23%, whereas in insulation glasses the Al₂O₃ content is generally less than 5% and the CaO content is generally between 5% and 10%. Silica, however, is still the most prevalent oxide in E-glasses, and as the backbone of the glass structure, it takes on great importance.

Silica

The most critical raw material for the manufacture of textile fiberglass is the silica sand source. Because the glass composition is limited in allowable alkali content as described previously, the glass is much harder to melt than an insulation fiberglass composition. Furnaces melting these glasses operate at temperatures that are hundreds of degrees higher than those found in furnaces melting insulation glass compositions. In order for furnaces melting E-glass to produce a daily quantity of high-quality glass large enough to be economically viable, it is necessary for the particle size of the silica source to be finer than that of insulation glasses. Stated another way, unless the silica sand is much finer in particle size than that used in insulation glasses, the furnace pull rate would be so low as to be financially impractical.

The fiberglass manufacturer will specify that the silica supplier grind or mill the sand into silica flour with a particle-size distribution having 90% or more of the particles smaller than 45 µm (325 mesh), with essentially no particles as coarse as 250 µm

(60 mesh). The chemical requirements of the ground silica are essentially the same as those for glass-grade sands used for insulation fiberglass; the SiO₂ content is greater than 99% and must be held between ±0.4% of the nominal value. The Fe₂O₃ content is generally less than 0.1% and cannot vary more than ±0.03%. Trace impurities that are refractory in nature and will not melt in the glass furnace are unacceptable, similar to what was described for sand usage in insulation glasses.

Borates

Where the glass composition calls for the inclusion of B₂O₃, boric acid, colemanite, and 5-mol borax are the minerals usually specified.

Boric acid has the chemical composition of H₃BO₃. The B₂O₃ available to enter the glass structure is 56%, with the balance being chemically combined water. Colemanite is a naturally occurring calcium borate mineral that contains from 25% to 28% CaO and 41% to 43% B₂O₃, with impurities of SiO₂, Al₂O₃, Na₂O, MgO, and strontium oxide (SrO) that range from 0.2% in the case of sodium oxide to more than 4% for SiO₂. Because colemanite is lower in B₂O₃ than boric acid, and because it is less highly refined and contains more impurities, many fiberglass manufacturers prefer boric acid over colemanite. One advantage that colemanite has over boric acid is it contains a lower amount of chemically combined water, 25%, versus 44% for boric acid.

Five-mol borax was described in the section on insulation fiberglass. Because 5-mol borax contains 21.7% sodium oxide, and because textile fiberglass compositions are limited in the allowable alkali content, the use of 5-mol borax as a batch material is limited. For a general purpose E-glass composition where the B₂O₃ content can be as high as 10%, however, a typical batch will employ two of the borate minerals in a mixed-borate formulation. The practice is to add 5-mol borax until the sodium oxide requirement of the final glass composition is satisfied. Then either boric acid or colemanite is used to satisfy the balance of the boron content of the glass.

Alkali

Because alkali oxides in textile glass compositions are limited to 2% or less, the use of alkali-containing minerals is much lower compared to glasses used to produce insulation fiberglass. Five-mol borax or soda ash can be used to supply the limited alkali content of these glasses. In cases where lithium oxide is added, the practice described in the section on insulation fiberglass is applicable for E-glasses as well.

Alkaline Earth

For textile fiberglass, limestone or quicklime is used to provide CaO to the glass, and dolomite or dolomitic quicklime is used to supply MgO. The chemical requirements described in the section for insulation fiberglass are applicable to textile fiberglass as well.

The requirement for the particle-size distribution of limestone used in the manufacture of textile fiberglass is generally that 80% of the product must be finer than 75 µm (200 mesh), and less than 1% can be as coarse as 250 µm (60 mesh). For quicklime or dolomitic quicklime, the particle-size requirements described in the section on insulation fiberglass apply here as well.

Alumina

In the manufacture of textile fiberglass, the primary source of Al₂O₃ is air-floated kaolin produced in the southeastern United States. It is the preferred source of Al₂O₃ because it is low in alkali content and is consistent with the requirement that the glass be low in alkali. Kaolin clay contains 45% SiO₂, consistent within ±0.5%, and 38.5% Al₂O₃, also consistent within ±0.5%. The particle-size

Table 2. Composition ranges, descriptions, and uses for other textile fiberglass compositions

Oxide	C-Glass, wt %	D-Glass, wt %	E-CR Glass, wt %	AR Glass, wt %	R-Glass, wt %	S-2 Glass, wt %
SiO ₂	64–68	72–75	54–62	55–75	55–65	64–66
Al ₂ O ₃	3–5	0–1	9–15	0–5	15–30	24–25
B ₂ O ₃	4–6	21–24		0–8		
CaO	11–15	0–1	17–25	1–10	9–25	0–0.1
MgO	2–4		0–4		3–8	9.5–10
ZnO 2–5						
BaO 0–1						
Li ₂ O				0–1.5		
Na ₂ O + K ₂ O	7–10	0–4	0–2	11–21	0–1	0–0.2
TiO ₂			0–4	0–12		
ZrO ₂				1–18		
Fe ₂ O ₃	0–0.8	0–0.3	0–0.8	0–5		0–0.1
F ₂				0–5	0–0.3	
Descriptions and Uses						
C-Glass	D-Glass	E-CR Glass	AR Glass	R-Glass	S-2 Glass	
Chemical stability in corrosive acid environment	Low dielectric constant for electrical applications	Where strength, electrical resistivity and acid corrosion resistance are needed	Alkali resistant glasses for reinforcing cement and concrete	For reinforcements where added strength and acid corrosion resistance are needed	High strength, modulus, and stability under extreme temperature and corrosive environments	

requirement for kaolin clay is that 97% or more must be finer than 45 μm (325 mesh). By convenience, this nearly matches the particle-size distribution of the ground silica. This means that two of the major raw materials for textile glasses are similar in particle-size distribution. This is beneficial in preventing batch segregation in mixed batches. Trace amounts of TiO₂ and K₂O are present in clay, as well as iron oxide. TiO₂ can be as high as 1.7% and K₂O can be as high as 0.3%. Low-iron clays would be defined as having an iron oxide content as low as 0.5%; in high-iron clays, Fe₂O₃ may approach 1%. The supplier must control the iron oxide content of the clay to approximately $\pm 0.05\%$ of the nominal value.

Fluorspar

Fluorspar is also sometimes used in the manufacture of these types of fiberglass compositions, and the requirements are essentially identical to those outlined in the section on insulation fiberglass.

Iron Oxide

Some manufacturers use fine-ground iron oxide to control the total iron content of the glass by compensating for the variation of iron in all the batch ingredients. This is done to control the oxidation–reduction state of the glass and is important for optimizing the heat transmission characteristics of the glass.

Other Glass Compositions

Although E-glass represents the bulk of volume of textile fiberglass produced, other glass compositions are in use in the industry. Table 2 lists some of these alternate compositions and their uses. For some of the glasses listed in Table 2, other batch materials like titanium dioxide and zircon sands are required.

Titanium Dioxide

A 99% pure grade of granular rutile (TiO₂) is often used. Low levels of iron oxide, phosphorus pentoxide, and sulfur trioxide are present as impurities. The particle-size distribution of this material

shows a significant percentage being coarser than 425 μm (40 mesh) with only 1%–2% being finer than 45 μm (325 mesh).

Zircon Flour

Zircon flour, which is used as the source of zirconium dioxide (ZrO₂) in the special glass formulations shown in Table 2, is composed of 66% ZrO₂ and 32% SiO₂ with trace quantities of Fe₂O₃, TiO₂, and Al₂O₃. Hafnium is typically present along with zirconium in the ore body in a 50:1 zirconium to hafnium ratio. Thorium and uranium are also present in concentrations up to several hundred parts per million. Particle-size requirements are similar to those for silica flour, namely 95% or greater being finer than 45 μm (325 mesh).

THE USES OF FIBERGLASS AND MARKETS SERVED

Insulation Fiberglass

Insulation fiberglass is made into many shapes and forms and sold into many markets. The sections that follow describe some of the common applications for insulation fiberglass.

Building Insulation Products

Fiberglass batts, blankets, rolls, and loose fill–blown-in insulation find common application in insulating buildings of all types, from residential homes and light commercial buildings that use wood frame construction to commercial buildings that use metal frame construction. Building insulation is identified and labeled by R-value. “R” stands for resistance to heat flow, with high R-value products having greater insulating power. Commonly available products range in insulating value from R-11 to R-38. Batts and rolls are available unfaced or often with vapor-retarding facings already applied. These facings usually consist of asphalt-coated kraft paper, aluminum foil, or plastic film. The vapor barrier’s purpose is to resist the movement of moisture to cold surfaces where it could condense to liquid water and damage the building. Batts are sold in nominal sizes in lengths ranging from 1,194 mm (47 in.) to 2,438 mm (96 in.) and widths

ranging from 279 mm (11 in.) to 610 mm (24 in.). Rolls come in lengths of 11.94 m (39 ft 2 in.) to 21.49 m (70 ft 6 in.) and in widths of 279 mm (11 in.) to 584 mm (23 in.). A recent development is to encapsulate light-density batts in plastic sheathing to provide an easier handling product that has less associated dust and itch. This type of insulation is installed in exterior and interior wall cavities, ceilings, basements, and crawl spaces. In addition to providing thermal protection, it is also used for its acoustic properties of providing sound control.

Air Handling Systems

Fiberglass duct board, duct wrap, and duct liners are used to insulate air handling systems. Duct board is designed for easy fabrication into rectangular ductwork. In some ducts, the fiberglass board products are part of a system that also consists of coating products and air turning vanes. These smooth interior coatings provide a low resistance to air flow, will not support microbial growth, and resist penetration of incidental water into the fiberglass wool core. Duct liners are designed for lining sheet metal ducts in heating, ventilating, and air-conditioning (HVAC) systems. They provide good thermal insulation and their acoustic properties also dampen sound. Duct wrap is used as thermal insulation for the exterior of HVAC systems where temperature control is required. In many instances, these products meet surface burn-through requirements because of their limited combustibility.

HVAC Systems

Fiberglass blanket and board insulation products find common use in air conditioners, furnaces, and other HVAC equipment. In some cases, the blanket is faced with a smooth, durable, nonwoven mat that is used as a thermal and acoustical control liner in HVAC equipment. In others, acrylic coatings are applied. These insulation products have low air friction, are resilient and flexible, have high tensile strength, and are easy to install. They are incombustible and nonhygroscopic. Some come with acrylic coating formulated with antimicrobial agents to protect against microbial growth. There are requirements for corrosiveness, moisture vapor sorption, fungi resistance, temperature and erosion resistance, odor emissions, surface burn characteristics, thermal conductivity, and sound absorption coefficients.

Pipe Insulation

Fiberglass pipe insulation is made from glass fibers bonded with a thermosetting resin, jacketed with a reinforced vapor retarder facing, and equipped with an adhesive closure system for sealing. It is used to insulate pipe where temperatures range from -20°C (-4°F) to as high as 454°C (850°F). Section lengths can be as long as 1.2 m (4 ft). For some applications, precision V-grooves are machined into the insulation making for a more precise fit. For large diameter shapes such as pipes, tanks, ducts, vessels, and other round and irregular shapes, a high-temperature, semirigid blanket bonded to a flexible facing is used. These products are sold as rolled goods in 0.92-m (3-ft) or 1.22-m (4-ft) widths with thickness up to 102 mm (4 in.).

Acoustics

For acoustical applications, fiberglass board products find wide use in office furniture, office partitions, ceiling panels, and wall panels where high thermal and acoustical efficiency in a minimum space is required. In some applications, these products have a fiberglass mat facing on one or both sides. Requirements for these products include high tensile strength and resiliency; light weight; and resistance to vibration, settling, and shock down. These products are incombustible and will not support microbial growth.

Appliances

Fiberglass board and blanket-type insulation products find common application in household appliances such as ranges, refrigerators, freezers, and water heaters where thermal and acoustical requirements must be met. Certain products are designed specifically for low-temperature applications found in freezers and refrigerators. For application in ovens and ranges, the insulation must be designed to emit minimal smoke and odor. None of these products contribute to or absorb odors, and all pass UL fire hazard classifications.

Aircraft Insulation

Insulation for use in aircraft fuselage wall cavities is made from blankets composed of ultrafine glass fibers. These products must be lightweight and flexible, with superior thermal and acoustical properties and excellent dimensional stability. Where bonded insulation is required, blankets are furnished with water and oil-repellent thermosetting phenolic binders, which also make the products flame resistant and nonpinking. The water repellency is critical for areas where high-altitude moisture condensation occurs. In some areas, contact with oils or oil-based liquids can occur, and providing protection against this type of contact is also necessary. In higher-temperature applications, unbonded insulation is required. The absence of binders and oils eliminates potential contamination from outgassing or binder vaporization. Because of the fine-diameter fibers, these products are ultralightweight and superior in acoustic and thermal performance per unit weight of insulation used. Bulk density of these products may be as low as 9.6 kg per m^3 (0.6 lb per ft^3). Special binderless fiberglass felts are also used to insulate aircraft and jet engines. These felts are intended for continuous exposure to hot face temperatures up to 482°C (900°F). Again, because these products do not contain binder chemicals, there is no outgassing or binder vaporization.

Automotive

Fiberglass insulation is used in molded hoodliners, headliner substrates, dashboard insulators, and other automotive acoustical components. To reduce objectionable dust generated during installation of these parts, glass fibers are bonded with latex binders to encapsulate the intersections of the fibers, allowing them to bend without shattering. These products have excellent dimensional stability and strength, and acoustical and thermal properties. They are also lightweight, flexible and odorless, easy to mold, and they bond well to decorative facings.

Marine Applications

Fiberglass blanket and board products are used for insulating marine products and ship hulls and decks, in shipboard heating and air-conditioning systems, and on drilling rig platforms. Some of these products are characterized by low organic content to improve their performance in combustibility testing. In these applications, key characteristics are high thermal performance, light weight, and low combustibility.

Cryogenics

A fiberglass blanket bonded with melamine resin is used to insulate cryogenic tanks containing liquefied gases such as oxygen, nitrogen, argon, and helium.

Filtration

Fiberglass roll goods are made into bag or pleated filters for industrial and commercial air filtration applications such as ASHRAE (American Society of Heating, Refrigerating, and Air-Conditioning Engineers) high efficiency particulate air (HEPA), and ultralow

penetration air (ULPA) filters for clean rooms, face masks, respirators, vacuum bags, panel filters and filters for HVAC systems, and paint spray booths. They are also used for Food and Drug Administration (FDA) applications. In liquid filtration applications, both cured and uncured roll goods are used in liquid/gas separators, liquid/liquid coalescers, oil and gas coalescing, solids/liquids and solids/gas filter cartridges and filter pads.

Microfibers

Microfibers are glass fibers with diameters ranging from less than 0.5 μm to 2.5 μm . They are used in HEP A and ULPA filters in clean-room applications for many industries, including the manufacture of microchips. Microfibers are also supplied to the lead-acid battery market for use as battery separators in automotive, heavy equipment, and machinery batteries. In some highly specialized applications in the health care industry, microfibers are used for filtering blood particles.

Textile Fiberglass

Textile fiberglass is produced in a variety of forms that are necessary to describe before discussing the markets into which they are sold.

Textile Products

A strand is defined by the diameter of its filaments, its linear weight or tex count (grams per kilometer), the direction of twist, and the number of turns per meter. Single yarn undergoes a single twist operation with between 20 and 40 turns per meter. Plied yarn is made from two or more single yarns twisted together in the opposite direction to the original twist. The yarn is supplied on a cone and can be used directly on industrial process machinery for uses such as weaving, braiding, covering, and so forth. Once it has been transformed by textile processing, it is most often used as a reinforcement or support for various materials such as synthetic resin, bitumen, mica, paper, or adhesive.

Roving

Roving is produced either directly from the bushing by drawing a large number of filaments, or by assembling several strands in parallel, with no twisting. Roving consisting of filaments from 10 to 24 μm in diameter is most often used in linear weights or counts of 600, 1,200, 2,400 and 4,800 tex. Presented as a spool wound on a tube, roving unwinds very easily. The characteristics of roving are stiffness, equal tension of fibers, lubricity, and ease of cutting. Roving can be used in different processes such as weaving, continuous impregnation, or chopping.

Chopped Strands

Basic strands, which are generally cut to lengths from 3 to 12 mm ($1/8$ to $1/2$ in.), have numerous applications. They are used mainly in large series processes to reinforce thermoplastic and thermoset resins and are also used to reinforce plaster, cement, and paper. The characteristics with respect to integrity, flowability, and compatibility will differ depending on the application.

Continuous Filament Mats

Continuous filament mats are felts of continuous filaments distributed in uniform layers as they leave the bushing. They are held together by a binder, and the type and content of the binder depend on the intended application. These mats are particularly well suited to molding between matched molds, and to the production of continuous profiles and circuit boards. They are also used for foam

reinforcement. They are easy to draw and are a simple way to obtain "pre-forms" of the shape of the part to be molded.

Chopped Strand Mats

Chopped strand mats are felts or mats consisting of glass strands chopped to lengths of mostly 50 mm (2 in.) and held together by a binder that is soluble in styrene. The binder content may vary from 3% to 6%, depending on the requirements in terms of processing of the mat and the characteristics of the finished product. Chopped strand mats are particularly suited to contact molding and to continuous molding between layers of film.

Woven Rovings

Woven roving fabrics are made of roving glass strands. The fabrics are manufactured mostly as fabrics with a uniform warp and weft setting but also as unidirectional fabrics and as tapes. They are used for hand lay-up, injection molding, and press molding for the production of laminated glass-reinforced plastics for use in industry, transport, sports, and leisure activities.

Glass Mat

Glass mat is a nonwoven material, composed of uniformly distributed glass strands. These are bound by means of organic additives, mainly thermosetting resins. These form a paper which, after polymerization, is rolled up and packaged ready for use. Glass mat is not susceptible to atmospheric agents or to ultraviolet rays, is supple and traction-resistant, will not rot, and is dimensionally stable. Its porosity makes it easy to impregnate. It also demonstrates good chemical resistance and possesses excellent waterproofing, anticorrosion, and fire protection characteristics. The two processes used to manufacture glass mats—the wet and dry processes—produce different types of paper. Their diverse applications satisfy the technical requirements of a range of sectors such as insulation, automotive, roofing, and construction.

Textile Fiberglass Markets

Markets into which textile fiberglass is sold are described in the following sections.

Transportation

Fiberglass composites are used in a number of applications within the transportation market. These include exterior door panels, radiators and ignition components on passenger vehicles, side panels on light- and heavy-duty trucks, hoods, hatchbacks, roof and truck panels, wing mirrors, rear light units, brake linings, ignition components, and mufflers. The benefits of using composites include greater fuel efficiency, corrosion resistance, low weight and high strength, impact resistance, freedom from rust, and the ability to apply a high-quality finish.

Structural and semistructural parts made of composites have good flexural strength and rigidity. Parts often having a high glass content are front-end panels, flooring, engine blocks, bumper beams, leaf springs, spare wheels and covers, fuel tank supports, inlet manifolds, cooling modules, and oil pans.

Construction

Composite applications in the construction market are numerous. They extend from the exterior walls and the roof to the interior of the home or building. In some cases, glass strands are visible, and in others, the glass is incorporated in a plastic or cement matrix. For exterior applications, composites are used in the following areas:

- Doors and windows
- Gutters, downspouts, and outlets

- Columns, pedestals, domes, and cornices for exterior design
- Paneling, cladding, covering for protection, and insulation panels
- Shingles and other roofing applications
- Translucent flat or corrugated sheets and facing for decorative fascia
- Renovation of fascia using glass-cement composites
- External insulation and coatings of facades where dimensional stability and prevention against cracking are required
- Molds for concrete

Interior applications for composites are also numerous and include

- Gypsum boards and wall partitions
- Composite panels
- Glass-reinforced plaster
- Dry-wall tapes
- Flooring
- Wash basins, showers, sinks, and toilets
- Blinds and shades for decoration and protection from the sun
- Aesthetic coverings for use on walls, partitions, ceilings, and doors
- Decor and furnishings
- Decorative items

Advantages that composites bring to the construction market are dimensional stability, high strength, reduced weight, impact resistance, low flammability, low maintenance, and design flexibility.

Infrastructure

In this market, fiberglass composites have numerous applications:

- In primary structural items, composites are found in pilings, bridge decks, and cable stays.
- In infrastructure restoration, composites are found in column wrapping, pipes, and structural cladding, and are used for in-situ repair of structures.
- In hybrid structural items, composites are combined with conventional materials like wood, steel, or concrete.
- In electric power transmission, composites are used in utility poles, transmission poles, and cross-arm members.
- In highway safety and roadside installations, composites are used in sign supports, guardrails, posts and supports, and noise barriers.
- In seismic-resistant applications, composites are used to repair damaged structures, to upgrade existing structures, and to build new construction that is less prone to earthquake damage.
- In bridge construction, composites provide a high load capacity with low material weight.
- In pavement reinforcing, composites are also used.

Other infrastructure applications are composite reinforcing for concrete products such as dowel bars, reinforcing bars, and post-tensioning and prestressed tendons.

In these applications, composite materials bring a number of benefits, including high strength, reduced weight, corrosion resistance, low maintenance, dimensional stability, low installation costs, and design flexibility. Composites are very durable and will not corrode like steel or rot like wood, so maintenance and replacement costs are reduced.

Corrosion Resistance

Unlike other materials, composites are ideally suited for corrosive environments. Applications in this market include pipes, fume-handling ducts, underground petroleum tanks, sucker rods, flood control, and navigational waterway structures like dam gates and weirs, energy production structures for oil and gas production like offshore platforms, and miscellaneous process equipment.

Recreational

Composites are found in a variety of consumer goods, particularly recreational and sporting goods products. These products include water and snow skis, kayaks, snowboards, golf club shafts, golf carts, fishing rods, and swimming pools. The benefits of using composites for consumer goods include strength, low weight, resilience, flexibility, and corrosion resistance.

Marine

Composite materials are used in a variety of applications in the marine market, including the materials used in the construction, maintenance, repair, and equipping of powerboats, sailboats, and other watercraft. Composites bring myriad benefits to marine applications, including high strength, reduced weight, corrosion resistance, dimensional stability, and design flexibility.

Appliances and Business Equipment

Composites are used in a number of different applications in this market, including gears, pans, housings, and other components for household appliances such as washers, washing-machine drums, dryers, waste disposal units, air conditioners, and humidifiers. Composites are also used in computer terminal housings and in business equipment such as copiers, cash registers, and mailing equipment.

Electrical and Electronics

Composite applications for electrical and electronics markets include light poles, circuit boards, electrical junction boxes, ladder rails, antennas, fuse boxes, lamp housings, street light shells, and switchgear cabinets.

As sheathings used in conjunction with lacquers and coatings, composites are used for covering wires and cables as insulators. The mechanical and electrical characteristics of composites allow very thin coverings to be produced, thereby reducing the volume of electrical equipment.

Glass strand fabrics play an important part in the electronics industry, where they are used to produce copper-plated laminates in printed circuit board manufacturing. The benefits of using composites in these applications include high strength, low weight, dimensional stability, design flexibility, cost performance, and corrosion resistance.

Aerospace and Aircraft

Aerospace and aircraft applications include overhead storage bins, aircraft toilets, and helicopter rotor blades. Benefits from using composites for these applications include cost performance, dimensional stability, and corrosion resistance. Composite materials are light in weight, can withstand heavy loads, and provide excellent resistance to bumps and impact.

FIBERGLASS MARKET TRENDS AND FORECASTS

In a report published by the Freedonia Group (2003), a leading international database business research company, by 2007, the U.S. demand for glass fibers is projected to increase 2% per year to 3.1 billion kg (6.9 billion lb), having a market value of \$6.8 billion.

The segment projected to have strong growth is the fiber-reinforced plastics (FRP) market, where the growth rate is expected to be between 2.5% and 3.0%. The size of this segment is estimated to grow to more than 0.5 billion kg (1 billion lb). Opportunities in FRP will stem from their advantages over competitive materials, where products made from FRP are lighter in weight, are superior in corrosion resistance, and have a favorable cost/performance profile. Building products and motor vehicles will be the leading applications. Good growth is also expected for electrical and electronic markets, which continue to be stimulated by rapid advances in computer and telecommunications technology.

Demand in other reinforcements applications, such as asphalt construction products, mechanical rubber products, paper products, and fabrics is projected to rise 2.3% yearly to 0.6 billion kg (1.3 billion lb). The best prospects are expected in mechanical rubber reinforcement applications, based on usage in a broad range of industrial component applications. Asphalt construction products will continue to account for a large portion of overall demand as a result of above-average growth for laminated shingles, which utilize 30% more glass fiber than standard asphalt shingles. Among nonreinforcement uses, filtration and other smaller markets such as battery separators will provide good opportunities based on rising demand in high-efficiency filtration and other applications.

In the insulation segment, overall demand is forecast to increase 1.7% annually to 1.9 billion kg (4.1 billion lb), with residential construction accounting for approximately 70% of the total. A projected deceleration in residential construction activity will strongly limit growth prospects, but reductions in single-unit conventional housing starts will be somewhat offset by a growing after-market demand, as well as by more intensive use of fiberglass insulation per new housing unit. The best opportunities are anticipated in nonresidential construction because of rebounds in office, commercial, and industrial construction applications.

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Flat Glass

Ed McCullah

HISTORY

“Flat glass” is a designation given to glass that was historically produced for windows with the purpose of keeping out wind and rain while letting in light. As processes for producing flat glass improved and evolved, other uses were developed to take advantage of the product’s improved flatness, more uniform thickness, stronger durability, and better optical quality.

The flat glass industry has undergone two technological revolutions in the twentieth century. The first of these, occurring in the period between World War I and World War II, transformed flat glass manufacturing from a batch to a continuous process. This period included the development of several commercially successful sheet glass production techniques, such as the Colburn, Fourcault, and Pittsburgh processes. In addition, plate glass manufacturing was developing to the point that, by the start of World War II, the technology for continuous twin grinding and polishing of the plate ribbon was in commercial use.

The second revolution, which has taken place in the last 50 years, has involved the development of processes for forming flat glass on a substrate of molten tin—the development of float glass technology. The history of float glass (a type of flat glass) actually began in the mid-nineteenth century when Henry Bessemer became the first person to recognize the advantages and filed an early patent (Bessemer 1848). The first U.S. patent describing the manufacture of flat glass by pouring molten glass onto a liquid metal bath and then drawing the bath into an annealing lehr was issued to William Heal in 1902. Further work led to another U.S. patent issued to H.K. Hitchcock in 1905. The Hitchcock patent dealt with the compartmentalization of the tin bath to provide temperature control of the glass ribbon.

The great breakthrough in float glass was made by Pilkington Brothers in the 1950s. Starting from a clear, well-defined objective—to fire-polish rolled glass on a liquid metal substrate and thus avoid the grinding and polishing operations—they were able to develop the first commercially successful process. The development took 7 years of massive effort and expenditure. Its success is a direct result of the vision and pertinacity of the workers involved and to the patience and economic courage of Pilkington Brothers’ management. The problems encountered during these years (until approximately 1962) were primarily of an engineering and chemical nature. It was the solution to these problems that ended the first phase of float glass development. The U.S. patent by Pilkington Brothers was issued in 1965.

Up to now, most activity has centered on the development of techniques for making a float glass ribbon thicker and thinner than the so-called “base/equilibrium” thickness, which is 6 mm. As the process matured, it was capable of displacing plate glass in the mid-1960s and was, by the 1970s, clearly capable of replacing sheet glass as well. The advantages of higher quality, more flexibility, higher production volumes, and economics became very obvious.

FLAT GLASS PRODUCTION

Batching

Batching is the process of unloading, storing, weighing, mixing, and conveying the raw material to the melting furnace. The plant of today is essentially fully automated with some type of computer or controller. Each part of this process must be tightly controlled to minimize cross contamination of raw materials and to achieve accurate weighing and optimum mixing. All processes also include some type of cullet (broken glass) recycling, not only from in-house losses but also from customer-returned product. For lines that use several colorants to produce different colors and products, the storing and controlled recycling of cullet can be extremely critical. Very small amounts of cullet with colorants not accurately compensated for can lead to off-color and out-of-specification product. Although sometimes taken for granted, the batching area is the first step toward a good product. A mistake in this area cannot be corrected later in the process.

The importance of a consistent supply of raw materials cannot be overemphasized. Tight controls, along with monitoring of each raw material for composition, grain size, and impurities, are required. Slight variations can result in major problems. Transportation of the raw materials is just as important. Dedicated railcars and trucks are preferred, but not always available. In situations where other materials are involved, an agreed-upon and documented cleaning procedure may be necessary.

Melting

The float glass furnaces of today, although similar to those of the 1960s, are continually changing. The furnace has been the heart of the process and typically the limiting factor. The driving force for improvement has been the ultimate cost and quality of the final product. The key areas of improvement in the past 40 years have been product quality, volume produced, furnace life, and energy usage. These items are interrelated in that changing one also has a

direct impact on the others. Instrumentation, computers, and modeling, for example, have allowed monitoring and control to drastically improve. Better refractories, materials, construction, and hot-repair techniques have helped increase the life of the furnace (the campaign), to the point that the campaign has increased from 5 years to current targets of 15 years. Improved insulation packages and better combustion control have improved fuel efficiencies. Furnace size increases and design changes have helped in all areas.

Although most U.S. furnaces use natural gas for fuel, a few use oil. Some use oxygen/gas burners for extra melting capacity to increase production and improve quality. There are currently three 100% oxygen/gas-fired float lines. Some electric boost is being used for furnaces that melt high-iron automotive glasses. With the rising energy costs facing the producers today, much work is being done to optimize current technology and to look for new methods and fuels for the future.

Furnaces are normally considered to have three main areas: a melter where the raw materials are melted and liquefied, a refiner to allow gas bubbles to escape, and a working end where the glass is cooled before exiting into the bath. Melting temperatures in excess of 1,600°C are common.

Forming in the Bath

The float bath, which contains >100 t of molten tin, is electrically heated and then purged with a nitrogen-hydrogen mixture. The glass is poured onto molten tin where it “floats” because of the density difference between the glass and the tin. The continuous ribbon of glass moves through the bath where it is controlled with heat and top-roll machines to form a desired thickness and width. The glass is pulled by a system of rollers that conveys the glass through the entire process. Glass enters the bath in the temperature range of 1,050° to 1,200°C and exits at 575° to 625°C. Glass thicknesses from 0.3 mm to 25 mm have been produced. After more than 40 years of use, the float bath still remains the primary method for producing flat glass in high volumes at low cost.

Annealing

Once the ribbon of glass is formed in the bath, it enters the annealing lehr. The lehr has two functions and areas: the permanent and the temporary. The annealing range (550° to 490°C) determines the strength, flatness, and cutting properties that the glass will have at room temperature. This is termed the permanent zone because these properties will remain with the glass unless it is reheated or tempered. Below the annealing range, the glass enters the temporary zone where the goal is to rapidly cool the glass to room temperature for cutting. Once the glass reaches room temperature, the temporary properties are gone and only the permanent remain. Improper cooling rates and too much stress buildup can result in breakage, flatness problems, or cutting problems.

Inspection

Once the ribbon passes through the lehr, it is inspected and out-of-spec defects are marked. Most lines today are using automatic inspection systems that employ lasers or camera systems, or both, for detection. The higher production speeds and requirements for smaller defect detection and identification are continually pushing the limit for the current equipment.

Cutting and Packing

The final step is the cutting and packing of the products. Today's customers require an almost endless number of sizes that range from 130 in. × 230 in. down to 12 in. × 12 in. This has required greater flexibility in the cutting systems and has led to complete computer-

ization. Packing is evolving from a totally manual process to one that uses automatic equipment. Once again, the packing equipment needs the flexibility to pack any number of different sizes.

Environmental Concerns

The impact of changing environmental regulations has not bypassed the glass producer. Like all other manufacturers, the impact has been absorbed into the product cost. In the United States, the major areas of environmental concern are nitrogen oxides (NO_x), sulfur oxides (SO_x), and particulates. The particulates can be controlled in several ways, but the electrostatic precipitator (EP) has proven to be the main method. SO_x can also be controlled inside the EP using a soda ash slurry that is injected into the exhaust stream and collected. NO_x has proven to be more of a problem, and many different methods for its reduction are being practiced throughout the float and other glass industries. Depending on the location of the plant, different levels of NO_x are allowed, and this may dictate the method or practices to be used. Controlling NO_x without damaging the furnace or shortening its life, while maintaining cost controls, has become a tight balance.

Production Locations in North America

Table 1 lists the current operating float glass production lines by company. The impact of the global company influence is evidenced by the fact that the AFG (Asahi Glass) and Pilkington (formerly LOF) companies are both foreign owned.

RAW MATERIALS USED IN PRODUCTION

Base Batch Ingredients

There is no set or standard composition used by all the glass manufacturers, but they typically run in a close range for the major ingredients, especially for clear glass. Table 2 shows a typical base for clear float glass.

Although these are the base ingredients, a typical composition also includes numerous minor elements. Their types and amounts will vary with the location of the mine, quarry, or process, but these minor ingredients are typically potassium (K₂O), titania (TiO₂), alumina (Al₂O₃), zirconia (ZrO₂), manganese (MnO₂), and iron (Fe₂O₃). Today a full analysis of all the ingredients is compiled and input to a computer, which calculates the batch recipe. The processing, sizing, and transportation of these materials are also very important to the glassmaker to ensure no contamination, consistent melting, and reliable delivery. Some contaminants can be disastrous to the producer when they arrive as larger particles that do not have enough time and/or temperature in the process to melt. Two of the most difficult to handle are chromite and alumina.

Additives for Color, Properties, and Forming

For automotive glasses, the composition for many years used a higher level of iron (0.4% to 0.6% Fe₂O₃), which gave a green product. Sometimes a small amount of cobalt was used with the iron to give a green/blue tint. As the automotive industry became more concerned with air conditioning and heat buildup in vehicles, compositions with higher iron levels were used to absorb/reflect more of the solar heat and ultraviolet (UV) radiation. Some compositions used cerium and titania for improved UV protection to prevent fabric fading and protect passengers. With the production of minivans and sport utility vehicles (SUVs) came even more glass usage, which again caused air-conditioning and heat-buildup concerns. Glass manufacturers responded with what has been labeled as “privacy” glass, which is a very dark product that again helps control solar and UV properties. These glasses are made with iron (Fe₂O₃) levels >0.8% up to 1.5% and different combinations and amounts of cobalt, selenium, nickel oxide, titania, cerium, niter, and manganese,

Table 1. Producing companies and locations (North America)

Company and Location	Float Glass Production
AFG (Asahi Glass)	
Church Hill, Tennessee	2 lines
Cinnaminson, New Jersey	
Jerry Run, West Virginia	
Richmond, Kentucky	
Spring Hill, Kansas	
Victorville, California	
Quebec, Canada	
Mexicali, Mexico	Joint with Vitro
Cardinal Glass	
Menomonie, Wisconsin	
Portage, Wisconsin	
Mooreville, North Carolina	
Durant, Oklahoma	
Guardian Glass	
Carleton, Michigan	2 lines
Geneva, New York	
De Witt, Iowa	
Florence, Pennsylvania	
Richburg, South Carolina	
Corsicana, Texas	
Kingsburg, California	
Pilkington Glass	
Rossford, Ohio	2 lines
Ottawa, Illinois	
Lathrop, California	
Laurinburg, North Carolina	2 lines
PPG Industries	
Carlisle, Pennsylvania	2 lines
Meadville, Pennsylvania	2 lines
Mt. Zion, Illinois	2 lines
Wichita Falls, Texas	2 lines
Fresno, California	
Owen Sound, Canada	
Visteon	
Nashville, Tennessee	
Tulsa, Oklahoma	2 lines

among others. The color can be controlled to produce a green, gray, blue, or bronze product tint using combinations of the colorants and tight control of the furnace redox.

For architectural glasses, mostly gray and bronze products are used, but several blue, blue-green, and green products are also on the market. These use essentially the same colorants as the automotive privacy glasses. Several of the newer products are essentially the automotive products under a different name. Once again, it is control of the solar properties that is critical in the building design in addition to the beautiful colors that can be selected.

Specialty glasses such as a low-iron product are being made for furniture, glass shelving, industrial needs, solar products, and so forth. These glasses sometimes have less than 0.015% iron. They require that the raw materials contain very low levels of iron. Tight furnace control of the redox conditions is needed to maintain the iron at the desired color shade. A more oxidized glass will cause the remaining iron to turn yellow, and this sometimes requires the addition of a small amount of cerium and niter. If a blue shade is

Table 2. Typical base for clear float glass

Oxide	Percentage Range	Source
SiO ₂	71.5–73.2	Silica, silicon dioxide (SiO ₂), silica sand
Na ₂ O	13.4–14.2	Sodium carbonate (Na ₂ CO ₃), soda ash
CaO	8.4–8.9	Lime, limestone (CaCO ₃)
MgO	3.6–4.3	Magnesium, dolomite (CaMgCO ₃)
Al ₂ O ₃	0.1–1.2	Alumina, nepheline, feldspar, slag
Fe ₂ O ₃	0.08–0.12	Iron, iron oxide (Fe ₂ O ₃)
SO ₃	0.15–0.30	Sulfate, sodium sulfate (Na ₂ SO ₄), calcium sulfate (CaSO ₄)

desired, the furnace is operated under reducing conditions and a small amount of cobalt might be added.

FLOAT GLASS PRODUCTS

Market Breakdown by Section

Although the market end use for glass varies with the introduction of new products, it has remained reasonably stable for several years. The increasing number of cars has been offset by windows (both residential and architectural/commercial) that use multiple panes of glass. The latest numbers from the AFG Marketing Group (2003 data) indicates a breakdown in the sectors as follows:

Automotive	23%
Residential	42%
Architectural	24%
Specialty	11%

Automotive Glass

As designers continue to develop the new looks of today's vehicles, the role of glass has continued to be an integral part of that design. Today's designers are concerned about color, solar heat, UV rays, weight, styling, and security. Each of these items has forced changes to the basic glass product and continues to challenge the producers.

Originally, basic automotive glass was clear. This changed to green tints (achieved with Fe₂O₃) in the 1970s as the desire to increase sun shading became important. As designers began to increase the amount of glass used, the heat buildup in a parked car and the air conditioning required to keep a car cool were added to the list of concerns. The first move was to increase the amount of iron used to darken the green color, which lowers the light and solar transmittance. This approach was limited by a federal standard that requires a minimum of 70% light transmittance in all passenger car glass. For SUVs, mini vans, trucks, and so forth, this law applies to the windshield and the front-door glass only. The concern about UV rays also came to the fore at this time in connection not only with personal health, but also with fabric and dash fading. Glassmakers found that they could optimize the solar and UV protection by controlling furnace redox and/or using small amounts of cerium, titania, or both.

With the success of minivans in the 1980s, SUVs in the 1990s, and passenger-styled trucks recently, the privacy glass wave of products evolved. Light transmissions were reduced to less than 20% in some products to further reduce solar heat and UV rays. This has also allowed color to be more of a choice. Today's designers can use, for example, green, gray, blue, and bronze shades of glass, and engineers can design smaller air-conditioning systems. These glasses have been a real challenge to the producers not only in the melting area, but also in the seemingly continuous color transition that generate tons of off-color product to be recycled.

As the glass composition options became limited by the 70% light transmittance regulation, the use of coatings on the glass and

laminating materials with additives has increased. These have allowed further decreases in solar and UV transmittance while continuing to meet the 70% minimum for light transmittance.

The continuing cycle of concern about fuel mileage has led to the use of thinner glass products in an effort to reduce overall vehicle weight. Although this is not a melting concern, it is a forming problem for the bath. Thinner products normally result in poorer optical properties. The old standard to improve optics is to run slower and produce less, but this leads to higher production costs. Glass less than 1 mm has been used, but problems with fabricating parts, breakage, and road and wind noise, among others, continue to limit the reduction in thickness.

Styling is a designer's dream but often a producer's nightmare. The windshields that lay down seemingly almost horizontal result in increased optical problems. This, combined with thinner glasses, results in very tight control ranges. The large wraparound pieces are very difficult to bend and form without problems. The many bends, numerous holes, and curvy shapes also increase the fabricator's difficulties.

Security is probably the latest item of concern to fabricators. The standard for many years has been laminated windshields and tempered side and back glass. Tempered glass, although tough to break, can be broken, resulting in very quick entry into the vehicle. Several of the high-end cars today are also using a laminated product for side glass. Instead of a single 3.6-mm tempered glass piece, the new units are two pieces of 1.6- to 1.8-mm laminated glass.

Residential/Window Glass

The traditional glass of choice has been and continues to be a clear product. Just as the automotive designers began to be concerned about heat buildup, heat loss, and UV rays, the homeowners have done likewise. Unfortunately, glass cannot be made to control and mitigate these concerns without decreasing the light transmittance, which is totally undesired in this application. The first step was to improve the thermal barrier by the use of insulated glass (IG) units that consist of 2 and sometimes 3 lites of glass, sealed in a unit with an air space separating each lite. These units continue to be refined in design by using different and more efficient construction materials, spacers, and gas filling. The next step was to further control the heat escaping from the house and the solar heat and UV rays entering the house. This has been accomplished with the use of coatings and a group of products termed Low E, which stands for low emissivity. Low E glass is coated with microscopically thin, virtually invisible metal or metallic oxide layers to reduce the U-factor by suppressing the radiative heat flow through the window. Low E coatings can be applied on the float line (pyrolytic) or ofline (sputtered). The coatings differ in their durability—the on-line pyrolytic type is the most durable, which allows it to be exposed to the weather and outside conditions. Because the sputtered products are less durable, they must be glazed inside an IG unit.

The coatings have been further refined to include products that are better in colder climates than in warmer climates. Color control is also a key control for the coatings, as slight variations can change the color from a neutral to a blue or green shade, among others, when viewed in reflection.

In areas where hurricanes and high winds are a risk, some building codes are now requiring that the glass be laminated like a car windshield.

Architectural/Commercial

Color and solar control are at the top of the designer's list of considerations when it comes to large applications. The old standby colors of the past were the gray and bronze tints, but today's palette is almost endless. The base glass can now be of several tints, most

of which have been developed for automotive applications. These can be several shades of green, blue, blue-green, gray, bronze, and so forth. On top of the basic glass, an almost endless list of colors and properties can be added with the coating technology. Both pyrolytic and soft coat products are used for these applications.

Specialty Products

One of the fastest growing areas is the glass for solar collectors. This glass requires the maximum amount of light transmittance possible to obtain peak efficiency. As a result, the iron levels are being reduced to the limit of the available raw materials. Products with <0.015% Fe₂O₃ are being produced. Sometimes small amounts of cerium and niobium are used to control the redox state of the iron to further increase light transmittance.

Other uses of the low-iron products are found in glass for furniture, table tops, shelving, appliances, and lighting fixtures where the traditional dark green edge can be a soft green, a light blue, or almost colorless.

Products for liquid crystal displays, personal computers, touch screens, TVs, computers, and many other electronic and commercial uses are also increasing in volume. These products require very tight quality controls and very thin thicknesses in some applications. Again, coatings are playing a major role in several of these applications.

FUTURE MARKETS AND TRENDS

The forecast for glass sales continues to show a gradual increase in volume in the coming years for the U.S. and North American markets. Unfortunately, the supply and demand in the United States still is on the supply side, resulting in a very competitive commodity market. Glass is a commodity product, worldwide quality is improving, and more imports will most likely be coming to U.S. shores in increasing numbers.

Flat glass producers appear to be following the same path as other manufacturers because the majority of the world's new production facilities are being built in the Far East, particularly in China. China, which is undergoing the largest expansion in the world today, is and will continue to be the biggest concern for the industry. With today's float plant cost pushing \$100 million for a basic plant and glass prices still very soft, the price of labor and energy are key variables.

Technology and productivity improvements have kept the U.S. manufacturers competitive for a long time. This trend must continue. Other areas that must continue to grow are the value-added and specialty products, many of which involve coatings. These niches allow for increased profits only until the technology spreads and others enter the market. At that time, a profitable value-added product becomes a commodity.

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Specialty Glass

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INTRODUCTION

Specialty glasses include that very broad range of glass types, compositions, and end uses that are not flat (window) glass, container glass, or fiberglass. In earlier texts this broad group was sometimes referred to as “pressed and blown ware,” but this definition is not completely satisfactory because it is not specific in terms of composition, nor is it inclusive in capturing the process of forming the product. The U.S. Department of Commerce has published glass-production data that includes fiberglass with the specialty glass data, which clouds the subject somewhat.

Examples of specialty glasses include lighting products (incandescent bulbs and fluorescent tubes), laboratory ware, cathode-ray tubes (CRTs) for television and computer monitors, liquid crystal display flat glass, optical and ophthalmic glasses, glass-ceramic cooking and table ware, soda-lime and borosilicate tableware, and lead crystal and other art glasses including color sticks. Fused silica is a glassy form of silicon dioxide (SiO_2) and is sometimes included in the group, although it is not formed by normal glass-making processes. Optical fiberglass, produced by the flame pyrolysis of silicon compounds, is not considered in this chapter.

The complexity of the subject is reflected in the fact that at one time a leading specialty glassmaker listed nearly 1,000 glass compositions used to manufacture about 60,000 different products (Edwards and Copley 1977). More than 20 different industrial minerals are consumed in the glass industry (O'Driscoll 1990), and the number of specialty chemicals consumed is even greater. Indeed, the dividing line between minerals and specialty chemicals can become blurred as the specialty glassmaker places increasingly stringent demands on the raw material producer by requiring minerals to be more highly processed. At that point it becomes difficult to say whether they have lost their original mineralogical identity and become refined chemicals.

Many specialty glass products, such as tableware and float glass (window glass produced by floating molten glass on a pool of molten tin), use glass formulations which, although specific to the end use, are similar to the great bulk of container glass in that they are soda-lime glasses, formulated with SiO_2 , soda (NaO), calcia (CaO), and small amounts of alumina (Al_2O_3) and perhaps magnesia (MgO) as a stabilizer.

This chapter gives a brief overview of selected specialty glasses and their manufacturing processes but focuses more on some of the industrial minerals used in their production. For greater

detail on glass-manufacturing techniques, consult *The Handbook of Glass Manufacture* by F.V. Tooley (1984).

The glass industry as a whole refers to the oxide when discussing the composition of a mineral or chemical, and this convention is used here, referring to, for example, the potassium content of a feldspar in the form of K_2O , or potash, rather than as the element potassium. This convention is useful for the glassmaker in that most glasses are described by their content of glass formers (SiO_2 , boron oxide [B_2O_3], etc.), intermediates (Al_2O_3 , titania [TiO_2], etc.), and modifiers (MgO , lithia [Li_2O], CaO , etc.), and such an expression is used to calculate the oxide contribution of any given raw material in the batch to the desired oxide composition of the final glass. This in turn facilitates the calculation of the batch composition needed in producing the glass, because in general, glassmaking is a continuous process for which the raw materials are prepared discontinuously in discrete batches, then added to the continuous melting and forming stages.

SPECIALTY GLASS PROCESSES

Lighting

Lighting products such as lamp envelopes (light bulbs) are made from a variety of glass types, including borosilicate, soda lime, and aluminosilicate, although this list is not exhaustive. The processes used in manufacturing these lamp envelopes can be generalized into two categories: (1) lamp blanks (preliminary shapes from which finished articles are made) formed directly in some type of blowing process (such as the ribbon machine); or (2) lamp blanks formed by the lampworking of previously manufactured glass tubing. Glass quality requirements vary among the different applications but are most critical for halogen-type bulbs because of the high operating temperature of the lamp.

Vello, downdraw, and Danner forming processes are used to manufacture tubing (Tooley 1984). Historically, the Danner process was preferred until the Vello process, which greatly increased production rates, was developed. The Danner process is still in use in many developing countries, and for a very few selected products requiring particular dimensional characteristics. The Danner process is a much simpler process than the Vello but is limited by the gravitational flow of the viscous glass, and the stability of that flow down the forming mandrel to provide dimensional control. The Vello process could be thought of as a pultrusion process, where the glass is literally pulled through an annular opening by

the cutting machine at the cold end of the process. The downdraw process differs from the Vello primarily in scale and size of products, ranging upward from roughly an outside diameter (OD) of 51.0 mm (2.0 in.). It is also characterized by being a completely vertical process, whereas Danner and Vello are horizontal.

The variety of sizes produced range from less than 6.0 mm (0.25 in.) OD to as much as 305 mm (12 in.) OD for a downdraw operation, with a variety of possible wall thicknesses. Probably the largest application is for soda-lime fluorescent tubing.

Amid the variety of blowing processes, the ribbon machine for standard light bulbs is the best known. The ribbon machine is capable of making a variety of bulb blank sizes, up to larger specialty bulbs for x-ray tubes and stadium lighting, for example. A stream of glass is formed into a relatively thin ribbon and pulled across the top of a bank of molds. The glass is pressed into the top of each mold and blown out into a bulb. The finished bulb is cracked off the ribbon, and the majority of the ribbon is returned for recycling. Larger bulbs can also be made on gob-and-blow machines, where a small gob of glass is extruded from an orifice, cut and pressed into a patty, and then sagged and blown into a rotating mold. This latter process produces blanks without mold seams because the mold rotates around the glass piece, cushioned by a film of steam.

In developing countries, many such lighting products are produced by hand.

Glass quality requirements for lighting applications can be challenging because the products are relatively thin-walled, leaving no room for inclusions that might be tolerated in thicker ware, such as a bottle. For process stability in high-speed manufacturing processes, a constant and stable viscosity is required, implying that the glass composition must be very stable and also requiring tight control of raw material assays and thorough mixing.

Laboratory Ware and Pharmaceutical Glass

Glasses produced for this industry segment are nearly all borosilicates of one type or another, which have the highest chemical durabilities of common glass compositions.

The durability and inertness is a result of the composition, which is more than 80% silica in the case of heat-resistant glass, with the remainder being boron, soda, and alumina. The resulting low coefficient of thermal expansion also makes this hard borosilicate especially useful in the laboratory where it can withstand direct heating without suffering thermal shock damage. The high amount of silica in the composition also makes this glass relatively difficult to melt, and so the selection of the particle-size distribution of the silica sand used is the most critical element of the raw materials portfolio. Many melting studies have been performed in an attempt to understand the melting dynamics of any particular sand, and although no definitive conclusion has been reached, sands for borosilicate glass are generally finer than those used for other applications. More subtle differences, such as whether the sand source is a rounded beach grain, or a crushed, angular, fractured grain, will also affect the melting process.

The basic forming processes for laboratory ware are similar to those for lighting, with tubing and blownware being the primary manufacturing products. From these basic components, a great variety of products are produced through secondary manufacturing, based on the lampworking process—reheating, shaping, and connecting previously made components. A small sampling of products would include petcocks, distillation and condensation apparatus, reaction vessels, and transfer piping. Nearly every research university with any reasonable interest in chemistry will

have a lampworking department (or at least an expert individual) to custom fabricate the desired process glassware.

The glasses for pharmaceutical applications retain most of the chemical durability attributes of the heat-resistant glass but do so with much less silica in the composition, which makes the glass a bit easier to melt and manufacture. These compositions will also contain varying amounts of potash and calcia, and likely higher amounts of alumina, soda, and boron. They also have the distinction of being produced in an amber color, for ultraviolet (UV) light protection of the contents. Although easier to melt because of lesser amounts of silica, their quality is difficult to maintain because of sensitivity to the oxidation state of the glass, a function of trace residual organics in the raw materials interacting with the melting process. This can affect not only the glass color but also the number of small gas bubbles retained in the melt. Pharmaceutical glass is most often produced as a glass tube initially, with a secondary product forming into an ampoule.

Cathode-Ray Tubes

CRTs, such as television tubes and computer monitors, were developed in the 1930s and 1940s and became a major manufacturing activity in the 1950s and 1960s in North America. The advent of color television in the 1950s required further improvements in the glass compositions, and larger tube sizes pushed the limits of pressing capability.

The composition of the faceplate (panel) glass is based on the need for x-ray absorption to protect the viewer from the radiation produced within the tube when the electron beam is generated to excite the fluorescent coating on the inside surface of the optical-quality faceplate. The glass composition has generally been high in the heavy alkaline earth components and with a small amount of lead to provide the x-ray absorption. With the advent of computer monitors and their problem with x-ray browning (burned-in ghost images), the composition evolved once more to exclude lead and add zirconia (ZrO_2) instead. The funnel glass (so named for its shape) continues to be a high-lead composition, as browning is of no consequence there. The neck tubing for the electron beam source is also high in lead.

Pressing is the most common process for manufacturing panel and funnel glass. A large, precious-metal-clad or refractory gobber is used at the delivery end of the process to extrude the desired quantity of glass (the gob) through an orifice. The gob is then cut, falls into a mold, and is pressed to the desired shape. Once cool enough (a limiting factor because of the relatively high thickness of the panel glass), the glass has a variety of metal components imbedded. It is then annealed and made ready for tube production, which involves applying phosphors; installing various metal components; and welding together the glass parts of the tube, followed by evacuation and sealing.

Because of the stringent quality requirements for the panel glass and the large amount of glass required to produce a panel (in excess of 45 kg [100 lb] each for large specialty tubes), a great deal of effort has been expended to study melting characteristics of various raw materials, working toward the goal of defect-free glass. The high amount of fluxes and modifiers in the composition means that melting (e.g., sand grain dissolution) is not necessarily the primary concern. Instead, residual bubbles, cord (glass inhomogeneities), and refractory dissolution and interactions are the critical criteria for successful production.

The production of CRTs has been, until recently, a premier activity of any glassmaker. In North America and Western Europe, however, the last few years have been extraordinarily difficult for

the CRT glass producer. Significant capacity increases, as well as efficiency improvements, have been implemented in Asia. Economically, only the top-of-the-line products can be manufactured profitably in the developed countries, but as technical and manufacturing capabilities continue their rapid progression in Asia, it is expected that more of these products will be moved there as well. It is not very likely that any primary glass manufacturing will remain in North America by 2010, and the pressures will be very similar in Western Europe.

In any case, the rapidly increasing popularity of flat-screen displays for televisions and computers means that these sheet-glass displays will likely replace the CRT in most applications within a few years.

Liquid Crystal Display Glass

The popularity of thin, flat displays for computer monitors and home entertainment has driven recent rapid growth in this segment of the specialty glass industry, although development has been under way for at least 30 years. The basic forming technology was developed 30–40 years ago with the intention of producing window and automotive glass by a smaller scale alternative to the float glass process.

Although tonnage produced is small, these products are highly profitable for their producers and have evolved into important and proprietary businesses. Assuming that product costs follow the decay curve seen in most newly developed electronic items, flat display panels are expected to replace the CRT as the preferred product for television sets and computer monitors within a few years' time.

The glass material used for these flat-panel displays is unusual in that soda and potash are contaminants to the ensuing semiconductor application and must be controlled to absolutely minimum levels. Often trace levels of alkalis in the raw materials are sources of serious product performance problems for the glass. In addition, the variabilities of the contaminants and material assay cause major instabilities in the melting process.

Because of the semiconductor application requirements, the composition has an extremely high softening point, requiring melting temperatures that exceed 1,700°C (3,092°F) and special materials in the construction of the melting furnaces and glass-handling equipment. Primary melting is powered by gas/oxygen combustion in combination with joule heating. The glass is refined, often in a vacuum-fining process, before proceeding through a platinum-clad mixing, conditioning, and stirring section.

One major producer's forming process consists of a trough that allows glass to overflow both sides and flow down to rejoin below the trough to form a vertical sheet with two optically perfect air-contact surfaces. A sheet is produced up to 2 m (6.6 ft) in width, and as thin as 0.7 mm (0.03 in.) at the current state of the technology. It is then inspected and graded for quality and allocated to its optimum utilization, depending on its quality grade. All processes after the forming pipe are in tightly controlled, clean-room environments.

Optical and Ophthalmic Glass

Optical glasses are extremely specialized, low-volume products. Raw material purity and stability requirements are demanding, often pushing the limits of suppliers' processes and approaching specialty chemical specifications. Because nearly perfect homogeneity is necessary for optical transparency and image formation, glass/refractory contact is often minimized through the extensive use of precious metals, at least in the conditioning and stirring sections of the process. Very precise control of the refractive index is also key to producing these materials.

Ophthalmic glasses are nearly as demanding in terms of quality and purity requirements and often employ similar melting technologies, including precious metals and intense stirring. One of the key product criteria, refractive index control, is a direct result of stable raw material assays. Photosensitive ophthalmic glasses have been produced that include precipitated silver halide crystals that react to ambient UV light levels and, therefore, adjust their degree of tint. Production of these glasses has been eroded by the advent of plastic lenses with similar performance and, undoubtedly, the increased popularity of contact lenses and corrective surgery.

Glass Ceramics

Glass ceramics is an interesting family of materials that are melted and formed as glasses and then, through subsequent heat treatment, grow crystalline phases to take on many attributes of ceramics. They are extremely resistant to thermal shock and have very high mechanical strength. Many of the compositions that have been manufactured have been based on lithia compound crystallization, which has historically made this segment one of the larger consumers of lithia minerals.

Although there are a variety of technical and scientific applications of this type of material, the best-known applications are bakeware and stove-top consumer products. The manufacture of these products has decreased greatly in recent years, and it is not clear whether any are still manufactured in the United States. A few products have been replaced by a variety of traditional ceramic materials. Currently, stove-top surfaces and woodstove windows are still produced from glass ceramics and take great advantage of the thermal shock resistance of this family of materials. Overall production is certainly well below historical levels and likely to continue at that reduced level.

Soda-Lime Table and Cookware

Consumer products cover a broad spectrum of products and glass compositions as well. Soda lime, borosilicate, fluorine opal, laminated glass, and glass ceramic materials have all been used to make products such as measuring cups, bakeware, dishes, and mixing bowls. Primary forming is typically done by pressing, and decorating can be a multistep silkscreen printing process using ceramic-based inks that are then fired onto the ware. Melting furnaces for these products are typical of other glass operations for large-volume commodity glass manufacturing, although the production of opal glasses carries the burden of managing fluorine emissions. For this reason, cold-top melters are so metimes used, greatly reducing emissions and assisting in fluorine retention.

Because the consumer does not have strict technical requirements for the glass material, this has been a field where "look-alike" products have often been applied successfully to produce ware at reduced cost. As one example, instead of making a product from the more expensive and more difficult-to-melt borosilicate composition, some producers have manufactured products from soda lime and then heat-treated the products to result in the improved strength and thermal shock resistance that approaches the performance of borosilicate products. Similarly, some glass ceramic and opal products have been replaced with traditional ceramic bodies, using glazes chosen to mimic the surface quality of the original glassware.

As if recycling glass were not challenging enough, it is further complicated by the mixture of products and materials found within the broad field of consumer products and by variations among producers. Glass ceramics and pottery, if mixed with cullet in postconsumer recycling operations, do not melt well when introduced into the glass furnace.

Art Glass

Because there are few specific technical requirements for this class of applications, the glass compositions vary according to producers and their company traditions and practices, including high lead and soda-lime compositions. Individual studio producers often use one of several standardized glass compositions from the soda-lime family, commercially available in cullet form and as premixed batch.

Lampworking applications tend to be separated into two general families: soda lime and borosilicate. Within any given application, however, there are technical requirements for colorant compatibility and proper annealing.

Larger producers are more likely to employ continuous melters, which require either 2 or 3 daily production shifts, 7 days per week, to support the melting volume and produce consistently reliable quality. Smaller producers are more likely to use pot melters, which offer the advantages of limited production rates (1 shift per day, 1 or more production days per week), while still producing good quality ware. Typically, because this type of ware is produced by hand blowing and forming, the character of these businesses is dominated by the atmosphere of an artisan's workshop, not necessarily a technologically sophisticated industrial approach.

Lead glass, commonly referred to as lead crystal, can range from 22%–30% lead oxide and is the preferred material where its high index of refraction is required to improve the sparkle of the resulting products. The high density of the resulting glass also contributes to the distinctive chime when lead crystal glasses are tapped. Color quality is of utmost importance to these applications, so the concentration of coloring oxides present in the raw materials must be minimized. Some producers will also add decolorizers to produce a neutral grayed color to mask the presence of iron oxide (and other coloring oxides) instead of or in addition to minimizing the iron oxide in the raw materials, most notably from the silica and lead oxide sources. A few producers have investigated melting lead-free compositions, instead using other heavy metal oxides, such as silver and barium, to provide the high refractive index and density.

Soda-lime glass is probably the most commonly used composition in the art glass field; it is the most readily available and has the fewest environmental ramifications. Some colors are easier to produce with soda lime, particularly those requiring reducing conditions, which would precipitate metallic lead within the glass or on its surface. A huge variety of "color sticks" are available to support soda-lime production, and often the producers melt only one or two colors (e.g., clear and opal), and achieve all other coloration with these highly concentrated colorants.

INDIVIDUAL INDUSTRIAL MINERALS AND CHEMICALS

The following sections give an overview of individual industrial minerals and chemicals as used in the glass industry (Harben 2002), with some details of the specific requirements of the specialty glass industry.

Most of the raw materials used in specialty glasses are essentially the same as those used in the larger volume commodity glasses, but with special conditions to fit special requirements. Generally the special conditions involve the level of purity or freedom from contamination of various kinds, but may also include the physical form of the raw material. In many cases the specialty glass in question may have purity requirements that prohibit the use of minerals, no matter how highly refined. An example of this might be the use of strontium carbonate rather than celestite in the production of CRT glasses because the formulation and manufacturing process of these glasses is intolerant of sulfur.

Alumina

The majority of glasses used for large-volume commodity applications, such as containers and windows, contain a small amount of aluminum oxide to enhance mechanical and chemical durability. Generally these glasses, and many specialty glasses as well, derive their alumina from one of the various forms of feldspar. Others, however, must be largely free of one or more of the normal constituents of feldspars, such as soda, requiring some form of alumina or alumina hydrate. The ore mineral bauxite is rarely if ever used as an alumina source in glass because of impurities, but can be used in glass after it is refined into alumina.

Glass ceramics, usually produced to exploit their low coefficient of thermal expansion, cannot contain much soda, so they must get their alumina content from special calcined aluminas. Liquid crystal display (LCD) flat sheet-glass production requires a soda content below 20 ppm to meet the semiconductor application requirements.

Alumina is produced as one step in the Bayer process of reducing the bauxite ore to aluminum metal. The Bayer process involves digesting bauxite in a caustic soda solution at elevated temperatures. The alumina trihydrate produced in this way is electrolytically reduced to aluminum metal via the Hall-Héroult process, or is further processed for use in various industries, including ceramics and glass.

Depending on the purity demands, several alumina products are used in specialty glasses, including calcined alumina produced by firing Bayer-process alumina trihydrate, low-sodium alumina, and high- to ultra-high-purity alumina.

Barium Carbonate

Barium carbonate (BaCO_3) is produced from the mineral barite by high-temperature reduction of the barium sulfate in the presence of sodium carbonate.

Barium carbonate finds significant use in CRTs where the large nuclear cross-section of barium is useful in blocking the x-rays produced by the electron beam impinging on metals within the tube. The baria also serves as a flux and stabilizer.

Baria also increases the index of refraction of the glass, giving decorative glassware greater brilliance. Pure grades of barium carbonate are used to make optical glass, and also to increase the index of refraction. Barium carbonate is also used in LCD glasses.

Boron Minerals and Compounds

Borates—minerals containing B_2O_3 —are relatively rare in nature. The borate minerals used in glass manufacture are restricted to desert regions that are also actively volcanic and where lakes have been present to dissolve the soluble borates before evaporation and deposition. Their high solubility means that borate deposits do not survive for long on the surface; they are readily washed away when the climate turns wetter.

The most commonly used borate minerals and chemicals are tincal ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), anhydrous borax ($\text{Na}_2\text{B}_4\text{O}_7$), sodium pentaborate ($\text{Na}_2\text{O} \cdot 5\text{B}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$), colemanite ($\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$), ulexite ($\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$), and boric acid (H_3BO_3).

Even though detergent and fire retardant uses consume significant amounts of borates, glass is by far the largest consumer of these minerals. B_2O_3 contributes a number of desirable attributes to the glass, including reducing the coefficient of thermal expansion, chemical and mechanical durability, easier melting (it is a powerful flux), and increasing the index of refraction.

The form selected for use depends on the composition of the glass. Formulations that include sodium and calcium can use the

lower cost ulexite, but glasses that can tolerate no alkalis or alkaline earths must use boric acid, or even anhydrous boric acid, a glassy product made by melting boric acid to drive off the water, leaving only B_2O_3 .

Glass articles produced with borate minerals and chemicals include cookware, laboratory ware, vessels for the chemical industry, laboratory glassware, and LCDs (Harben 2002).

Borate minerals find major applications in the fiberglass industry, which is covered in a separate chapter.

Calcium Carbonate, Limestone, and Dolomites

By far the largest use of calcium and magnesium minerals in the glass industry is as limestone in soda-lime container glass. Although a reasonable standard of purity and consistency is required for container applications, the dominant characteristic controlling the glassmaker's choice of limestone is price, and because transportation is a major part of the delivered price, most limestones are mined close to where they are consumed.

Carbonate rocks and minerals comprise a wide and varied range of geological circumstances. Included in this group are limestone, chalk, marble, carbonatite, vein calcite, aragonite, sand, and others.

The use of the calcium and magnesium carbonates in the specialty glass field is governed by the requirements of the individual glass compositions, which need to be free of specific contaminants.

Special limitations placed on the calcium carbonate used by the specialty glassmaker may include iron oxide (Fe_2O_3), chlorides, and sulfates. The restrictions may be so tight that the glassmaker will resort to precipitated calcium carbonate, even reagent grade, for limited usage. Few natural calcium carbonate sources, such as limestone or vein calcite, will routinely yield products with Fe_2O_3 of less than 0.05% and this level of iron may be too high for some optical applications. The nature of the glass being made will also dictate whether dolomite or calcite is used, as some of the glasses are not tolerant of significant amounts of MgO.

In any case the use of calcium carbonate rocks and minerals in glass is a very small percentage of the total worldwide consumption of these materials when compared to the huge tonnages consumed in aggregate production and the making of portland and other cements. Ground calcium carbonate, if sufficiently high in whiteness, is used in papermaking, as fillers in plastics and coatings, and in other industrial uses.

Cerium and Other Rare Earths

Along with cerium, some of the other rare earths include elements in the lanthanide series, including lanthanum, praseodymium, erbium, and neodymium. Together or individually, these elements are used to control index of refraction, to reduce optical dispersion, and to introduce various colors. They are also used as oxide coatings on the surface of optics to control reflection properties (Tooley 1984).

Rare earth is quite a misnomer, as the mineral sources of these elements are fairly common in the earth's crust. Overall, these elements are more common than silver, and cerium and lanthanum are more common than lead (Harben 2002). Two minerals, bastnaesite and monazite, serve as the ore sources for most of the rare earths, including cerium and lanthanum. These minerals occur in carbonatite bodies, which are a rare class of igneous rocks consisting mainly of carbonates and phosphates. Carbonatites in China, Russia, and the United States supply the majority of rare earth minerals.

Cerium oxide (CeO) is used as a polish in optical and other glass production. It serves a dual use in the production of CRTs, because it is used both as an ingredient in the faceplate glass and as a polish in the finishing of the ware. Cerium oxide can also be used to

decolorize glass by modifying the valence state of the iron contained in the glass.

Erbium imparts a distinctive pink color to glass.

Other rare earths, particularly yttrium and europium along with cerium, are used in the "phosphors" which fluoresce to produce the colored image on the screen of the CRT when struck by electrons from the electron gun.

Uses of rare earths other than in glass include petroleum-cracking catalysts, specialty ceramics, electronics, and minor medical applications.

Coloring Oxides

One of the most useful characteristics of glass is that it can be colored many different shades and intensities, indeed over the entire visible spectrum. This attribute is used in industrial and technical applications but is of particular value in consumer ware and art glass. The "coloring oxides" include cadmium, chromium, cobalt, cerium, copper, gold, iron, manganese, selenium, nickel, neodymium, and uranium. Sulfur is used in combination with iron to impart the familiar color to brown beer bottles.

Cadmium is introduced as the sulfide (along with some selenium) to produce a ruby red color, or without the selenium to produce a strong yellow. This application has been of considerable commercial importance in turn-signal lamps for automobiles.

Chromium imparts the bright green to many container glasses such as some beer bottles. The element is produced as the mineral chromite, often used directly in the metallurgical trade. Chromite itself tends to be highly insoluble in most glasses, and for this reason chromium is usually batched as the potassium dichromate, $K_2Cr_2O_7$. Chromic oxide is also used in some specialty situations where alkalis are not tolerated.

Cobalt is an extremely powerful coloring agent, just a few fractions of a percent yielding the familiar deep blue seen in much container ware and tableware. The principle use of cobalt other than as a colorant in glass and glazes is as a hardening alloy in steel. Most cobalt is a by-product of nickel mining.

Copper, usually added as one of the oxides, imparts a blue-green color to an oxidized glass. Under reducing conditions, it can produce a red coloration.

Iron will color oxidized glasses green, while under reducing conditions it produces a gray or brown tint. Magnetite is utilized for glasses needing reduced iron, as arsenic derite ($FeCO_3$) or ferrous oxalate (FeC_2O_4). In most glass raw materials, iron is regarded as one of the major contaminants, and most producers of sand, limestone, feldspar, and similar raw materials strive to produce the lowest iron products possible. If the glassmaker wishes an iron color, the glassmaker prefers to add the iron during the glassmaking process. Silica sands for specialty art and optical glass must have Fe_2O_3 contents less than a few parts per million. Pure and carefully sized Fe_2O_3 , termed rouge, is employed as a fine polishing compound in some glass operations.

Manganese is usually employed as the dioxide, MnO_2 . The naturally occurring manganese dioxide mineral pyrolusite is used unless extreme levels of purity are required, in which case purified manganese dioxide or potassium permanganate ($KMnO_4$) are used. Manganese can impart a lavender color to the glass, or in small quantities can be used to counteract the coloration imparted by iron, and thus serve as a decolorizer.

Neodymium, praseodymium, and other rare earths are sometimes employed as coloring oxides. Neodymium and praseodymium often occur together, and can be used in the oxide or carbonate form to produce a purple color. Like manganese, this combination can be used as a decolorizer. When used by itself,

praseodymium yields a green color. There are many specific and small applications for other rare earths where special colors are required in optical or other applications.

Nickel imparts violet hues to glasses and is sometimes used in the oxide form to decolor lead glasses. Nickel is also used to produce CRT faceplate glass, in conjunction with lesser amounts of cobalt and chromium, to produce the desired neutral gray color.

Selenium is used in elemental form as a metal powder. Selenium is widely used as a decolorizer to counteract contamination with iron. In larger amounts and with cadmium it is used to produce a ruby red. Selenium is largely a by-product of the smelting of copper ores.

Uranium has been used in various chemical forms to impart a distinctive green color with fluorescent effects. This color is sometimes seen in antique glassware, but uranium glasses have only limited production today because of industrial hygiene considerations relative to handling of the uranium compounds.

Feldspar and Nepheline Syenite

The term feldspar as used in industry covers a wide range of minerals and rocks, and usually includes nepheline syenite, a plite, and feldspathic sands, all of which are used in various glass applications as sources of alumina, and to a lesser degree of potash, soda, and silica. These are alkali-aluminosilicates containing a range of sodium, potassium, and calcium in a solid solution series (Harben 2002).

Potassium feldspars include microcline and orthoclase, both $KAlSi_3O_8$ in the pure state. Plagioclase feldspars are a series with sodium-rich and calcium-rich end members. Calcium-bearing feldspars include bytownite, labradorite, and anorthite, the last being a calcium aluminosilicate.

Most commercial feldspar deposits are mixtures of feldspars or contain feldspars intermediate between the pure end members. The terminology of the feldspar trade is not always clear, but if potash predominates over soda, usually in the amount of 10% or greater, the feldspar is called a potash feldspar, whereas a soda feldspar will have soda predominating, usually at the level of 7% or more soda.

Feldspars are very common minerals, constituting some 60% of the crust of the earth. They frequently occur in various types of igneous rocks, but feldspars weather easily to clay and soluble alkali carbonates. For this reason commercial deposits of feldspars are usually restricted to mountain regions where masses of relatively fresh, unweathered or partially weathered feldspar-containing rocks are accessible.

Rapid erosion of granitic areas may produce unconsolidated sands enriched in grains of feldspars that have not yet chemically weathered, and these feldspathic sands are exploited for glassmaking in several places, particularly in California, Italy, and Spain.

Nepheline syenite is an igneous rock similar to granite in some aspects but undersaturated in silica, the result being that it does not contain quartz but does contain a silica-deficient feldspathoid called nepheline with the composition $(Na, K)AlSi_3O_4$. This relative enrichment in Al_2O_3 relative to the alkalis and silica makes nepheline syenite of interest to the glassmaker as a source of alumina. Nepheline syenite is produced in a few localities, notably Brazil, Canada, and Norway.

The majority of feldspar and related materials is consumed by the glass industry (Bolger 1995). Specialty glassmakers use these sources of alumina to the greatest extent possible, always considering the levels of purity required. CRT glass production has traditionally been a major consumer of potash feldspar but has used the relatively high-potash nepheline syenite from Blue Mountain, Ontario, in recent years.

The various feldspathic materials compete among themselves for market share, and often the cost of transportation is the deciding factor, questions of chemical composition and purity aside.

Residual organics from the froth flotation process (or other processing) used to beneficiate feldspars can cause problems in specialty glass production in that they can change the oxidation state of the glass. This in turn may result in a color change by varying the amounts of iron in the +2 and +3 valence states. In some borosilicate glasses (neutral borosilicates in particular), this variability in oxidation state can cause bubble defects in the ware produced. Stabilization and control of the amount of residual organics may help some glass producers.

Fluorspar

The only significant commercial source of fluorine is the mineral fluorite (CaF_2), known industrially as fluorspar. Other fluorine minerals include cryolite (Na_3AlF_6), sellaite (MgF_2), bastnasite (a complex rare earth carbonate with fluorine), and fluorapatite (a calcium phosphate with carbonate and fluorine). The great majority of fluorspar production goes to the manufacture of hydrofluoric acid and other fluorine chemicals.

Fluorspar is used in glassmaking as a flux and to produce a white opalescence.

In some specialty glasses, sodium fluorosilicate (Na_2SiF_6), called "sodium silico fluoride" by glassmakers, is used to produce the opalescence.

Fluorine is volatile, and much of the fluorine introduced to the glass in the batch is lost to volatilization, usually into the combustion gases. This requires treatment of the effluent gases, often by wet scrubbing, or an alternative melting process such as a cold-crown furnace. This added cost has resulted in a reduction of the use of fluorine in glassmaking over the past several years.

Lead

Lead compounds, usually oxides, have long been used in glassware because they produce a high index of refraction, which gives the ware an attractive brilliance and sparkle. Lead is usually added as litharge (PbO) or red lead (Pb_3O_4), which are formed by high-temperature roasting of lead metal, and not directly from the lead sulfide mineral galena.

Red lead and litharge are dusty, and present a significant industrial hygiene hazard in handling and batching. To counter this problem, lead producers developed lead silicates, with about 25% SiO_2 , which are safer to handle. Nevertheless, the melting process volatilizes a significant amount of lead, and the use of lead in many large-volume specialty glasses such as CRTs, where it serves to block the transmission of x-rays, has declined significantly in recent years. Lead continues to be used for x-ray protection in the neck and funnel glasses of CRTs, but its use in the faceplate of the tube has been essentially discontinued because of the tendency of lead-containing glasses to turn brown after prolonged exposure to x-rays.

Lead continues to find use in small-volume art crystal and optical glasses.

Lithium

Lithium, the lightest of the alkali metals, has traditionally been produced from pegmatites as the silicate minerals spodumene, petalite, and lepidolite. During the 1990s, the bulk of production shifted from spodumene mined in North America to lithium carbonate produced from desert dry lake brines in Chile. Some dry lake brine production has existed in the United States and China for several years. Australia, Canada, and Zimbabwe continue to produce silicate-sourced lithium, but at reduced volumes compared to historical levels.

In the Sal de Atacama of Chile, shallow-well brines are pumped to large evaporating ponds where they are concentrated by solar evaporation. The resulting lithium chloride-enriched liquor is reacted with soda ash to precipitate the lithium carbonate.

Lithium finds use in many specialty glasses at small fractional percentage additions—usually less than 0.2% by weight. It is a powerful flux and can be used to reduce the melting temperature and viscosity of the glass, or to increase furnace throughput. The reduced viscosity has been shown to increase the rate of fining of the liquid glass (fining is the process by which bubbles are removed from the freshly melted glass).

Lithium can be used as a flux in place of fluorspar in CRT glass.

A major consumption of lithium has been glass ceramics for cooking and tableware, where the element is an integral part of the microcrystalline structure of the finished ware. For many years this was the major application of petalite from Zimbabwe, and spodumene from Manitoba, Canada. These minerals constituted a large portion of the batch for these glass ceramics. Production of this kind of glass-ceramic ware has ceased, at least in North America.

Magnesia

Most MgO in glass compositions comes from dolomite or dolomitic limestone. The term “high-calcium” is sometimes applied to limestones with CaO contents of up to 56%; “dolomitic limestones” have up to 25% of the CaO replaced by MgO. In most applications the MgO serves to stabilize the glass matrix, reducing devitrification (a defect in the glass caused by crystallization of certain mineral phases) and improving mechanical and chemical durability.

Pure MgO as periclase (dead-burned magnesia) is produced from seawater or brines, either desert lake brines or deep well brines, and finds limited use in specialty glasses where the glass matrix cannot tolerate calcium. Glass ceramics, some of which are lithium-magnesium aluminosilicates, require pure grades of periclase or magnesium hydroxide. In these compositions the MgO acts as a flux and melting aid, as well as serving an essential role as an intrinsic part of the glass matrix.

Potash

Generally the term “potash” refers to various salts of potassium (Harben 2002), and specifically to the oxide K_2O . The bulk of potash consumed in specialty glasses comes in the form of potash feldspars, discussed earlier.

For glasses where potash is needed but low limits of Al_2O_3 or other alkalis preclude the use of a feldspar source, the glassmaker will resort to more expensive potassium salts such as the carbonate (K_2CO_3) or nitrate (KNO_3). Potassium carbonate is somewhat hygroscopic and can be difficult to handle and store. A hydrated form is known as “pearl ash” or glassmaker’s potash (Tooley 1984).

Potassium nitrate is generally used in CRT faceplate glass production to force the molten glass composition toward a more highly oxidized state, helping to remove any trace organics introduced with the raw materials and cullet, thus stabilizing the coloring effect of Fe_2O_3 in the glass.

Silica Sand

The specialty glass industry places special demands on the sand supplier, because in many cases the volume glass sands produced for the container industry (which consumes the bulk of glass sands) are too coarse or contain an unacceptable level of impurities.

Specialty silica sands can be specially sized—for example, 100 mesh (150 μm) for borosilicate glasses—or of greater than ordinary purity. Some of the more sophisticated glass producers

have developed proprietary theories about whether rounded sand grains or angular sand grains provide worthwhile melting benefits, and may have specification requirements relative to grain shape.

High-purity silica sands are generally considered to be those with less than 300 ppm of total impurities, while ultra-high-purity silica sands are those with less than 30 ppm total impurities.

CRT glassmakers often require 50-mesh (300 μm) sands, or even finer, to allow faster dissolution of the quartz grains, although some producers express a preference for coarser sands (35 mesh [500 μm]) to minimize the number of gas bubbles produced during the dissolution of the individual grains.

As impurities are reduced, the cost of production, recovery, and handling restrictions all increase, so ultra-high-purity grades are priced as much as US\$1/lb. The total production of such rarefied grades is relatively modest, probably not exceeding 40,000 t worldwide in 2001.

Markets for such grades of silica sand are complex, consisting of many highly fragmented and isolated individual market segments. Much ultra-high-purity silica is used to make fused quartzware. Note that fused quartz is derived from natural quartz, whereas fused silica is synthetic, being derived from chemicals such as silicon tetrachloride. About half of the quartzware is used in the semiconductor industry to manufacture crucibles for single-crystal silicon production.

Other specialty glass sectors have individual restrictions. Lead crystal makers often prefer 50-mesh (300 μm) gradings, and may have Fe_2O_3 restrictions close to the ultra-high-purity level. Large-sized art crystal pieces may require sands with Fe_2O_3 as low as 5 ppm maximum to achieve the desired clarity.

Zirconium

Zirconium is used in small amounts in a limited number of glass compositions, usually to increase the index of refraction. It also is effective in blocking x-ray transmission in CRTs and raises the viscosity and chemical durability of the glass. Zirconium is used as the refined oxide, ZrO_2 , or as the mineral zircon, $ZrSiO_4$. Zircon is one of the heavy minerals and is produced from heavy mineral sands along with the titanium minerals ilmenite, rutile, and similar dense detrital minerals (Harben 2002). Baddeleyite, a naturally occurring ZrO_2 mineral, has been produced from carbonatites by open-pit mining. It has also been reported from mineral sands.

PACKAGING AND TRANSPORTATION ISSUES

Specialty glassmakers have similar issues with packaging and transportation as do makers of other types of glass, except where limitations on contamination may demand an extra degree of cleanliness. Thus, bulk shipment of sand and feldspar, common in many glass operations, may be ruled out because shipping modes cannot be kept sufficiently free of contamination.

It is possible to achieve a surprisingly high level of cleanliness, even in bulk shipments of industrial minerals on ocean-going vessels. Bulk shipments of lithium minerals bound for specialty glass consumption have been done on bulk ocean freighters with little or no contamination, but each hold of the vessel required a special cleaning crew to remove scale and wash down the hold, followed by inspections, before the cargo could be accepted. An experienced agent of the receiving customer must do such inspections.

In a similar manner, motor trucks or railcars for bulk shipment of specialty industrial minerals may require individual cleaning and inspection by trained personnel before being certified as acceptable for use.

Many specialty glassmakers receive all their raw materials in some kind of packaging to protect them from contamination. The

most common packaging for such raw materials is the multilayer kraft paper bag with a ply of polymer film for moisture proofing. Such bags usually contain about 25.0 kg (55.1 lb) of material.

“Super sacks” of woven polymer may offer a semibulk solution to large volume materials that must be kept clean. These contain a nominal 1 ton of material, and can be handled aboard ship or on rail with relative ease. A forklift truck, for example, can lift one of the sacks for loading or unloading, or for discharge into a dump hopper.

Other containers, such as fiber drums of varying capacities, are also used where suitable, but these present some difficulty in handling. Usually a polymer film lining is included as added protection against moisture and other contaminants.

All containers of the kinds discussed here present the end user with problems of disposal, and attention must be paid to any questions of environmental or industrial hygiene hazards arising from the material contained.

CONSIDERATIONS FOR POTENTIAL SUPPLIERS

The contemporary glass industry, including specialty glass, consists of a group of producers who have survived a prolonged period of downsizing and consolidation. They are sensitive to costs, and have limited in-house resources for quality control. Industrial mineral producers wishing to become suppliers to the glass industry will be met with demands for consistency of supply, and for effective protection from upsets caused by contaminated or off-specification materials. The vendor must provide these assurances without placing undue demands on the customer's personnel.

Although the lowest possible delivered cost is a given, the glassmaker will also insist on assurances of on-time delivery of in-specification raw materials, and such assurances may be built into the purchasing agreement, with severe penalties for failure to comply.

Consequently, any industrial mineral producer seeking to gain greater penetration into the glass industry will have to be prepared to act as a provider of service rather than, or in addition to, just supplying a commodity. For example, certificates of analysis should be provided electronically to the glassmaker before the shipment arrives at the glass plant, thus avoiding any possibility of contaminating (with off-specification material) any in-specification material already in storage at the receiving plant. In fact, the vendor should reject off-specification shipments independently without waiting for the receiving plant to notice a discrepancy.

Although ISO certification alone is not proof of process control or of good quality of product, it is proof of a minimum level of record keeping, a necessary step in process control.

In many cases the specialty glassmaker will have purity or consistency requirements, or both, that are sufficiently strict to require the industrial mineral vendor to maintain an analytical laboratory capable of performing tests set forth by the glassmaker to ensure in-specification material.

A powerful marketing tool for any vendor is independent or joint research into the behavior of his industrial minerals in the glass. Forward-looking vendors should be expected to take part in glass research and raw material development, both to develop new products and to improve existing ones.

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Agglomeration Processes— Pelletizing and Sintering

Joseph J. Poveromo

This chapter focuses on industrial minerals, including fluxes, used in the processes that produce iron-bearing agglomerates (pellets and sinter) for ironmaking. The predominant ironmaking process is the blast furnace, which produces liquid pig iron (hot metal) for feeding to the steelmaking vessel—an oxygen converter called the basic oxygen furnace (BOF) in North America and the L-D converter elsewhere in the world. Another important steel production process is the electric arc furnace (EAF), which relies mainly on steel scrap as a feed material. For example, in the United States, nearly 50% of the steel production is from EAF operations. Because the scrap used in EAF operations may carry As, Cu, Ni, Cr, and other deleterious contaminants, EAF operators may require additions of “clean” iron units in the form of direct reduced iron (DRI). In scrap-deficient regions, DRI may be the principal feed material. DRI is produced by the solid-state reduction of iron ore, mainly pellets, most commonly in a shaft furnace. As a prelude to the discussion of agglomerating processes, an overview of steel production and ironmaking processes is presented. All units are metric unless otherwise noted.

IRON AND STEEL PRODUCTION PROCESSES

The blast furnace continues to be the primary method of producing hot metal in large-scale steel production. Many attempts have been

made to replace it with various other process options, including direct reduction and coke-free smelting reduction. Although these new technologies are being adopted in appropriate niches, the blast furnace process has met the challenge by being amenable to continuous improvement. The current status of the competitive direct reduction processes can be summarized by noting that several (e.g., Midrex and HyL) are well established whereas others are under development but not yet fully proven. After 40 years of effort, North American (excluding Mexican) DRI production is less than 2 Mtpy whereas worldwide DRI production is about 50 Mtpy. World hot metal production, however, is more than 600 Mtpy. Thus the blast furnace process produces more than 90% of the clean (virgin) iron units. Table 1 gives world iron and steel production data from the International Iron and Steel Institute (IISI).

Growth in steel production has been dramatic in recent years, led mainly by sharp growth in China; available data indicate that world pig-iron production increased to 650.3 Mt in 2003, with the growth in China from 169 to 202 Mt being the major contributor. Steel production, based on the blast furnace process (BF/BOF), will also grow in low-cost areas such as Brazil and India, whereas regions rich in natural gas resources, such as the Middle East and Venezuela, will see growth based on the integrated DRI/EAF steel production route.

Table 1. World iron and steel production data, Mt/year

Region	2002			2001		
	Pig Iron Production	Crude Steel Production	Pig Iron/ Crude Steel	BOF, %	EAF, %	Other Production, %
European Union (EU)	89.7	158.6	0.56	58.9	41.1	0.0
Other Europe	22.9	45.0	0.51	60.4	39.2	0.5
Commonwealth of Independent States (CIS)	77.9	99.9	0.78	55.4	12.5	32.1
North America	52.9	123.6	0.43	51.5	48.5	0.0
South America	33.4	40.9	0.82	63.9	34.9	1.3
Africa	7.1	15.7	0.45	48.5	51.5	0.0
Mideast	2.2	11.9	0.18	18.8	81.2	0.0
Asia	308.9	381.9	0.81	59.9	31.8	8.3
China	169.1	181.7	0.93	57.7	24.2	18.1
Oceania	6.7	8.3	0.81	83.4	16.6	0.0
Totals	601.7	884.9	0.68	57.7	35.0	7.3

Table 2. Typical pellet chemistry, %

Chemistry	Blast Furnace Pellets			
	Acid	Fluxed	Low SiO ₂ , Fluxed	DR-Grade Pellets
Fe	65.10	65.60	63.30	65.10
SiO ₂	5.20	4.50	3.75	2.50
Al ₂ O ₃	0.50	0.50	0.50	0.45
CaO/SiO ₂	0.12	0.13	0.98	0.90
CaO	0.60	0.60	3.68	2.25
MgO	0.25	0.25	1.30	1.50

Table 3. Development of iron ore production in the western world, 1960–1994

Iron Ore Type	1960	1975	1994
Pellet, %	4	21	34
Fine ores, %	48	49	46
Lump ores, %	48	30	20
Total production, Mtpy	340	580	617

Source: Poveromo 1999.

Table 4. Consumption of ore type by application in 2000

For Direct Reduction, Mtpy	
Fines	2.5
Lump	12.6
Pellets	52.5
For Blast Furnace/Sinter Plant, Mtpy	
Fines	687.0
Lump	121.0
Pellets	208.0
Total	1083.6

Source: Poveromo 1999.

IRON-BEARING RAW MATERIALS FOR IRONMAKING

Historically, the feedstock for the world's blast furnaces was naturally occurring lump ores. The depletion of deposits of higher quality lump ores in the 1950s forced the development of low-grade ores that required fine grinding for concentration. These fine, high-grade concentrates had to be agglomerated, most commonly as sinter or pellets, ahead of the blast furnace. These agglomerates, in turn, sharply improved blast furnace performance and led to a major shift in blast furnace burdening.

Iron Ore—Sintering Ore Fines

Historically, iron ore was sourced primarily from local or regional mines. Sometimes this ore was low grade when options were limited. In the last four decades, seaborne trade of iron ore has grown dramatically, aided by the construction of large vessels and thus reduced shipping costs. Now iron ore from higher-grade ore deposits in Australia, Africa, South America, Canada, India, Sweden, and other locations can be delivered economically worldwide. The ready availability of these high-grade ores, which are ideal sinter feed, allowed steel companies to gain the advantages that uniform sinter feed can provide to the blast furnace by reducing operating costs and improving the competitive position. For most of the world, the sintering process, based on coarse high-grade ore fines, is the primary means of producing ferrous raw material feed. High-

grade ore fines are characterized by high iron content (64% to 69%), moderate levels of acidic gangue (i.e., SiO₂ and Al₂O₃ are less than 6%), low levels of key impurities (e.g., Mn, S, P, and alkalis), and trace amounts of other elements.

Iron Ore—Pelletizing

In North America, depletion of higher-grade ore reserves promoted the development of low-grade “taconite” ores, which require very fine grinding for beneficiation. These fine concentrates were not amenable to conventional sintering and led to development of the pelletizing process. The decline in hot metal production in the 1980s, along with excess modern pellet plant capacity and environmental issues, caused a reduction in sintering capacity. The subsequent development of fluxed pellets and improvement of acid pellet properties have made pellets the prime feed material in North America and parts of Europe and a valuable supplementary feed material elsewhere. Table 2 shows typical pellet chemistry.

Iron Ore—Sintering

For blast furnace operations where sinter is the principal burden material (65% to 90%), imported or local sintering ores are the prime feed material, followed by waste oxides and then fluxes. With an average iron ore SiO₂ level of 5.0%, the CaO–SiO₂ ratio is set at about 1.5 to 2.5 to ensure good sinter physical and metallurgical properties and sufficient flux to minimize or eliminate the need to charge raw flux directly to the blast furnace. The flux must contain some MgO to ensure good sinter metallurgical properties and also a certain MgO level in the blast furnace slag. The blast furnace slag MgO target varies worldwide, however, according to different strategies for slag chemistry optimization. In any event, sinter typically has the following chemistry: 55% Fe (in the form of Fe₂O₃ at 71% and FeO at 7%); 5% SiO₂; 10% CaO; 2% MgO; 1% Al₂O₃; and 4% other. This composition implies considerable (>20%) addition of raw flux, mainly in the form of limestone and dolomite, given calcination losses of about 50%.

Iron-Bearing Raw Material Usage

Sinter is the primary iron-bearing raw material worldwide. Accurate production data for sinter are not compiled, but world sinter production can be safely estimated to be well over 600 Mtpy to support pig-iron production of more than 600 Mtpy. Worldwide pellet plant capacity is about 300 Mt, but this capacity is focused in three regions: the former Soviet Union (more than 70 Mt); North America (United States, 55 Mt; Canada, 27 Mt; and Mexico, 14 Mt); and Brazil (47 Mt). Significant production also comes from Sweden (16 Mt), Iran (13 Mt), India (about 10 Mt), and Venezuela (about 10 Mt). Pelletizing capacity is growing rapidly in China (by the time of publication, this total could reach or surpass 40 Mtpy). Individual pellet plants are also operated in Chile, Peru, Netherlands, Bahrain, Japan, and Turkey. Table 3 shows long-term trends by type of iron ore.

Table 3 shows how pellet use grew dramatically at the expense of lump ore. The fine ore percentage, mainly for sinter plant use, decreased only slightly; but given the dramatic overall increase in ore production, the absolute consumption of fine ores increased sharply. Iron ore production data are now compiled for the world; total world iron ore production exceeded 1,200 Mt in 2003 (Ericsson 2004). The breakdown among ore types is not known precisely, but it is believed that the lump ore proportion is somewhat lower and pellet and fine ore proportions are somewhat higher. Sinter and fluxed pellets contribute equally well to improved blast furnace production; the choice is based on ore availability and other local economic factors. Table 4 shows iron ore consumption in 2000, by reduction process and ore type.

These data indicate that ore demand for the blast furnace route dominates the iron ore trade, but pellets dominate demand for direct reduction ore.

World Iron Ore Market

World iron ore production exceeded 1,100 Mt in 2002, with six areas (Brazil, Australia, China, the Commonwealth of Independent States [CIS], India, and United States–Canada) accounting for 86% of total output. Brazil and Australia are the largest producers, with nearly a 40% combined share; the United States and Canada together produce about 10%; China is the world's largest iron ore miner at about 230 Mt, but much of this is low-grade ore. The CIS countries of Russia and Ukraine are the third largest iron ore producer at 150 Mt. World trade in iron ore reached 500 Mt in 2002. China and Japan dominate world iron ore importing, with Asia and Europe accounting for 50% and 40% of imports, respectively.

Exports as a share of world iron ore output have been on a long-term upward trend (from 35% in 1980 to 50% in 2000), reflecting the growth and importance of ore-dependent Asia. Brazil and Australia dominate the world iron ore export market, accounting for more than 70% of seaborne exports. Other important seaborne exporters are India, South Africa, Sweden, Canada, Venezuela, and Mauritania. Russia and Ukraine export major tonnages by rail to neighboring countries.

North American Iron Ore Supply

Pellets make up 90% of North American iron ore supply, whereas sinter (10%) plays a lesser role than elsewhere in the world, largely because of environmental considerations. One pellet plant is dedicated to supplying its equity owner, Mittal Steel North America, and all the other pellet plants supply both merchant customers and equity owners (in parentheses): Minntac and Keetac (USS); Hibbing (Mittal Steel, Stelco); QCM (Dofasco); Tilden (Stelco); Empire (Ispat); and Wabush (Stelco, Dofasco). Cleveland-Cliffs dominates pellet merchant supply, selling to Algoma, Mittal Steel, WCI, Severstal NA, and other steel companies from Northshore, Hibbing, United, Empire, Tilden, and Wabush. The three Canadian producers—IOC, QCM, and Wabush—also export significant tonnage worldwide. Imports, mainly from Brazil, are less than 10% of North American supply.

AGGLOMERATION PROCESSES

Need for Agglomerates and Desired Agglomerate Quality

The blast furnace is a countercurrent gas–solid reactor in which the solid charge materials move downward while the hot reducing gases flow upward. The best possible contact between the solids and the reducing gas is obtained with a permeable burden, which permits not only a high rate of gas flow but also a uniform gas flow, with a minimum of channeling of the gas. The primary purpose of agglomeration is to improve burden permeability and gas–solid contact, and thereby reduce blast furnace coke rates and increase the rate of reduction. A secondary consideration is to reduce the amount of fine material blown out of the blast furnace into the gas recovery system.

The leading direct reduction processes such as Midrex and HyL also are shaft furnaces that rely on countercurrent gas–solid contact, so the principles of burden sizing are similar but even more important in the blast furnace, because the ferrous materials are the only solids in these furnaces.

A good agglomerate for blast furnace use should contain at least 60% iron, a minimum of undesirable constituents, a minimum of material less than 6 mm (1/4 in.) in size, and a minimum of material larger than 25 mm (1 in.). The agglomerate should be strong

enough to withstand degradation during stockpiling, handling, and transportation so as to arrive at the furnace skip containing a minimum of 85% to 95% of +6 mm (+1/4 in.) material. In addition, the agglomerate must be able to withstand the high temperature and degradation forces within the furnace without decrepitation. The agglomerate also should be able to be reduced at a satisfactorily high rate in the blast furnace. In the last several decades, different standards have developed for the two leading agglomerate forms, sinter and pellets. Table 5 is a summary of desirable sinter and pellet properties; a more comprehensive discussion is available in Kortmann, Lungen, and Ritz (1992).

Choice of Agglomerating Process

Four types of agglomerating processes have been developed: sintering, pelletizing, briquetting, and nodulizing. Sintering and pelletizing are the processes of major importance. Careful evaluation should be made of the processes, the material to be agglomerated, and the product desired before arriving at a final decision on a commercial installation. Quite often the origin of the material to be agglomerated, together with material handling and transportation considerations, will dictate which process is chosen. Fine concentrates such as those made from magnetite taconite are not easily shipped because of dusting and freezing problems, but once made into pellets, are easy to handle and transport with minimal degradation. Consequently if there is a considerable distance between the mine and the blast furnace, it is preferable to locate pellet plants near the mine site. Materials that do not have the particle-size distribution and characteristics required for pelletizing can be agglomerated by sintering. Besides natural ore fines, typical sinter feed materials include fines generated during ore transport, steelmaking slag fines, flue dust, mill scale, and concentrates that are too coarse for pelletizing. Sinter plants tend to be located near blast furnaces because sinter degrades badly during shipment and because the steelmaking facilities are the point of origin of many of the materials that can be agglomerated. For blast furnace operations relying mainly on sinter, the sinter plants are larger and fed mainly with natural ore fines. For blast furnace operations relying primarily on pellets and lump ore, the sinter plants are smaller and more reliant on in-plant recycled materials.

Energy cost and the uncertainty of fuels availability are important factors in all processes and have been the incentives to reduce fuel consumption and to use substitute fuels. Better recycling of hot gases for heat recuperation has lowered fuel costs. Additionally, converting pelletizing operations from oil and gas to coal firing has resulted in a more reliable fuel source.

The Sintering Process

Sintering has been referred to as the art of burning a fuel mixed with ore under controlled conditions. The flexibility of the process enables the converting of a variety of materials into a clinker-like aggregate that is well suited for use in the blast furnace. These include natural fine ores and ore fines from screening operations, flue dust, ore concentrates, and other iron-bearing materials of small particle size.

The continuous sintering process shown schematically in Figure 1 is carried out on a traveling grate that conveys a bed of ore fines or other finely divided iron-bearing material, mixed intimately with approximately 5% of a finely divided fuel such as coke breeze or anthracite. Near the head or feed end of the grate, gas burners ignite the bed surface and, as the mixture moves along, downdraft combustion burning the fuel pulls air down through the mixture. As the grates (or pallets) move continuously over the wind boxes toward the discharge end of the strand, the combustion

Table 5. Desirable sinter and pellet properties

Sinter		Blast Furnace Pellets	
Chemistry		Physical Properties	
FeO	5.0%–6.0%	Grain structure	
Mn	≈0.2% (as low as possible)	>16 mm	max 5%
P	≈0.04% (as low as possible)	8–16 mm	Minimum (min) 85%
SiO ₂	5.0%–5.5%	<6.3 mm	max 5%
Al ₂ O ₃	1.0%–1.3%	Cold compression strength	
TiO ₂	– (as low as possible)	Pellets 10–12.5 mm (ISO 4700)	
Na ₂ O + K ₂ O	<0.08% (as low as possible)	Average	min 2,500 N
CaO	8%–10%	<2,000 N	max 10%
MgO	1.4%–2.0%	<1,500 N	max 5%
CaO/SiO ₂	>1.8	Tumbler strength (ISO 3271)	
Physical Properties		>6.3 mm	min 95%
ISO strength (ISO 3271)		<0.5 mm	max 5%
>6.3 mm	70%–80%	Metallurgical Properties	
Grain structure		Low-temperature disintegration, dynamic test (SEP 1771/82)	
<5 mm or <6 mm	Maximum (max) 5%	>6.3 mm	min 80%
<10 mm	max 30%	<0.5 mm	max 15%
>50 mm	max 10%	Reduction Properties under Load (ISO 7992)	
Metallurgical Properties		80% degree of reduction	max 15 mm WG
Disintegration in the static test		Reducibility R40 value (ISO 4695)	
RDI		min 0.8 %/min	
<2.8 mm	max 20%–30%	Swelling (ISO DP 4698)	
<3.15 mm	max 35%	max 20%	
ISO 4696			
<3.15 mm	max 30%–33%		
Reducibility (ISO 4695)			
1.4%–1.6%/minute			

Adapted from Kortmann, Lungen, and Ritz 1992.

front in the bed moves progressively downward. This creates sufficient heat between 1,300°C and 1,480°C (2,370°F and 2,700°F) to sinter the fine iron-rich particles together into porous clinkers. The location along the traveling grate where the combustion front touches the bottom of the bed is called the burnthrough point. By the time the discharge end of the machine is reached, sintering will have taken place throughout the depth of the bed.

Although simple in principle, sintering plants require important design and operation criteria to attain optimum performance, and intimate mixing of the feed materials is one of the most important factors. Sintering ores, steel plant waste oxides, fluxes, and solid fuels are premixed in a bedding and blending operation in most modern sinter plants. This blended feed is supplemented by small trim amounts of flux and solid fuel. Water is then added to the total feed mixture in a mixing device such as a balling drum, or a disc or pug mill. These mixers produce small, rice-size nodules that significantly improve the permeability of the sinter bed. In many plants, burnt lime added to the feed mixture promotes granulation, especially to process ultrafine materials. Improved permeability, in turn, results in more rapid and uniform sintering. Desirable mixer retention times vary from about 1 minute for sticky hematite ores to 4 minutes for ores that are more difficult to ball.

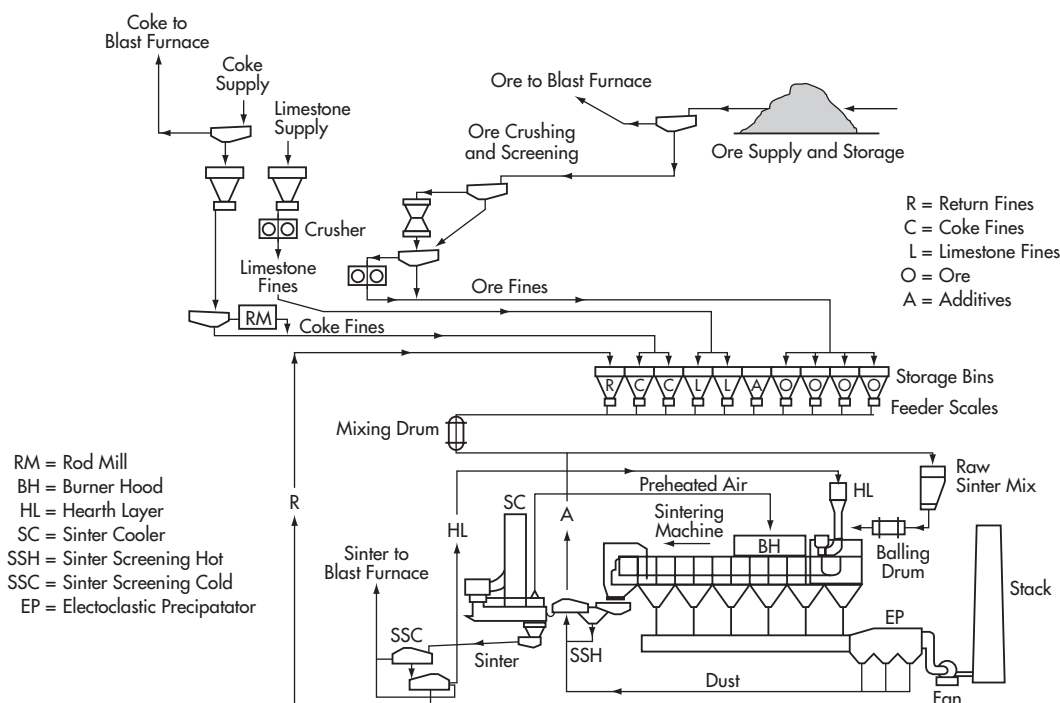
Depending on the characteristics of the ore materials and the sintering conditions, daily average production rates of 22.4 to 42.9 t/m²/day (2.3 to 4.4 st/ft²/day) are expected, and individual daily rates in excess of 48.8 t/m²/day (5 st/ft²/day) have been achieved. The area refers to the dimensions of the grate.

Cooling the sinter below 150°C (302°F) is an important part of the operation, which allows it to be handled on conveyor belts. Sinter coolers such as the rotary type are typically used; it is best to avoid a water quench because it adversely affects sinter properties. The exhaust air from these coolers is normally too cool to permit the economical recovery of heat, although such systems have been installed in countries with high energy costs, such as in Japan.

Benefits of Fluxed Sinter to Blast Furnace Performance

Sinter is preferred to lump ore or acid pellets as blast furnace material. Improvements have been obtained (1) by incorporating the blast furnace flux into the sinter rather than charging it separately to the top of the furnace, as was formerly done; (2) by using sized sinter; and (3) by virtue of improved high-temperature properties. The available data on the use of fluxed sinter, sometimes called self-fluxing sinter, indicate that for each 100 kg (200 lb/st) of limestone per ton of hot metal removed from the blast furnace burden and charged into the sinter plant to make a fluxed sinter, approximately 10 kg (20 lb/st) of metallurgical coke per ton of hot metal are saved. The savings in coke result primarily from calcining limestone on the sintering grate rather than in the blast furnace. Limestone in the form of fluxing fines for producing sinter is made by crushing and screening methods that result in a product meeting size specifications.

Using sized sinter is desirable because it further increases iron production rates in the blast furnace. Plant tests have demonstrated significant increases in iron production rate as a result of screening out small-sized material in sinter before it is charged to the furnace.



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Figure 1. Schematic flow diagram of continuous iron ore sintering process

Other tests have shown that sized sinter, which contains 85% to 90% of 25 mm \times 6 mm (1 in. \times 1/4 in.) material compared with 60% in unsized sinter, has a much higher permeability than unsized sinter and performs as well as pellets of comparable size. It also appears that crushing to -25 mm (-1 in.) at the sinter plant yields a more stable sinter because the smaller size fractions are more resistant to degradation.

In the last several decades, researchers have shown that fluxed sinter (and also fluxed pellets) has superior high-temperature properties in the blast furnace compared to lump ore and acid pellets. These improvements include higher softening and melting temperatures and higher levels of reducibility.

The above description of sintering is only an introduction to the topic. Earlier references (before 1980) are useful for North American and former Eastern Bloc sinter plant operations, most of which were built in the 1950s and 1960s. Some more recent references describe advances in sintering relevant to large, modern sinter plant operations, which are predominant in Europe and the Asia-Pacific area.

It has been demonstrated in North America and in the Scandinavian countries that blast furnace performances with fluxed, sized sinter also can be achieved with pellets that are properly sized and fluxed with either limestone/dolomite mixtures or olivine.

Pelletizing—General Considerations

Pelletizing differs from sintering in that a green unbaked pellet or ball is formed and then hardened by heating. Experimental work on the concentration and agglomeration of low-grade iron ores, started many years ago by E.W. Davis and his associates at the University of Minnesota, showed that it was possible to ball or pelletize fine magnetite concentrate in a balling drum, and that if the balls were fired at sufficiently high temperature (usually below the point of

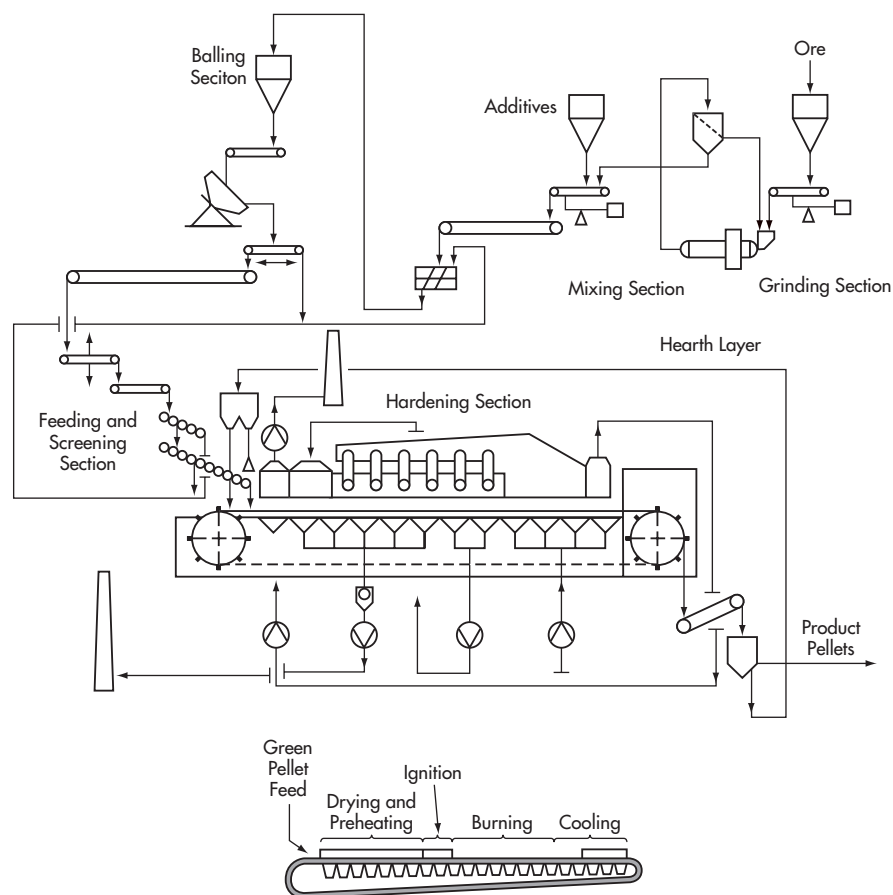
incipient fusion), a hard, indurated pellet could be made that was well adapted for use in the blast furnace. Consequently, despite the unquestioned benefits of sinter on blast furnace performance, intense interest in the pelletizing process had developed because of the outstanding performance achieved by steel producers in extended operations with pellets as the principal iron-bearing material in the blast furnace burden. In North America this interest was promoted further because of the absence of coarse sintering ores coupled with the opportunity to effectively use abundant reserves of low-grade taconite ore.

In general, the pelletizing process is desirable for agglomeration of finely divided concentrates because they are normally of a size that can be formed into a green ball with little difficulty. Concentrates and high-grade ores not suitable for pelletizing are in some cases ground to the required size when pellets are desired as the final product.

Pelletizing Feed Preparation

The balling drum and the disc pelletizer are the most widely used devices for forming green balls. Compared with the balling drum, the disc has the advantages of lighter weight and greater possibility for adjustment. Its inherent design averages out the effect of instantaneous fluctuations in the feed, whereas the drum cannot. Also, the classifying action of the disc promotes discharge of balls of more uniform size. The capacity of the discs is low, however, and discs generally require closer control than drums. Best control of ball size is achieved when the balling device is in closed circuit with a screen to remove and recycle the undersize material.

Binders such as bentonite clay or hydrated lime are generally used to raise the wet strength of green balls to more acceptable levels for handling. Bentonite consumption at 6.3 to 10 kg/t of feed is a significant cost element and adds to the silica content of



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Figure 2. Schematic diagram of the traveling grate system for iron ore pelletizing

the final product. Considerable effort has been directed at reducing bentonite usage and developing cheaper substitutes. The ballability and strength of green balls are influenced by the additives and the moisture content and particle-size distribution of the concentrates. Optimum moisture content for good balling is usually in the 9% to 12% range. It appears that balling characteristics are relatively independent of the chemical composition of a concentrate but strongly affected by its physical properties. For example, specular hematite is more difficult to ball than are magnetite concentrates because of the plate-like structure of the former. In any case, satisfactory pellet formation usually is achieved by regrinding to about 80% to 90% of $-43\ \mu\text{m}$ (-325 mesh). Normally any material considered for pelletizing should contain at least 70% of $-43\ \mu\text{m}$ (-325 mesh) and have a specific surface area (Blaine) $>1,200\ \text{cm}^2/\text{g}$ for proper balling characteristics.

Both the drop and compressive strengths of green pellets are important, but compression strength is most important because dried pellets are not required to withstand much handling. The strength of fired pellets is important in minimizing degradation during handling and shipping, and in the blast furnace. Strong bonding in pellets is believed to be caused by grain growth from the accompanying oxidation of magnetite to hematite or recrystallization of hematite. Although slag bonding may promote more rapid strengthening at slightly lower firing temperatures, pellet strength is normally decreased, especially its resistance to thermal shock. Fired pellet

strength is determined most commonly by compression and tumble tests. Compressive strengths of individual pellets depend on the mineralogical composition and physical properties of the concentrate, the additives used, the balling method, pellet size, firing technique, and temperature. The compressive strengths of commercially acceptable pellets are usually between 200 kg and 350 kg for pellets between $-13\ \text{mm}$ and $+9\ \text{mm}$. In the tumbler test, 11.4 kg (25 lb) of $+6\ \text{mm}$ pellets are tumbled at 25 rpm for 8 minutes in a drum tumbler (ISO 3271: 1995) and then screened. A satisfactory commercial pellet should contain no more than about 5% of $-0.6\ \text{mm}$ (-28 mesh) fines, and 94% or more of $+6\ \text{mm}$ size, after tumbler testing. A minimum of broken pellet fines between 6 mm and 0.6 mm is also desirable. Other important properties of fired pellets for blast furnace feed are reducibility, porosity, and bulk density.

Pellet Plant Flowsheet

The flowsheet of a pelletizing process is similar in many respects to the sintering process, particularly in the materials handling area. Usually the associated mining, concentrating, and grinding installations are operated as a feed preparation section of the pellet plant. The three most important pelletizing systems are the traveling grate (Figure 2), the grate-kiln (Figure 3), and the shaft furnace. Figure 2 shows the overall layout of the pellet plant for the traveling grate system; it would be the same for the other indurating systems. Each system has been used commercially to make quality pellets, and so

capital and operating costs are usually the deciding factors involved in choosing one or the other. Fuel requirements for these pelletizing systems vary from about 500,000 to 1 MkJ/t of pellets, depending on the feed material. Oxidizing magnetite to hematite during pelletizing will produce a significant proportion (about 400,000 kJ/t) of the heat requirement in all of the systems. For pelletizing hematites, using coke breeze (or some carbon source) in the pellet feed mixture has become a common practice, producing the additional endothermic energy normally produced by magnetite oxidation. Pelletizing processes are being improved constantly, and sources in the bibliography give further details on their technology and development. Self-fluxing pellets is an example of an innovation that has been accepted on a commercial scale and has led to major advances in blast furnace performance.

Traveling Grate

The traveling grate system for producing pellets, illustrated in Figure 2, is essentially a modification of the sintering process. The green balls are fed onto the grate continuously to give a bed depth of about 300 to 400 mm (12 to 16 in.) and are dried in the first few wind boxes by updraft air recovered from the firing zone; this is followed by downdraft drying using recovered air from the cooler. This arrangement of hot air flow limits pellet damage from condensation of moisture in the bed. Following drying, downdraft air from the cooling zone preheats the pellets. Firing is done downdraft in the combustion zone by burning fuel oil or natural gas with hot air from the cooling zone. The cooling zone follows the combustion zone and uses updraft fresh air.

Fuel consumption in the traveling grate system is about 350,000 to 600,000 kJ/t of pellets produced from magnetite and up to 1 MkJ/t from pelletizing hematite. The system offers good temperature control in the firing zone. Pellet consistency throughout the bed is achieved by recirculating some fired pellets to form hearth and side layers on the grate. The largest grate machines are 4 m (13 ft) wide and can produce more than 3 Mt of pellets per year. Circular grate machines also have been designed, and one such machine is in operation.

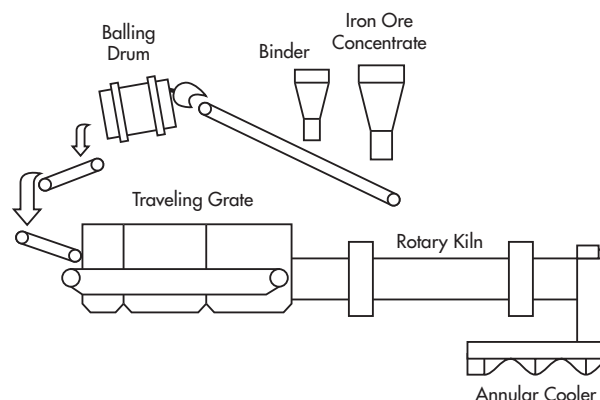
Grate-Kiln System

The grate-kiln system, depicted in Figure 3, consists of a traveling grate for drying and preheating the pellets to about 1,040°C (1,902°F), a rotary kiln for uniformly heating the throughput to the final induration temperature of 1,315°C (2,400°F), and an annular cooler for cooling the product and recuperating heat. A central oil, gas, coal, or waste wood burner at the discharge end of the kiln supplies heat for firing. Hot gases produced in the kiln are used for downdraft preheating of the pellets. Hot air from the cooler supports combustion in the kiln; it also is recovered to the traveling grate for drying and tempering preheat.

The grate-kiln system offers excellent temperature control in all stages of the process and produces a consistently uniform product. Fuel consumption is 300,000 to 400,000 kJ/t of standard pellets produced when using magnetite ore and up to 700,000 kJ/t of standard pellets produced when the feed is hematite. Fuel consumption increases by 250,000 kJ/t when producing fluxed pellets. Power consumption, from balling to pellet loadout, is 23 kW-hr/t. Grate-kiln systems can be designed for production tonnages up to 6 Mtpy per line.

Briquetting

Briquetting is an old art of agglomerating or forming small or large lumps of regular shape from a wide variety of materials, including wood, coal, lignite, chars, cokes, ores, and flue dust. Various designs



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Figure 3. Schematic diagram of the grate-kiln system for iron ore pelletizing

of punch and roll presses are or have been used. Briquetting of cold or unheated material had not been successful for producing satisfactory agglomerates for the blast furnace until recently. Briquettes usually are formed using a binder and do not possess the strength that high-temperature heating gives pellets and sinter. The shutdown of sinter plants in North America and Scandinavia has led to improvements in briquetting technology by recycling waste oxides. Such briquettes can be used at 3% to 10% of the furnace burden without difficulty; the poor high-temperature properties preclude higher consumption levels.

Consumption of Fluxes in Sintering

The level of flux consumption in sintering can be estimated from data from sinter plant operations in Asia, Europe, and North America. The fluxes used are limestone, dolomite, olivine, serpentine, and burnt lime.

Limestone

Limestone is composed primarily of the mineral calcite (CaCO_3) and is the most widely used flux. Its calcium combines with iron to form calcium ferrites that bond sinter particles together and give the sinter the physical strength and high-temperature properties that are desirable in blast furnace raw material. Limestone consumption rates average between 100 and 125 kg/t of sinter. With sinter production exceeding 600 Mtpy, limestone consumption would exceed 60 Mtpy accordingly and could approach 90 Mtpy worldwide. Limestone deposits are common, so for any given operation it is sourced locally or regionally. The chemical and physical specifications for limestone (and dolomite) are listed in the chapter on metallurgical fluxes in this volume. For limestone, the key physical attribute in sintering is a size range of 1 to 3 mm. Particles that are too coarse will not melt and be assimilated properly into the sintered matrix, whereas ultrafine particles may be carried through to the sinter waste gas system.

Olivine (Serpentine, Dunite)

Olivine (solid solution series composition: Mg_2SiO_4 and Fe_2SiO_4) fluxes are used selectively worldwide. The objective is to achieve the desired MgO level in blast furnace slag, and the SiO_2 helps increase the final sinter SiO_2 target level to about 5% or higher. The

sinter SiO_2 by itself is helpful only to the extent that it allows an increase in total CaO input at a given target CaO/ SiO_2 level. The CaO helps to “hold the sinter together,” and the CaO/ SiO_2 ratio must be high enough to flux the iron ore gangue and coke ash compounds in the blast furnace raw materials. The upper limit of the CaO/ SiO_2 ratio in sinter (and therefore blast furnace slag) is limited by slag viscosity and slag alkali removal considerations. Typical sinter CaO/ SiO_2 levels are between 1.5 and 2.2 depending on the overall sinter percentage. The SiO_2 input is required for European and Asian sinter plants that use large amounts of iron ore from Brazil and Sweden, which have low SiO_2 levels. The prime Australian ores also have SiO_2 levels well below 5%.

Olivine and serpentine are more desirable sources of MgO than dolomite because olivine does not require calcination; serpentine, however, does require the removal of water. These materials are viewed as enhancements to the sintering process, whereas dolomite is regarded as detrimental and necessary only to meet blast furnace slag chemistry requirements. Both MgO sources improve the high-temperature properties of sinter.

Olivine is a magnesium-iron silicate with an average composition of 93% forsterite (Mg_2SiO_4) and 7% fayalite (Fe_2SiO_4). A typical chemical composition follows:

Oxide	%	Oxide	%
MgO	49.0	Al_2O_3	0.5
SiO_2	41.0	NiO	0.3
FeO	7.0	MnO	0.1
Cr_2O_3	0.3	CaO	0.05

Olivine composition can range from 100% Mg_2SiO_4 to 100% Fe_2SiO_4 because it is a solid solution series. The melting temperature of fayalite is low, so the Mg:Fe ratio in olivine is one of the critical specifications in assessing the suitability of different olivine compositions for use as fluxing agents. Additional details are given in the chapter on olivine in this volume.

Typical addition rates for olivine are 25 to 40 kg/t in European sinter mixes. Use of olivine to replace dolomite began in 1975 in Europe and is now universally accepted. European consumption is estimated at 3 Mtpy and is sourced mainly from Norway.

Dunite is a rock composed primarily of olivine, whereas serpentine is a hydrated magnesium-iron silicate. The Fe:Mg ratio varies from one deposit to the next. Generally, the chemical specifications apply as they do for olivine.

The choice of olivine, dunite, or serpentine depends on availability and logistics. Olivine is readily available in the Atlantic basin, mainly from Norway; dunite and serpentine are more readily available in the Asia-Pacific regions.

Dolomite

Dolomite is used mainly in North American sinter mixes to achieve the desired MgO level in the blast furnace slag. Worldwide, some dolomite is used in Asia and Europe. In North America, only one sinter plant operation, which uses significant amounts of low-silica Brazilian ore (Operation A in Table 6), uses olivine. The remaining operations achieve adequate SiO_2 levels from recycled materials such as steelmaking slag, so any additional SiO_2 from olivine would be detrimental. Therefore dolomite is the convenient choice for addition of MgO as well as for CaO. The chemical and physical specifications for dolomite are given in the chapter on metallurgical fluxes in this volume.

Burnt Lime

Burnt lime is introduced as a binder in the sinter plant mixing drum to promote the agglomeration of ultrafine particles (0.1–1.0 mm).

The objective of using the mixing drum is to add the proper amount of water and binder (burnt lime) to promote agglomeration so that the particles will exceed 1 mm in diameter when they exit the mixing drum. Such particles enhance the permeability of the mix, increasing gas flow and thus accelerating sintering. Using burnt lime is particularly effective when the sinter mix contains significant levels of finer sized iron ore concentrates and other fine ores. Burnt lime is used extensively in European sinter plants and to a lesser extent in Asian sinter plants, where the predominant feed materials are coarser Australian iron ores. Burnt lime is used in only one plant in the United States, which is shown as Operation A in Table 6.

Typical consumption rates for burnt lime are 5 to 15 kg/t of sinter. A rule of thumb is that a 1% addition (10 to 15 kg/t) increases sinter production by as much as 10%; the incremental benefit at higher addition rates, however, is much lower. Because burnt lime is more costly than other flux materials, most sinter plant operators target burnt lime addition rates at about the 1% level.

Burnt lime is identical to the high-calcium lime used in steel-making in the BOF, as described in the chapters on fluxes in this volume; the chapter on lime gives additional information.

Other Industrial Mineral Applications in Sintering

The only other known application of industrial minerals in sintering is spraying a solution of CaCl_2 onto the hot sinter as it exits the sinter strand. The objective is to increase the reduction-degradation index (RDI) of the sinter. This metallurgical property of sinter is important in avoiding excessive generation of fines in the upper stack of the blast furnace during the initial reduction of hematite to magnetite. Only a few sinter operations worldwide use this technique.

Consumption of Binders, Fluxes, and Coatings in Pelletizing

Additives to the iron ore mixture in pelletizing include binders and fluxes. The fluxes mainly modify the chemical composition of the slag-forming constituents of pellets; some of these additives such as lime and magnesium lime compounds, and siliceous compounds such as quartz and olivine, also may have binding properties. Some recycled materials called “reverts” also may have binding properties, but the use of such steel plant oxides is limited.

Binders

Binders help form pellets and maintain their strength before and after firing. The type of binder used depends on the type of ore to be pelletized. Finely ground natural ores with clay-like textures are readily agglomerated and require little or no binder addition. Such ores typically have significant Al_2O_3 levels that provide this clay-like behavior; these ores are found in Venezuela, Australia, India, and, to a lesser extent, Brazil. Iron ore concentrates produced from the beneficiation of taconite ores in the United States and specular hematite ores in Canada are not readily self-agglomerating and so require binders. The binders aid agglomeration and impart sufficient strength to unfired green pellets.

Table 7 lists binder use for selected pellet plants in North America and in world plants, i.e., those in South America, Europe, and the Asia-Pacific regions. Bentonite use is predominant in North American plants, but its use is also significant in some pellet plants overseas. One North American plant has been able to replace bentonite with an organic binder. Other materials used as binders are hydrated lime and caustic soda. Many other materials such as peat moss, starch, bitumen, and others have been proposed as binders, but only three have found widespread use: bentonite, hydrated lime, and organic binders.

Table 6. Typical sinter plant data

Company*	Europe							United States		Asia
	A	B	C	D	E	F	G	A	B	A
Sinter area, m ²	444	400	180	400	525	520	336	352	125	420
Production, 1,000 Mt	6,050	4,750	1,830	3,300	5,700	6,650	3,725	3,190	1,037	4,950
Productivity, t/m ² /day	40	35	32	26	34	37	34	27	23	36
Raw mix, kg/t										
Concentrates	101	164	323	144	126	160	190	125	140	43
Hematite ore	739	656	394	656	504	640	570	661	22	689
Magnetite ore	0	0	0	60	122	50	0	0	8	22
Dust and sludges	15	7	40	0	30	10	20	4	15	19
Other reverts, >60% Fe	25	35	40	0	20	10	40	91	283	164
Other reverts, <60% Fe	20	10	70	40	30	20	0	45	434	5
Limestone	135	120	125	160	150	130	140	109	95	167
Dolomite	0	0	0	0	0	0	0	39	0	18
Burnt lime	15	15	7	0	5	15	0	7	0	3
Olivine	25	35	20	25	25	25	40	40	0	0
Serpentine	0	0	0	0	0	0	0	0	0	14
Total fresh feed, kg/t	1,075	1,042	1,019	1,085	1,012	1,060	1,003	1,120	1,120	1,235
Total return fines, kg/t	430	480	350	490	365	420	370	451	280	254
Total mix, kg/t	1,505	1,522	1,369	1,575	1,377	1,480	1,373	1,571	1,400	1,490
Solid fuels, breeze, etc., kg/t	50	53	55	50	51	45	45	54	15	55
Operating data										
Bed depth (mix), mm	530	550	380	440	490	605	590	508	432	569
Moisture, %	6	5	5	6	5	6	6	6	5	6
Sintering time, min	21	22	22	29	24	na†	25	27	na	na
Product chemistry, %										
Fe	57.9	58.1	58.9	58.2	57.1	57.7	54.5	56.3	49.6	55.7
Fe ⁺⁺	5.1	7.9	4.6	4.4	6.2	4.7	5.1	6.4	0.0	4.8
SiO ₂	5.1	5.4	5.0	5.6	5.6	5.3	6.4	5.1	7.1	5.3
CaO	9.7	8.7	8.8	8.5	10.1	9.4	10.8	9.3	15.3	11.5
CaO/SiO ₂	1.9	1.6	1.8	1.5	1.8	1.6	1.7	1.8	2.0	2.2
MgO	1.7	2.1	1.2	1.4	1.7	1.6	2.3	3.1	3.3	1.3
Al ₂ O ₃	1.0	1.2	1.1	1.4	1.2	1.2	1.4	1.2	2.1	1.8

* Company names withheld to avoid disclosing proprietary data.

† na = not available.

Bentonite

Bentonite is the binder of choice in North America and is extensively used worldwide as well. Consumption rates fall in a narrow band of 8 to 10 kg/t, except where other binders supplement bentonite. The total consumption in North America would be just above 500,000 t, with the U.S. pellet producers supplied mainly from Wyoming and the Canadian pellet producers supplied mainly from the Greek island of Milos and also from India. Bentonite is described in more detail in the chapter on bentonite clays: in this volume. Bentonites used in pelletizing are the active sodium type from Wyoming and the sodium exchanged calcium type from Greece. The latter type is prepared by ion exchange of Ca⁺⁺ for Na⁺ by simply mixing it with soda ash. With both types, the bentonite expands with addition of water and promotes migration of water into iron ore particles; this in turn promotes agglomeration during the balling step. As the green balls are being indurated, bentonite promotes the formation of a slag bonding phase; this ultimately is responsible for the high strength of the fired pellet.

Bentonite is a rock composed primarily of clay minerals of the smectite group (including montmorillonite), which has the capacity to adsorb large volumes of water and expand to several times its original volume. This swelling property and the high thixotropic behavior are the most important characteristics for the bonding capacity of bentonite. The swelling capacity is defined by the Enslin value:

$$E_w = (V \times 100)/P$$

where

E_w = Enslin value, in %

V = absorbed water quantity, in cm³

P = bentonite quantity, in g

The chemical composition of various bentonites includes the following ranges of major components: SiO₂ (43.0% to 72.0%); Al₂O₃ (3.0% to 20.0%); Fe (0.67% to 14.0%); CaO (1.0% to 1.8%); MgO (2.0% to 3.5%); Na₂O (0.04% to 3.0%); K₂O (0.1% to 1.7%); and loss on ignition (LOI; 5.0% to 11.0%). The specific surface

Table 7. Binder use in pellet plants,* kg/t†

	North American Plants									
	A	B	C	D	E	F	G	GG	H	I
Bentonite	5.8		10.0	8.5	10.0	8.8	8.6	7.6	8.5	6.2
Organic		0.41		0.07						
Other	3.6 (hydrated lime)									0.2 (caustic soda)
	World Plants									
	A	B	C	D	E	F	G	H	I	J
Bentonite	5.1–5.5		8.4	5.0	8.5		10.0	8.0		5.0‡
Organic									0.024	
Other						Hydrated lime				0.400§

* Company names withheld to avoid disclosing proprietary data.

† Blank cells indicate a value of zero.

‡ Blast furnace.

§ Direct reduction.

area ranges from 3,000 to 8,000 cm²/g, whereas Enslin values range from 200% to 900%.

Bentonite contains alkalis such as Na₂O and K₂O, which are undesirable in the blast furnace, and SiO₂ and Al₂O₃, which are expensive to remove in the electric furnace (for direct reduction [DR]-grade pellets). Accordingly, some of the efforts to reduce bentonite consumption or to find substitutes for bentonite are driven by the desire to reduce the input of these undesirable elements into ironmaking and steelmaking furnaces.

Hydrated Lime

Hydrated lime (Ca(OH)₂) can be used with ores that already have some propensity for self-agglomeration. It is produced from limestone and is usually sourced locally; it is also less expensive than bentonite. Hydrated lime is discussed in the chapter on lime in this volume. Briefly, CaO is obtained by calcining limestone at temperatures >900°C (1,652°F). Calcium hydrate is produced from CaO by slaking with water. The oxide is converted to hydroxide in quenching units, and is then pulverized. Hydrated lime is transported in closed containers.

Hydrated lime acts as both a binder and a basic additive. During pellet induration, the basic additives react first with the “acid” gangue constituents to form a neutral or basic matrix between the iron oxide grains. Accordingly, hydrated lime has some advantage over bentonite, which adds acidic gangue to the pellet mix.

During the mixing process, hydrated lime greatly increases the specific surface area of the iron ore mixture. This in turn contributes to increased wet green ball and dried fired-pellet strength, even with more coarsely ground ores.

This substance, however, is less capable than bentonite of controlling water during pelletization and does not contribute to the cohesive/adhesive forces required to form and maintain green pellet integrity.

Organic Binders

Organic binders have been under development for some time and continue to be investigated. They are used both as the sole binder additive and in conjunction with others. These binders immobilize large amounts of water during the pelletization process and then release this water gradually during the drying process. They offer some key advantages relative to bentonite such as reduction of acidic gangue input and increased porosity, which can contribute to increased pellet reducibility and improvements in other metallurgical properties. The increased porosity results from burning off the organic binder during the indurating process.

The increase in porosity also poses challenges in maintaining fired-pellet strength; this has been one of the major roadblocks to more widespread use of organic binders. Fired pellet strength can be maintained with skillful modification of green-balling and indurating conditions, and also by using other additives such as limestone.

The two principal types of organic binders are one based on cellulose and the other based on a polymer. Both are noncontaminating to the iron ore pellets and contain no elements (such as sulfur, phosphorus, and alkalis) that are harmful in ironmaking and steelmaking. These binders produce carbon dioxide and water vapor when burned.

Organic binders are shipped as fine powders of <200 mesh. They are added directly in front of the balling step. Typical addition rates are 0.3 to 0.6 kg/t (0.03% to 0.06%). Such rates are about 10% of a typical bentonite rate, but the costs of these manufactured specialty chemicals are usually 10 times greater than bentonite.

Accordingly, the major incentives for using organic binders are focused on their benefits in ironmaking and steelmaking. In direct reduction ironmaking, the advantages are mainly realized in the subsequent electric furnace steelmaking step, where every 1.0% reduction in pellet SiO₂ content can reduce liquid steel costs from \$3.00 to \$5.00 per ton of DR pellet. In the blast furnace, an increase in pellet reducibility of 0.1% in the ISO R40 test (range of reducibility: 0.5 to 1.3) can decrease the coke rate by 5 kg/t and therefore reduce hot metal cost by \$0.50/t of hot metal or nearly \$0.75/t of pellets for an all-pellet burden.

Fluxes: Flux Additions to Blast Furnace Grade Pellets

The principal fluxes used in pelletizing are limestone, dolomite, and olivine. The other major additive used in pelletizing is coal, particularly for hematite pellets. Table 8 gives typical consumption levels. Fluxes can be broadly divided into three major categories: dolomitic-limestone, limestone, and olivine.

Dolomitic-Limestone Fluxed Pellets

Dolomitic-limestone fluxed pellets predominate in North America. Commercial pellet production began in North America in the 1950s with production of acid pellets (SiO₂ = 5% to 6%) with the sum of CaO and MgO <1.0%. Such pellets provided blast furnace performance that was superior to the use of lump ore but inferior compared to high-quality fluxed sinters. Research studies showed that pellet metallurgical properties such as reducibility, high-temperature softening, and melting temperatures could be increased with basic additives. Indeed, overseas pellet producers (e.g., in Japan) successfully demonstrated production and use of dolomitic fluxed pellets; in

Table 8. Additives—blast furnace pellets,* kg/t†

	North American Plants								
	A	B	C	D	E	F	G	H	I
Limestone	5	16	62	11	85–119	3–13	60‡ 4§	40–55‡ 12§	35‡ 4§
Dolomite	59		62		25–35		25‡	45–85‡ 10§	65‡ 10§
Olivine									
Coal	11		18					11‡ 10§	26‡ 21§
Other	Coke breeze								
	World Plants								
	A	C	E	F	G	H	I	J	
Limestone	35‡		15	15–73	25		48		37‡ 33§
Dolomite	13.5§			40–90			90		
Olivine		35				25			
Coal	13‡ 11§	6	20	4–9	5		6		16‡ 16§
Other	15‡ 24§			2–28 (serpentine) 20–35 (steelmaking dust)	Coke breeze				

* Company names withheld to avoid disclosing proprietary data.

‡ Fluxed.

† Blank cells indicate a value of zero.

§ Acid.

North America, however, it was not until the mid-1980s that researchers identified the right combinations of limestone and dolomite to improve metallurgical properties while maintaining satisfactory physical properties. By the early 1990s, most North American pellet plants were modified to produce fluxed pellets. The CaO–SiO₂ ratio is typically 0.9 to 1.0 but can be increased to 1.3, whereas MgO levels range from 0.6% to 1.8%. The MgO target specification determines the ratio of dolomite to limestone in the flux mixture. On a worldwide basis, dolomitic fluxed pellets are gaining popularity at the expense of limestone fluxed pellets.

Limestone Fluxed Pellets

Limestone fluxed pellets are still produced in some parts of the world, including Brazil. In some cases, adding limestone was an extension of using calcium hydrate as a binder. Depending on the ore type, limestone also may improve the physical and metallurgical properties of the pellets.

Olivine Fluxed Pellets

Olivine fluxed pellets play a key role in areas such as Sweden and the Netherlands where some Swedish ores are pelletized. In these areas, the ores being pelletized are very low in SiO₂. Producing an acid pellet from such ores could result in very high swelling values. Olivine is a convenient mineral that contributes both SiO₂ and MgO; the MgO improves the metallurgical properties of these pellets and the overall silicate structure gives them high physical strength. In the Asia-Pacific area, other types of magnesium-silicates such as serpentine (see Table 8) play the same role as olivine.

Flux additives also are playing an increasing role in improving the properties of acid pellets. Adding 1% to 2% of either limestone or dolomite can improve key physical and metallurgical properties such as tumbler and compression strength and resistance to swelling and low-temperature breakdown. Table 8 gives typical addition rates for blast furnace fluxed and acid pellets.

The data in Table 8 suggest total flux addition rates of about 100 kg/t, or 1.0%, for dolomitic fluxed pellets and <50 kg/t for limestone fluxed and olivine fluxed pellets. The lower addition rates for the latter are related to the lower SiO₂ levels of the ores being pelletized; this in turn requires less flux addition to achieve a given basicity target.

These flux additions do not dramatically affect green-ball formation but do play an important role during induration. The fluxes are ground to the same level of fineness as the ores being pelletized, preferably with separate grinding facilities. During induration the limestone reacts with the acidic gangue to produce a slag bonding phase and the dolomite reacts with the ore to produce a magnesian-wustite bonding phase. The resultant increase in porosity contributes to increased reducibility and the combination of slag bonding and oxide bonding contributes to the increase in softening and melting temperatures. In acid pellet production at elevated temperatures, wustite (FeO) combines with siliceous gangue to form low-melting temperature fayalite. This in turn increases contraction and extends the softening–melting temperature range.

For blast furnace acid pellet production, the primary additive is limestone, about 1% to 2% (10 to 20 kg/t). This increases pellet strength by creating a stronger slag bonding phase in the pellet. Some pellet producers also add up to 1% (10 kg/t) dolomite, which contributes mainly by its resistance to swelling.

Flux Consumption in Blast Furnace Pellet Production

North American fluxed pellet consumption is about 45 Mtpy. With flux consumption levels at about 10%, this implies consumption of limestone and dolomite together is > 4 Mtpy. The lesser use of fluxes in acid pellet production could bring this total to some what <5 Mtpy. Such fluxes are usually obtained from local or regional sources. The specifications for limestone and dolomite are in the chapters on metallurgical fluxes in this volume.

Table 9. Additives to direct reduction pellets,* kg/t†

	North American Plants	
	H	I
Limestone		3
Dolomite	20	14
Coal	12	22
Other		

	World Plants				
	A	B	D	H	J
Limestone		6	10–15		16
Dolomite	16	14		15	
Coal	12	16	6–10		16
Other		7.2 (waste oxides)			

* Company names withheld to avoid disclosing proprietary data.

† Blank cells indicate a value of zero.

Benefits of Fluxed Pellets to Blast Furnace Performance

The effect in the blast furnace of improved metallurgical properties of fluxed sinter or fluxed pellets (as compared to acid sinter, acid pellets, or lump ore) is a lower coke rate because of the combined benefits of improved reducibility and improved high-temperature properties. The latter manifest themselves in the shift of the blast furnace “cohesive” zone (where the iron-bearing raw materials initially soften and then melt off as liquid hot metal and slag). This shift of the cohesive zone lower in the furnace and closer to the furnace center increases the volume of the zone where gaseous reduction of iron oxides occurs. It is not possible to allocate the coke rate savings between the reducibility and cohesive zone shift phenomena. The shift in the cohesive zone also provides other process economic benefits, specifically extension of furnace campaign life as a reduced volume of hot gases strike the furnace wall, and reduction in hot metal silicon content (with attendant downstream benefits in the steelmaking BOF) as the volume for Si transfer in the furnace is reduced.

In blast furnace practice, the benefits of fluxed pellets relative to acid pellets include both reduced raw flux calcination and improved metallurgical properties. For converting a burden of 100% acid to a burden comprising at least 65% fluxed pellets, the process benefits could be quantified as follows.

- Coke rate savings of 25 to 30 kg/t hot metal owing to a combination of technical reasons: reduction of raw flux calcinations, improved pellet reducibility, cohesive zone shift, and ability to operate at higher flame temperatures. This is about twice the savings calculated for an acid pellet burden solely because of raw flux calcinations.
- Extension of campaign life through reduced lining wear as a result of reduced gas flow and thermal load at the furnace walls.
- Reduction in hot metal Si content caused by cohesive zone shift with attendant benefits in BOF operations.

The statement that the process benefits are realized with at least “65% fluxed pellets” is based on the observation that once the burden composition exceeds 65% of a dry iron-bearing material, the furnace behaves as if the entire iron-bearing component was that one material. Accordingly, most ironmakers operating with all-pellet burdens use about 65% to 80% fluxed pellets, with the balance mainly acid pellets. This practice also maximizes the consumption of other basic materials such as waste oxides like steelmaking (BOF) slag.

Although flux pellets account for about two thirds of North American pellet production, acid pellets still play a key role as a supplement to predominantly fluxed pellet or fluxed sinter burden or even in all-pellet operations where the plant hot metal requirement can be met by an all-acid-pellet burden.

Flux Additions to DR-Grade Pellets

Flux additions to DR-grade pellets are also significant, although less so in recent years. Table 9 lists some flux addition rates for DR-grade pellets. At one time, a number of DR-grade pellet producers, mainly in Brazil and Sweden, added about 5% of flux to reduce the “sticking” or “clustering” tendency of pellets during reduction in Midrex or HyL shaft reduction furnaces. As DR-grade pellets underwent reduction, metallic whiskers formed and attached or stuck to whiskers from adjacent pellets, forming clusters that could impede the downward flow of reduced pellets. The flux additions coated the metallic whiskers, thus minimizing cluster formation.

The development of pellet coating techniques provided a more cost-effective means of eliminating pellet clustering in DR shaft furnaces. Although additives such as CaO and MgO provided fluxes that would be used later in EAF steelmaking furnaces, adding higher levels of fluxes also reduced the Fe content and increased pellet costs. At present most DR pellet producers add 1% to 2% (10 to 20 kg/t) fluxes, mainly dolomite, to enhance pellet physical and metallurgical properties. Coal addition rates of 10 to 20 kg/t help meet indurating energy requirements for these predominantly hematite ores.

Coatings for DR-Grade Pellets

In the mid-1990s, pellet producers and shaft furnace operators worked together to develop and implement the concept of “coating” pellets. Pellet coating mixtures, mainly aqueous, of various finely ground oxides would be sprayed onto pellets as they exited the indurating furnaces. Such coatings are limestone, dolomite, bauxite, cement, and other substances. These coatings also can be applied just before pellets enter the Midrex or HyL shaft furnaces. In some practices, the pellets are coated twice, once at the pellet plant and then again just before the reduction furnace. By coating the surface of the pellet, metallic whiskers are encapsulated by the oxide coating.

Because of coatings technology, shaft furnaces are able to operate at higher temperatures (760°C [1,400°F] to as much as 1,000°C [1,832°F]) to increase both metallization and productivity. Furthermore, this ability to operate at higher shaft temperatures has encouraged the use of techniques such as oxygen enrichment that raise the bustle (inlet) temperature to these furnaces; this in turn increases the shaft temperature. Increases in productivity of 10% to 15% can be achieved and increases in metallization from 92% to 95% have also been realized. The EAF steelmaking furnace benefit of increased metallization is about \$0.70/t of DR pellet per 1% increase in metallization.

Table 10 gives some current coating practices.

Although coatings have been applied mainly to DR-grade pellets, one pellet producer has been exploring coatings for blast furnace pellets. The incentive is to minimize dust generation in the blast furnace shaft, improve furnace permeability, and increase pellet yield as flue dust generation is decreased.

Other Pelletizing and Briquetting Applications: DR and Alternative Ironmaking

Nearly all sintering and pelletizing applications in iron and steel production involve preparing iron-bearing raw materials for the major established reduction processes: the blast furnace and the

gas-based DR processes, Midrex and HyL. The latter account for more than 90% of the DRI production worldwide; some agglomeration applications, however, relate to other ironmaking processes to produce either liquid hot metal or DRI.

Corex Process

The same pellets used for the DR processes are also used in the Corex ironmaking process. Corex is a two-step process in which the prereduction step is a shaft furnace fed with pellets and lump ore on top and with a reducing gas on the bottom. This reducing gas is the off-gas (top-gas) from the smelting reduction vessel, which is fed with coal and oxygen. Commercial Corex hot metal plants are in operation in South Africa, India, and Korea; the total tonnage is <5 Mtpy. High capital costs are a barrier to widespread adoption, but additional Corex plants are expected to be built in regions where power generation from excess off-gas from this process may be as valuable as the hot metal produced.

Rotary Hearth Furnace Processes

Another class of processes to use fine iron ores is the rotary hearth furnace (RHF) DR processes. These processes require either a briquetting or a pelletizing step to prepare self-reducing agglomerates of iron ore fines, coal fines, waste oxides, binders, and fluxes for the RHF. These agglomerates are heated and reduced in one circumferential trip around the rotary hearth. The DRI produced can then be melted in a subsequent EAF or BOF steelmaking process or even in a blast furnace. In some process variants such as the Iron Dynamics, Inc. (IDI) process, the RHF is coupled to a submerged arc furnace (SAF). The hot DRI produced in the RHF is charged directly into the SAF to produce liquid hot metal for subsequent charging into an EAF. Another variant is the ITmk3 process in which the RHF is heated to a sufficiently high temperature to separate the reduced agglomerate into molten pig iron and slag while still on the RHF. The resultant pig-iron nugget can then be charged to an EAF. Both the IDI and ITmk3 processes are headed toward commercial development in the United States. The overall effect on flux consumption may not be significant, however, because the SAF and EAF process steps will still require fluxes for proper slag chemistry. Binders continue to be used to produce satisfactory self-reducing agglomerates. Other RHF processes use steel plant waste oxides along with some coal to produce a lower grade solid DRI product for subsequent use in an EAF, BOF, or blast furnace. Smaller scale (<300,000 tpy) RHF plants using various technologies (e.g., Fastmet, DryIron, Inmetco) are in commercial operation in the United States, Japan, and elsewhere.

Cold Bonding Processes

In some commercialized cold bonding processes, steel plant waste oxides, ore fines, coal/coke fines, etc., are agglomerated to produce a material suitable for charging into a blast furnace or cupola. The agglomeration process is usually a briquetting process, although pelletizing and brick-forming processes also have been developed. The produced agglomerate lacks the high-temperature strength of fired agglomerates such as sinter or pellets. Accordingly, such cold-bonded agglomerates can be used only as <5% of the iron-bearing charge to a blast furnace; otherwise blast furnace permeability and overall performance will be adversely affected. Therefore the scale (usually <100,000 tpy) of such plants is limited by both the consumption ability of the blast furnace and the availability of waste oxides in a given steel plant. The use, if any, of industrial minerals in these processes is usually for binders, with materials such as cement, molasses, and various proprietary mixtures commonly employed.

Table 10. Coatings for direct reduction pellets,* kg/t†

	North American Plants	
	H	I
Limestone		3
Dolomite	2.5–3.0	Used in winter
Bauxite		Used in winter
Cement		

	World Plants				
	A	B	D	H	J
Limestone	Rate unknown		1.5–2.0		
Dolomite				3.0	
Bauxite					2.0–2.5
Cement		Rate unknown			

* Company names withheld to avoid disclosing proprietary data.

† Blank cells indicate a value of zero.

Examples of such cold-bonded processes include several steel plants in North America without sinter plants that are using briquetting processes operated by outside companies to produce waste oxide briquettes composed of mill scale, ore fines, dusts, sludges, coke breeze, etc. In Sweden, a brick-forming processor consumes similar materials. In Japan, all steel companies have sinter plants, but cold-bonded pellets are made up of waste oxides not suitable for the sintering process.

All of the above produce agglomerates for blast furnace consumption. In Germany, a commercial plant (OxiCup Process) is being built to process “self-reducing” bricks (composed of waste oxides, coke breeze, etc.) in a cupola to produce liquid hot metal.

Alternative processes have a key objective of using iron ore fines (as well as waste oxide and coal fines in some cases) without relying on any prereduction process.

Hismelt, Smelting-Reduction Processes

Long-standing efforts to replace the blast furnace process are aimed mainly at replacing coke ovens and sinter plants and other processes that prepare raw materials for the blast furnace. The blast furnace itself is a highly efficient, environmentally compliant process. Alternative processes to the blast furnace involve smelting-reduction processes fed with iron ore fines, flux, and coal fines. The leading candidate is the Hismelt process, with commercial plants capable of producing 0.5 Mtpy of pig iron or hot metal starting up in Australia and China. Such plants would feed EAFs or small blast furnaces. Further scaleup, if successful, could enable Hismelt to replace small- to medium-size blast furnaces. The effect on flux consumption, however, would be minimal because fluxes currently used in sintering and pelletizing would then be charged directly into the Hismelt or other smelting-reduction vessels to obtain satisfactory slag chemistry.

Fines-Based Direct Reduction Processes

Included here are both fluidized bed processes using natural gas as a reductant and RHF processes using coal as a reductant. The latter are viable only if liquid iron or a pig-iron nugget can be produced or if only waste oxides are processed. The former include the Finmet process and its predecessor, the Fior process, in which iron ore fines are reduced in series of fluidized beds; the reduced fines are then hot-briquetted for subsequent shipment to mainly EAF steel-making furnaces. No binders or fluxes are used. Two commercial

plants have been built with a total capacity approaching 4 Mtpy. The capital costs at such plants are very high, and it is possible that no additional plants will be built.

FUTURE OF SINTERING AND PELLETIZING

The future of sintering and pelletizing is directly related to the future of those ironmaking processes that use sinter and pellets, mainly the blast furnace and the shaft furnace DR processes. The future of these processes in turn depends on worldwide steel production and consumption, which have been on an upward trend for the past century, with some important interruptions for events such as the Great Depression, the oil shocks, the fall of the Soviet Union, and the Asian financial crisis. Currently, global steel production is again on an upward trend, led by explosive growth in China, most of which is based on the blast furnace process. This growth has led to very strong demand for both pellets and sintering ore. Steel production in the rest of the world is expected to be reasonably stable through this decade. Some continual but gradual shifting toward EAF-based steelmaking at the expense of BF/BOF steelmaking will occur in North America and Western Europe. This will reduce sintering capacity in these regions, but global growth, mainly in China, will present an overall increase in sintering capacity. Worldwide pellet capacity will continue to grow to feed both blast furnace based expansions and DR/EAF based expansions, mainly in regions rich in natural gas, such as the Middle East.

Government, Environment, and Health Considerations

Globally, governments view steel production favorably because of the economic importance of the steel industry. Government attitudes about public ownership have shifted in favor of private investment, both locally and globally. The privatization trend has led to increased investment, improved energy efficiency, and planned growth. Growth in the steel industry has had a corresponding growth in agglomeration practice, whereas the use of uneconomic local lump ores continues to decline. The practice of producing sinter on-site has increased and is based on rich iron ores and pellets from local or seaborne sources, but mainly from seaborne trade. In North America, government actions concerning international trade have been favorable, but environmental mandates, currency appreciation, and tax and labor policies have presented challenges to the BF/BOF sector in particular. This has sharply reduced sintering capacity and led to consolidation of pellet plant capacity.

The sintering process in particular has been challenged by environmental interests. Worldwide, steel companies have made major capital investments to install or upgrade flue-gas scrubbing systems in sinter plants. For most of the world, sintering is the key iron-bearing feed preparation process, so these investments have been justified; steel companies, however, continue to face pressure on the issue of dioxin releases from sinter plants. Considerable technological progress has been made in this area in recent years, and it is now believed that the dioxin issue will not lead to widespread sinter plant shutdowns as originally feared. In North America, where relatively modern pellet plant capacity was available, steel companies shut down many smaller, older sinter plants that would have required significant capital spending to address these environmental concerns.

Most of the world's pelletizing capacity, including nearly all of that in North America, was built in the 1970s and 1980s with state-of-the-art equipment for air and water pollution control. Furthermore, most pelletizing capacity is at or near mine sites and

Table 11. Environmental emissions of agglomeration processes

Process	Emissions				
	SO ₂ , g/t	NO _x , g/t	CO, kg/t	CO ₂ , kg/t	Particulates, g/t
Sintering	1,670	640	38	220	260
Pelletizing, hematite ore	200	500	1	30	130
Pelletizing, magnetite ore	100	200	<1	25	125

Adapted from LKAB 2000.

typically in remote areas. By contrast, sinter plants are located within steel plants, which themselves are frequently located in or near densely populated urban areas. Accordingly, pellet plants have faced far less environmental pressure than have sinter plants. A portion of this is attributed to lower emissions, as indicated by the data in Table 11.

The differences shown in Table 11 arise mostly from fuel consumption. Magnetite ores have the lowest external fuel requirement due to the heat released when oxidizing magnetite to hematite at the start of the indurating process. Pelletizing hematite ores requires less fuel than sintering because of better heat utilization in the process. Hematite pellet producers use about 22 to 30 kg/t of coal or other carbonaceous fuels such as anthracite, coke breeze, or pet coke per ton of ore. Nearly all U.S. pellet plants process magnetite ores and Canadian pellet plants process mainly hematite ores. Worldwide, most of the pelletized ore is hematite, with some notable exceptions such as Sweden.

The issue of CO₂ emissions and the Kyoto Accord is also a concern. Because blast furnace ironmaking/steelmaking is a major contributor of CO₂ emissions, a solution must be found to avoid large-scale deindustrialization in developed countries. In the interim, the steel industry and iron ore pelletizing companies are demonstrating their commitment to minimizing CO₂ emissions, mainly by striving to minimize overall energy consumption.

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Fluxes for Metallurgy

Harold R. Kokal

INTRODUCTION

Although the use of fluxes in metallurgy spans the globe, this chapter is limited to include uses, consumption, and operations in the United States. The principles described, however, are universal in nature. Information on world sources, specific transportation issues, supply and demand, and marketing in foreign countries can be found in other chapters of this book, references in libraries, and, more recently, on the Internet (USGS 2004). Previous editions of *Industrial Minerals and Rocks* can be reviewed for an historical perspective on the industry (Boynton and Gutschick 1960, 1975; Gillson et al. 1960; Severinghaus 1960; Lawrence 1975).

The consumption of limestone, dolomite, and silica as metallurgical fluxes is small compared to the total consumption of crushed stone. Only about 10% of total consumption is used in the chemical and metallurgical industries, and only about 10% of that is used as flux (Tepordei 2002a). Therefore, the industrial use of fluxes is a specialized niche comprising only about 1% of total production within the much larger crushed stone industry. This chapter concentrates on flux uses in the iron and steel industry, because about 90% of all metal consumed in the United States and in the world is iron and steel (Habashi 1986; USBM 1991). The use of flux for processing several nonferrous metals is discussed only briefly.

This chapter is restricted to the uses of flux minerals in thermal processes; fluxing minerals as neutralizing agents in the hydrometallurgical processes and other chemical processes are not discussed. The latter subjects are covered elsewhere in this book. Also, the use of fluxes in welding and brazing is not discussed here, but the subject is covered well by Lawrence (1975) and in other chapters of this book.

THE CONCEPT OF FLUXES

A metallurgical flux is a substance that is combined with gangue (unwanted minerals) in ores during smelting, with impurities in a molten metal, or with other additives in metal refining to form a slag that can be separated from the metal. Slags are immiscible with the metallic melt and are of lower density, so that a clean separation of slag and metal occurs when the proper conditions are attained. Slag chemistries are adjusted to provide the proper melting point, viscosity, surface tension, conductivity, specific heat, density, or chemical properties for the particular metallurgical process. In addition to absorbing impurities from the metal, slag thermally

insulates the metal bath, protects the molten metal from the atmosphere, and controls the chemical potential of the system. Several excellent references on slags and metallurgical fluxes are available (Rosenqvist 1974; Boynton 1980; Turkdogan 1983; Fine and Gaskell 1984; Lankford et al. 1985).

Fluxes often are selected to make slags that perform different functions at different stages of a process prior to final melting. For example, slag composition and behavior will change as materials descend in the iron blast furnace and as materials melt in the early stages during steelmaking. Selection of slag chemistry might be influenced by factors other than their primary function; for example, blast furnace slags might be used to make cement, rock wool insulation, or aggregate. In some cases, steelmaking slags containing sufficiently high phosphorus content have been marketed as fertilizers. Slags containing sufficient quantities of valuable recoverable elements may be sold as raw materials for other processes. For example, during production of pig iron from titanium-rich ores by the Sorel process, a slag rich in titanium dioxide is made and used as a raw material for subsequent recovery of titanium metal (Knittel 1983). The U.S. Geological Survey (USGS) monitors slag as a separate mineral commodity (Kalyoncu 2001).

GENERAL USES OF FLUXES

The production of carbon steel of many types is accomplished by the reduction and smelting of iron-bearing materials (pellets, sinter, and lump ore) and fluxes in blast furnaces with subsequent refining of molten iron and scrap in oxygen-blown furnaces. Some carbon steels, as well as stainless steels, ferroalloys, and special alloys, are made in electric-arc furnaces. Limestone and lime are the major fluxes used in ironmaking and steelmaking, but dolomite, dolomitic lime, silica, alumina, and fluorspar also are used. Foundry cupolas also employ some limestone and dolomite (Boynton 1980), and small amounts of limestone and lime are used in nonferrous metallurgy.

In blast furnace ironmaking, the flux is added either by direct charging of sized lumps or through sinter and fluxed pellets. Silica and alumina sometimes are added to blast furnaces either by direct charging of sized lumps or through sinter. During steel refining in either oxygen-blown furnaces or electric-arc furnaces (EAFs), flux is added as lime and dolomitic lime either charged as lumps or injected as fines; sometimes a small amount of limestone is used. Occasionally, fluorspar is added as lumps or mixed with other fine materials in briquettes. During refining in ladles prior to casting

steel, special slags are made with compositions optimized for removal of impurities. In continuous casting, additional specialized fluxes are added.

Flux minerals sometimes are added to repair refractories. In the basic oxygen process for steelmaking, lime from the flux combines with silica (formed by oxidation of silicon from the metal) to form a slag. This slag will attack the magnesia refractory brick that lines the steelmaking vessel, so magnesia (MgO in some form) is added to help prevent damage to the refractory (Boynton 1980; Lankford et al. 1985). The selection of a flux material to repair the refractory lining of smelting and refining vessels depends on the type of refractory and the process itself. In copper smelting, an acid slag practice is used, and silica is added for repair of refractories in the smelting furnaces (Anderson 1961; Fowler 1961).

Fluxes contained in a slag that formed in one operation can also serve as flux in another. Slags that formed in refining operations often are recycled to smelting operations to provide flux materials and to recover elements that otherwise might be lost. For example, steelmaking slags are recycled to the blast furnace to recover unreacted, precalcined lime, and iron and manganese oxides. Impurities, particularly sulfur, phosphorus, and zinc, limit the recycling of steelmaking slag to the iron blast furnace. In copper smelting, converter slags are recycled to recover copper and flux; however, the extent of recycling depends on the level of impurities such as bismuth, antimony, and arsenic.

TYPES OF FLUXES

Fluxes often are referred to as *acid*, *basic*, or *neutral*. Acid fluxes are those that form acids in water, and basic fluxes form bases in water. Typical acid fluxes are silica, alumina, and phosphorus, although alumina may function as either an acid or base. Typical basic fluxes are lime and magnesia. Fluorspar, or calcium fluoride, is considered a neutral substance because it is viewed as the reaction product of a base and an acid. The degree of acidity (ratio of acids to bases) or basicity (ratio of bases to acids) often is specified to characterize slag chemistry for a particular system, which in turn might be referred to as acid or basic depending on the type of slag. For example, steelmaking is basic because it uses slags with more bases (lime and magnesia) than acids (silica and alumina).

The choice of minerals and compounds used as fluxes depends on the requirements of the process, availability, costs, requirements for recycling of intermediate products, and environmental concerns. Because slags are most often mixtures of oxides and silicates, fluxes are usually oxides, carbonates (which decompose to oxides), and silicates. Slags containing phosphates, borates, sulfides, carbides, or halides also have been used (Rosenqvist 1974; Moore 1981; Szekely, Carlsson, and Helle 1989). In ironmaking and steelmaking, slags are basic, so the primary flux is lime-bearing, although acidic components also may be added. In nonferrous processes, slags and fluxes are generally acidic (silica is the primary component), although small amounts of basic fluxes such as limestone or lime are used to modify slag properties, and some nonferrous refining slags are lime based.

Typical acid fluxes are siliceous sand and gravel, quartz rock, used silica brick, or raw siliceous ore (Lankford et al. 1985). Olivine, a magnesium-silicate mineral, has been added to iron blast furnaces to enhance removal of alkalis. Alumina-based fluxes include bauxite, aluminiferous clay, and recycled alumina brick. Alumina can function amphoterically, forming either aluminum silicate in high-silica slags or calcium aluminate in lime-bearing slags (Lankford et al. 1985).

The principal basic fluxes are limestone (calcium carbonate) and dolomite (calcium–magnesium carbonate), sometimes called

fluxstones (Boynton 1980), and their calcined forms, lime and dolomitic lime. The advantages of externally calcined fluxes are that they require less expensive forms of energy to effect decomposition than when they are used in the blast furnace (e.g., where coke is the main fuel), and they cause less boiling in steelmaking vessels because carbon dioxide gas is already removed. Limestone and dolomite are considerably less expensive than lime and dolomitic lime. The calcined forms are more difficult to handle and are highly reactive with water. Dolomite and dolomitic lime are used for their magnesia contents.

Fluorspar is a neutral flux once used widely in steelmaking slags to improve fluidity and also has been used together with lime as a primary slag in electroslag refining (Duckworth and Hoyle 1969). The lowest grade of fluorspar (metallurgical spar) often is used for steelmaking. When the price of fluorspar is high, substitutes, including aluminum smelting dross, borax, manganese ore, titania, iron oxides, silica sand, and calcium chloride, may be used (Peters 1982). Briquettes with various combinations of low-grade manganese ore fines, mill scale, precipitator dust, recycled slag, and fine fluorspar have been used as flux in steelmaking to form a fluid slag. Over the last decade, the use of fluorspar in the steel industry has been decreasing.

Fluorspar is employed widely in the manufacture of aluminum. High-grade fluorspar (acid-grade fluorspar used to make hydrofluoric acid) is used to make cryolite (AlF_3), which, along with fluorspar, is used in a molten bath to dissolve alumina and recover electrolytic aluminum (Miller 2002a).

Since about 1980, iron- and steelmakers have been using synthetic slags for external treatment of hot metal from the blast furnaces and for treatment of steel in ladles subsequent to basic oxygen furnace (BOF) and EAF processing. These treatments include flux additions for removal of silicon, sulfur, and phosphorus. Synthetic slags are made by adding magnesium or aluminum metal, magnesium–aluminum or calcium–silicon alloys, calcium carbide, prefused calcium aluminate, and mixtures of some of these to coke, lime, and fluorspar (Stubbles 1984). Sodium carbonate (soda ash) can be used for desulfurization and dephosphorization of steel (Yamamoto, Kajioka, and Nakamura 1980; Szekely, Carlsson, and Helle 1989). Special synthetic compounds also are used as mold fluxes in the continuous casting of steel (Branion 1987). Additional applications include nonferrous metallurgy, the ferroalloy industries, and foundries (Szekely, Carlsson, and Helle 1989).

PRODUCTION, CONSUMPTION, AND PRICING Sources of Flux Materials

Deposits of limestone and dolomite are widespread and often are found near ironmaking centers. In the United States, limestone and dolomite fluxes presently used for ironmaking and steelmaking originate primarily from Michigan. Historically, these fluxstones were of the type and purity useful for ironmaking and could readily and economically be transported to iron- and steel-producing centers. Small amounts of fluxstone also are obtained in Alabama, Ohio, Pennsylvania, and Illinois (Lawrence 1975; Lankford et al. 1985).

Minor flux materials used in ironmaking and steelmaking include alumina, silica, and fluorspar. In the United States there is a shortage of high-grade, alumina resources except for aluminiferous clays, which contain silica. Because alumina and silica must be added independently, bauxite (a form of alumina-bearing ore) must be imported from Greece, Turkey, or Jamaica. In contrast, siliceous materials are plentiful. Typical silica resources for blast furnaces include raw ore from iron mines and local siliceous gravel. Local siliceous sands, olivine, and other fine siliceous materials

are used to increase the silica content of sinter. Fluorspar for steel-making is imported to the United States from China, South Africa, and Mexico.

In the nonferrous industries, fluxes are largely siliceous, and lean ores or other nearby rocks often are used as fluxes, providing that impurities are low. In some instances, high-grade silica rock is used. Gypsum, a sulfate of calcium, has been used as a source of lime and sulfur in nickel smelting (Habashi 1986).

Transportation

Long-distance transportation of limestone and dolomite is uncommon because of their low unit values and widespread occurrence; however, if high purity is required, higher-cost lime and dolomitic lime might be transported over greater distances in some special cases. For example, low-impurity flux has been transported from Japan to Australia to supplement local impure sources for use in fluxed pellets.

In the United States, limestone and dolomite are transported to the steel-producing centers by ship on the Great Lakes, by barge on rivers, and by railroad. Sinter plants are often located at or near steel mills to take advantage of the availability of a variety of iron-bearing raw materials, coke fines, and slag. Some steel producers operate their own lime plants to produce both high-calcium lime and dolomitic lime, while others purchase their lime from independent producers. Captive lime plants often are located near steelmaking operations and in some cases are connected by conveyor belts. In other situations, lime is transported by truck, barge, or rail. The USGS publishes a directory of lime plants (Miller 2004).

The trend toward using fluxed pellets in blast furnaces has required a change in the transportation and distribution patterns of limestone and dolomite. In the United States, fluxed pellets are not made near the steel mills but instead at the iron ore mines in Minnesota and Michigan, which are located farther from the steel mills than from the limestone and dolomite quarries. Therefore, the limestone and dolomite fluxes must be backhauled to the mines by boat and railroad before being returned to the steel mills in the form of fluxed pellets. In some instances, fluxed pellets made in Minnesota with flux from Michigan have been transported as far as Alabama and Utah by railroad.

End Users

The sizes of stone used for flux are generally less than 150 mm but greater than 150 mesh (0.104 mm). The coarsest sizes are used for direct charging to shaft-type lime kilns and blast furnaces; intermediate sizes are used for manufacture of lime in rotary kilns and direct charging to blast furnaces; and the finer sizes are used for sinter. There is some flexibility in stone size if appropriate facilities for crushing, grinding, and sizing are available. The intermediate to fine sizes are used for fluxed pellets after additional crushing and grinding. Sizes below 150 mesh (0.104 mm) often contain impurities detrimental to ironmaking and steelmaking, and are either sold for agricultural use or disposed of as waste (see the chapters on lime, agglomeration processes, and limestone and dolomite for more details). For discussions on fluxed pellets and sinter production, refer to the Agglomeration Processes chapter, as well as Ball et al. (1973).

Lime often is added to sinter mixes to promote microagglomeration of fines and to serve as a source of calcium, or, in the case of dolomitic lime, as a source of calcium and magnesium. Lime and hydrated lime also have been investigated as binders in iron ore pellets; however, this can result in cracked pellets after induration (firing) of pellets caused by rapid release of the water of hydration (Ramos 1999).

High-calcium lime and dolomitic lime used as fluxes in steel-making have specific particle size requirements. The sizes of stone required for lime burning are fairly well fixed and are adjusted to make the required particle sizes of lime. In the nonferrous industries, lime, in addition to smelting and refining, is used to treat acid wastes and to control acidity in flotation and cyanidation plants.

Factors Affecting Pricing

Limestone and Dolomite

The USGS publishes information on the production, consumption, and value of crushed stone, which includes the flux minerals limestone and dolomite (Tepordei 2002a). Major sources of fluxstone used in the ferrous and nonferrous industries are domestic. Trends in the production, consumption, and value of fluxstone (limestone and dolomite), used predominately in the iron and steel industry, are shown in Table 1. The quantity used in the iron and steel industry is about 1% of total crushed limestone and dolomite consumption.

The total of crushed stone reported as flux is only slightly greater than the amount reported as fluxstone; the difference can be attributed to materials other than limestone and dolomite. During the period from 1998 to 2002, the reported amount of fluxstone used by the iron and steel industry decreased from about 7 Mtpy to less than 2.5 Mtpy. This not only reflects the depression in steel production during that period, but it also most likely reflects consumption from stock piles and underreporting by companies that were consolidating. During the same period, the average value of fluxstone increased from \$4.29/t to \$5.14/t.

Quantities and values of limestone and dolomite used within the chemical and metallurgical industries, including uses for lime making and flux, are shown in Table 2. The consumption of limestone is greater than the consumption of dolomite as flux.

Lime

The USGS publishes data related to production and consumption of lime (Miller 2002b). Most lime is produced domestically (Miller 2004), and the iron and steel industry contributes about one-third of the total lime demand (Table 1, which also shows trends for the period from 1998 to 2002); the decline in usage reflects the depression in the steel industry. The price of lime gradually increased from about \$58/t in 1998 to \$60/t in 2002. In 1989, the value of metallurgical lime was between \$50/t and \$55/t. In 2004, prices spiked dramatically for many raw materials, and the price of lime was also much higher than in 2002 and 2003.

The consumption and value of lime in the metallurgical industries between 1998 and 2002 are shown in Table 3, which also shows the uses of lime in the BOF and the EAF steelmaking processes. In 2002, lime use in the nonferrous industries, excluding smelting and refining, was about 18% of that used in ironmaking and steelmaking. This percentage has decreased steadily from 1998 to 2002.

Fluorspar

Table 1 shows fluorspar production and consumption. About 20% of total fluorspar demand is for crude steel production (Miller 2002c), which decreased from 1998 to 2002, from about 600,000 tpy to 450,000 tpy. The price for metallurgical purposes held relatively constant at \$89/t. The small decrease in price in 2001 reflects the slump in the steel industry as well as possible stockpile sales.

INDUSTRY STRUCTURE

Infrastructure

During the past decade, the flux industry has undergone dynamic and even abrupt changes because of large-scale consolidation within the iron, steel, and copper industries. A smaller number of

Table 1. Production or consumption and value for fluxstone, lime, and fluorspar in iron and steel production, 1998–2002

	1998	1999	2000	2001	2002
Fluxstone (Limestone and Dolomite)					
Fluxstone production (limestone and dolomite), <i>kt</i>	6,723	7,680	3,480	2,632	2,251
Total crushed stone used as flux, <i>kt</i>	6,880	8,080	4,010	2,900	2,380
Total limestone and dolomite, all uses, <i>kt</i>	1,064,000	1,084,000	1,099	1,131,000	1,075,400
Average value, \$/t* for fluxstone	4.29	4.37	4.70	4.67	5.14
Lime (Calcined Limestone and Dolomite)					
Lime production for iron and steel, <i>kt</i>	6,130	5,970	6,150	5,460	5,360
Total U.S. lime production including hydrated lime and deadburned dolomite, <i>kt</i>	20,100	19,700	19,500	18,900	17,900
Average value, \$/t† for lime in iron and steel	58.56	57.62	58.21	59.56	60.82
Fluorspar (Metallurgical)					
Imports, metallurgical grade, <i>kt</i>	41	59	39	27	28
Consumption in BOF, <i>kt</i>	7.33 W†	9.59 W	8.60 W	Not reported	Not reported
Consumption in EAF, <i>kt</i>	19.7 W	8.78 W	7.27 W	Not reported	Not reported
Total metallurgical consumption, <i>kt</i>	27.0 W	18.4 W	15.9 W	65.0	76.9
Total apparent consumption, U.S., <i>kt</i>	591	615	601	543	442
Average value, \$/t‡ for metallurgical uses	89	88	84	80	89

Adapted from Tepordei 2002a; Miller 2002a, 2002b.

* Average value—free on board (f.o.b.) quarry or plant.

† W = some data withheld to avoid disclosing company proprietary data.

‡ Average value—cost, insurance, and freight (CIF), U.S. port.

Table 2. Quantity and value of crushed limestone and dolomite sold or used within the chemical and metallurgical industries in the United States in 2002, by use

Use	Limestone		Dolomite	
	Quantity, <i>kt</i>	Value, \$/t	Quantity, <i>kt</i>	Value, \$/t
Lime manufacture	18,700	5.33	1,480	4.16
Fluxstone	1,440	5.51	811	4.48
Total, all uses	90,543*	4.74	2,386*	4.25

Adapted from Tepordei 2002a.

* Total does not include data withheld to protect proprietary information.

more efficient, larger producers now exist. In order to concentrate on their core business, many iron and steel producers sold captive limestone and dolomite operations. Most limestone and dolomite flux used in the steel industry now is supplied by less than a half dozen large producers (often the flux is supplied from the same quarries). A directory of principal producers of crushed stone, including limestone and dolomite, is published annually (Tepordei 2002b).

Some flux applications have changed, altering patterns of use and quantities. For example, limestone and dolomite fluxes used in blast furnace ironmaking previously were added directly to the blast furnaces or as flux through the sinter process, but today they are added as precalcined fluxes through the use of fluxed pellets. There also has been a large growth in mini-mill steelmaking with EAFs that rely primarily on scrap and direct reduced iron as sources of iron. These sources contain less gangue, thereby requiring less flux than the conventional blast furnace process.

Imports/Exports

Very small amounts of limestone, dolomite, lime, and dolomitic lime are imported and exported; however, USGS does not report quantities specifically used for flux. A small amount of fluorspar is

exported, although almost none is produced domestically. Some imports or excess inventories may be sold and reported as exports.

CHARACTERISTICS OF FLUX RAW MATERIALS

Selection of flux for a particular process depends on the chemical specifications to form a slag of the required composition. Ideally, only pure substances would be selected; however, these are seldom available in nature. Impurities in the flux should be minimal. Large amounts of impurities render the flux less effective, therefore requiring larger amounts of flux. Some minor impurities can have significant detrimental effects on the process or equipment. Once the chemistry is specified, particle size of the flux is determined largely by handling and gas-flow requirements of a particular process and, to a lesser extent, by the particle size or size distribution of flux available. Geographic location and economics may dictate the selection of a flux with the desired chemical or physical specifications; otherwise a new source may be explored.

Chemistry of Limestone and Dolomite

Limestone (CaCO_3) and dolomite ($(\text{Ca,Mg})\text{CO}_3$) are used in smelting iron ores to supply lime (CaO) and magnesia (MgO), respectively, to form a slag with acid components silica (SiO_2) and alumina (Al_2O_3). Table 4 gives typical chemical analyses for limestone, dolomite, and their respective calcined products. The ideal flux is low in acids (silica, alumina, and sometimes titania [TiO_2] and iron oxide), sulfur (S), phosphorus (P), alkali metals (sodium and potassium), and halides (chlorides and fluorides). All phosphorus in ironmaking raw materials, including iron ores or agglomerates, coke, and fluxstone, is reduced to the elemental state in the blast furnace and appears in the iron product; therefore, phosphorus must be minimized in the flux. This is particularly true with recycled slags, and it is the phosphorus content that often determines the amount of steelmaking slag that can be recycled to ironmaking. Because a major purpose of the ironmaking slag is to remove sulfur, sulfur in flux as well as other materials should be low. Alkali

Table 3. Quantity and value of lime sold or used in the metallurgical industries in the United States, by use, 1998–2002

Use	1998		1999		2000		2001		2002	
	Quantity, kt	Value, \$1,000	Quantity, kt	Value, \$1,000	Quantity, kt	Value, \$1,000	Quantity, kt	Value, \$1,000	Quantity, kt	Value, \$1,000
Metallurgy (hydrated lime)	46	3,810	22	1,560	19	1,650	23	1,790	23	1,740
Steel, BOF	4,280	245,000	3,860	219,000	4,000	229,000	3,260	194,000	3,600	218,000
Steel, EAF	1,650	102,000	1,870	111,000	1,840	111,000	1,960	117,000	1,510	92,900
Other steel and iron	206	13,000	239	14,700	300	17,900	250	14,000	255	14,700
Nonferrous metallurgy*	1,710	98,500	1,570	91,000	1,310	66,300	1,170	61,200	973	54,900
Total metallurgical†	7,840	458,000	7,550	435,000	7,450	424,000	6,630	386,000	6,330	381,000
Total lime, all uses	20,100	1,210,000	19,700	1,190,000	19,600	1,190,000	18,900	1,160,000	17,900	1,120,000

Adapted from Miller 2002b.

* Includes alumina and bauxite, magnesium, ore concentrate (copper, gold, etc.) and other.

† Data are rounded to no more than three significant digits; may not add to totals shown.

Table 4. Typical analyses of limestone, dolomite, and lime fluxes

Component	Limestone		Dolomite		Burnt Lime	
	Blast Furnace*	Sinter Plant	Blast Furnace*	Sinter Plant	High-Calcium	Dolomitic
One-year average, % weight					Calculated, % weight	
CaCO ₃	95.3	93.8	54.5	52.4		
MgCO ₃	3.1	3.6	42.0	40.0		
CaO	53.4	52.5	30.6	29.4	88.5	56.0
MgO	1.5	1.7	20.1	19.1	2.5	36.8
R ₂ O ₃ †	0.3	0.4	0.3	0.4	0.5	0.5
SiO ₂	0.7	1.8	2.6	6.8	1.2	4.7
Typical, % weight						
Fe ₂ O ₃	0.20	0.30	0.2	0.3		
Al ₂ O ₃	0.30	0.20	0.3	0.3		
Mn	0.01	0.02	0.01	0.03		
P	0.01	0.01	0.01	0.01		
S	0.03	0.04	0.05	0.03		
K ₂ O	0.10	0.10	0.10	0.10		
Na ₂ O	0.02	0.02	0.02	0.02		
LOI‡	43.40	46.10	6.00	1.00	1.0	2.0

* Also typical of flux used in fluxed pellets and as stone for lime production.

† R₂O₃ = Fe₂O₃ + Al₂O₃ + Cr₂O₃ + TiO₂.

‡ Loss on ignition.

metals are generally detrimental to the blast furnace operation, often forming deposits on the furnace walls; therefore, alkali inputs from raw materials should be minimized. During the production of fluxed pellets or sinter, the alkali metals, in combination with sulfur, chlorides, and fluorides, have been found to be extremely detrimental to some process equipment.

Adding silica to the blast furnace often is required to attain the proper ratio of basic to acid components in the slag. In traditional blast furnace practice, up to 5% silica in the flux was tolerated and 1% to 3% was common (Gault and Ames 1960). Today, silica levels are generally lower and the amount tolerated depends on whether the flux is used for making sinter or for direct charging; the levels of silica in other burden materials is also a factor. The allowable silica level also depends on the required slag chemistry, the volume of slag required for control of the furnace, and the amount of sulfur and alkali metals present.

The MgO content of limestone added to the blast furnace is often not critical. The amount tolerated depends on the MgO content

of all burden materials and the target slag chemistry. Higher MgO content keeps the slag fluid over a wider temperature range (Gault and Ames 1960; Rosenqvist 1974). Dolomite may be added to provide sufficient MgO to produce slag to meet a certain by-product specification, for example, slag for use as aggregate. MgO added in sufficient amounts increases the melting point, and this effect is used to advantage when making fluxed pellets for the blast furnace. The MgO content of limestone must be known when producing blends of limestone and dolomite for use in fluxed agglomerates.

Physical Properties of Limestone and Dolomite

Traditional ironmaking relied on direct charging of the iron blast furnace with flux materials up to 150 mm in size. Today the need for a uniformly sized and permeable burden requires that the size be more compatible with other burden materials; therefore, stone as fine as 50 × 12.5 mm has been used. By changing the size of stone, the location in the blast furnace where complete calcination occurs can be regulated (Lankford et al. 1985). Typically, flux added to

Table 5. Size analyses of typical fluxstone for blast furnace, sinter plant, lime plant, and fluxed pellet plant

Percentage Passing						
Size, cm	Blast Furnace or Lime Plant Stone		Mixed Blend 50:50 [*]	Sinter Flux		Pellet Flux 50:50 [†]
	Limestone	Dolomite		Limestone	Dolomite	
7.620			99.6			
6.350	87.6		99.0			
5.080	46.2	88.7	91.0			
4.445	18.7	72.7				
3.810	9.1	50.5	64.6			
3.175	4.4	26.4				
2.540	2.6	14.8	15.7			
1.905	1.7	2.0				
1.270			2.5			
0.952				99.8	100.0	
0.635			1.2			
Size, mm						
4.699				97.5	97.8	
3.327				90.6	86.1	
1.651				66.0	58.6	
0.589				20.3	20.0	
0.295				8.2	10.0	99.9
0.208						99.3
0.147				2.4	4.7	90.4
0.074				0.9	2.4	65.9
0.053						58.2
0.043						52.2
0.038						47.2
0.026						42.0

* Feed to crusher at fluxed pellet plant (50% limestone, 50% dolomite).

† Ball mill grinding.

sinter is in the range of –6.35 to –3.17 mm in size with 90% coarser than 150 mesh (0.104 mm). Some iron producers have adopted the use of fluxed pellets, which requires that the stone be ground to 60% to 80% passing 200 mesh (0.074 mm), a size more compatible with the formation of pellets from fine concentrates. Table 5 shows the size ranges of limestone and dolomite required for the blast furnace, lime plant, sinter plant, and fluxed pellet plant.

Thermal decrepitation and physical degradation of fluxstone are undesirable because the presence of fines reduces the permeability of the furnace burden. Experience has shown that fine-grained stone decrepitates less than coarse-grained stone in the blast furnace (Gault and Ames 1960). Resistance of stone to physical degradation during handling and transportation is also important in minimizing the amount of fines formed. If fines are deleterious to the process, they must be removed by screening. If fines have no alternate use, the cost of the flux is effectively increased.

Chemical Properties of Lime

Prior to use in steelmaking, limestone and dolomite are calcined or heated to drive off carbon dioxide. In the blast furnace, calcination of limestone begins at temperatures higher than 800°C and dolomite typically begins dissociating at about 700°C (Ricketts 1992).

Typical analyses of lime and dolomitic lime are shown in Table 4. In steelmaking, high-calcium lime with low silica content is specified because lime combines with silica formed by oxidation of silicon in the steel bath. Dolomitic lime is added in steelmaking

to control the MgO content in order to minimize wear of the basic refractory lining.

The available base (*AB*) for reaction with acidic components is important (Peters 1982; Lankford et al. 1985). The *AB* is calculated in either of two ways:

$$AB = \text{CaO}/(\text{SiO}_2 + \text{R}_2\text{O}_3),$$

$$\text{or } AB = \text{CaO} + \text{MgO} - \text{SiO}_2 - \text{R}_2\text{O}_3 - LOI,$$

where

R_2O_3 = the sum of the Fe_2O_3 , Al_2O_3 , Cr_2O_3 , and TiO_2 ;

LOI = loss on ignition.

The sulfur content of lime should be low, because absorption of sulfur that originates from either stone or fuel (or both) during calcining can be a major problem. The sulfur level in lime can be controlled by regulating oxygen content in the calcining system exit gas. Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) in fluxstone is undesirable because it is difficult to dissociate, but generally sulfur in pyrite (FeS_2) or pyrrhotite (Fe_{1-x}S , where $x = 0-0.2$) can be removed. Sulfur also occurs as organic sulfur in the stone. Sulfur levels of 0.03 % to 0.06% in the lime are typical.

After calcining, lime is hygroscopic and slakes to form calcium hydroxide. In addition, some uptake of carbon dioxide and sulfur dioxide can occur, forming a dense layer of calcium carbonate and/or gypsum on the surface. This layer can adversely affect the subsequent reaction rate of the lime. If lime is not completely calcined, a

core of unreacted limestone (or dolomite) will remain. Unreacted core, along with adsorbed water and carbon dioxide, will result in LOI when the lime is heated. Lime for steelmaking generally requires a low value LOI of 2% to 4% (or less); some plants actually require an LOI no higher than 0.5% (Boynton 1980).

Physical Properties of Lime

The particle size of lime used in steelmaking is typically 37 mm by 6.35 mm. Particle size is important because if sizes are too fine, the intense gas flow above the steelmaking vessel can remove them before the lime reacts to form slag. Typically, particles <3 mm in size are removed. Although considerable effort is made to minimize the creation of fines in the lime, degradation occurs during hydration and carbonation in storage and through physical handling. Lime placed in storage might contain between 5% and 20% fines less than 3 mm in size; however, after several days in storage, fully one third can degrade further, and up to one half will exist as fines that result from handling and transfers before use in steelmaking.

Several steelmaking processes use bottom blowing, and some use combined top and bottom blowing so that much finer flux can be used if injected. Fine lime can be pneumatically conveyed by oxygen or a carrier gas and injected through tuyeres (openings) in the vessel bottom. The high surface area of lime fines promotes rapid slag-metal reactions. The size of lime particles typically used in the injection process is about the same as (or finer than) those shown for pellet flux in Table 5 (Koros, Petrushka, and George 1991).

Requirements for Fluorspar

Fluorspar or calcium fluoride (CaF_2) sometimes is used as a flux along with lime to improve the fluidity of slag in steelmaking and subsequent ladle metallurgy processing. Typical consumption of fluorspar in steelmaking is 2 to 10 kg/t or 5% to 10% of the lime added (Peters 1982). In electroslag refining, fluorspar is used in a ratio of about 70 parts fluorspar to 30 parts lime (Duckworth and Hoyle 1969). The purpose in electroslag refining is to form a very conductive slag with the required melting point. In aluminum smelting, about 23 kg fluoride as AlF_3 equivalent is used per ton of aluminum (Miller 2002b).

The specification for metallurgical-grade fluorspar is 72% minimum effective fluorspar, where the effective fluorspar is calculated as follows:

$$\text{Effective CaF}_2 = \text{CaF}_2 - (2.5 \times \text{SiO}_2)$$

The major impurity in fluorspar is silica; the balance of impurities includes calcium carbonate and small amounts of barite (BaSO_4), lead, and zinc. Table 6 shows chemical analyses of typical fluorspars.

Fluorspar can be added as lumps, gravel-sized material, or fines incorporated in briquettes. Sizes of gravel and screen fines are shown in the footnotes to Table 6. Typically, 5% to 15% fluorspar fines are added to briquettes made with recycled slag fines or other steelmaking ingredients. The latter is often preferred to achieve better mixing of fluxes and better reaction with the slag. Any loose fines will be lost during the blow.

Other Materials

Silica-bearing materials sometimes are added to the blast furnace to control the basicity of the process and to counteract overaddition of basic fluxes, although additions are kept to a minimum. The chemistry of the material should be compatible with the process, and deleterious elements such as alkali metals, phosphorus, and sulfur are avoided. In ironmaking, typical silica sources are low-grade taconite ore, flint clay containing alumina, sandstone, siliceous gravel, or

Table 6. Composition of metallurgical-grade fluorspar (dry basis), wt %

Component	High-Grade	Medium-Grade*	Low-Grade†
CaF_2	92.7	89.1	82.0
SiO_2	3.5	3.9	8.9
Fe	0.09‡		
S	0.05‡		
CaCO_3	3.5	4.6	4.2
Effective CaF_2	83.9	79.3	59.7

* Gravel size: -6.35 cm, +0.95 cm.

† Screen fines: 78% -6.35 mm and +100 mesh (0.147 mm); 11% passing 325 mesh (0.043 mm).

‡ Oxides of iron and aluminum and sulfur can sometimes reach 1% in lower-grade products.

used brick. If the added material is low grade with respect to silica, a larger, measurable, and more controllable quantity can be used. For example, addition of taconite ore containing 50% silica and 35% iron allows extra iron units to be added to the furnace while providing a larger volume of material than if using pure silica. In copper smelting, low-grade ores or rock and sometimes high-grade silica are used. In any process, the size of the flux material should be compatible with the process: fine enough to react rapidly but not so fine as to cause permeability problems or to be lost as dust.

Testing Procedures

Many standard tests for characterizing lime and limestone (as well as dolomitic lime, dolomite, fluorspar, and other materials) have been developed by the American Society for Testing and Materials (ASTM) (ASTM 2003a, 2003b, 2003c). The ASTM tests commonly applied are listed in Table 7. Accurate sampling of stone is often a problem because of its large size or wide range of sizes. Sampling of lime and fluxstone is described in ASTM tests C-50 and D-75. Chemical analysis of limestone and dolomite is accomplished easily according to standard procedures defined in ASTM C-25 and C-1301 and by published or proprietary methods using modern analytical techniques. Methods for analysis of fluorspar are given in E-463 and E-815 (ASTM 1989). Physical testing is defined in ASTM C-110. The physical test most often done is sizing or screening of stone to determine size distribution described in ASTM E-11, C-136, E-276, and E-389. Degradation characteristics can be determined by the Los Angeles abrasion test for fine or coarse aggregates (ASTM C-131 and ASTM C-535). A drop test, approximating heights at which stone will be conveyed, is used to estimate amounts of degradation during handling and transportation (Fagerberg and Sandberg 1974).

The ASTM water reactivity test, ASTM C-110, is often used to test lime reactivity for steelmaking (Schlitt and Healy 1970). The American Water Works Association Standard B202-02 is similar. Although there is some correlation of water reactivity with slag formation, a crucible test is probably more directly related to lime behavior in steelmaking (Limes and Russel 1970).

TECHNOLOGY

Successful application of a particular slag in a metallurgical process depends on its chemistry and properties when molten, which are controlled by the selection of appropriate fluxes. Important properties of a slag are: melting point, viscosity, surface tension, density, and chemical activities of its components. In electro-slag smelting, conductivity also is important. The effects of composition on melting temperature in relation to its other properties often are

Table 7. ASTM standard physical and chemical tests and definitions applicable to limestone, dolomite, and fluorspar*

ASTM No.	Description
C 25-99	Chemical Analysis of Limestone, Quicklime, and Hydrated Lime
C 29/C29M-97(2003)	Bulk Density (Unit Weight) and Voids in Aggregate
C 50-00	Sampling, Sample Preparation, Packing and Marking of Lime and Limestone Products
C 51-05	Standard Terminology Relating to Lime and Limestone as Used by the Industry
C 70-94(2001)	Surface Moisture in Fine Aggregate
C 110-05	Physical Testing of Quicklime, Hydrated Lime, and Limestone
C117-04	Standard Test Method for Materials Finer than 75 μm (No. 200) Sieve in Mineral Aggregates by Washing
C 125-03	Definition of Terms Relating to Concrete and Concrete Aggregates
C 127-04	Density, Relative Density (Specific Gravity) and Absorption of Coarse Aggregate
C 128-04a	Density, Relative Density (Specific Gravity) and Absorption of Fine Aggregate
C 131-03	Resistance to Degradation of Small-Size Coarse Aggregate by Abrasion and Impact in the Los Angeles Machine
C 136-05	Sieve Analysis of Fine and Coarse Aggregates
C 184-94E1	Fineness of Hydraulic Cement by the 150 μm (No. 100) and 75 μm (No. 200) Sieves
C 204-00	Fineness of Hydraulic Cement by Air Permeability Apparatus
C 294-05	Standard Descriptive Nomenclature for Constituents of Concrete Aggregates
C 295-03	Petrographic Examination of Aggregates for Concrete
C 430-96(2003)	Fineness of Hydraulic Cement by the 45 μm (No. 325) Sieve
C 535-03e1	Resistance to Degradation of Large-Size Coarse Aggregate by Abrasion and Impact in the Los Angeles Machine
C 566-97(2004)	Total Evaporable Moisture Content of Aggregate by Drying
C 702-98(2003)	Reducing Samples of Aggregate to Testing Size
C 786-96(2003)	Fineness of Hydraulic Cement and Raw Materials by the 300 μm (No. 50), 150 μm (No. 100), and 75 μm (No. 200) Sieves by Wet Methods
C1301-95(2001)	Major and Trace Elements in Limestone and Lime by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP) and Atomic Absorption (AA)
D 75-03	Sampling Aggregates
E 11-04	Specification for Wire-cloth and Sieves for Testing Purposes
E 276-03	Particle Size or Screen Analysis at No. 4 (4.75 mm) Sieve and Finer for Metal Bearing Ores and Related Materials (including wet methods)
E 389-03	Particle Size or Screen Analysis at No. 4 (4.75 mm) and Coarser for Metal Bearing Ores and Related Materials (including wet methods)
E 463-03	Silica in Fluorspar by the Silico-Molybdate Visible Spectrometry Method
E 815-04	Test Method for Calcium Fluoride in Fluorspar by Complexometric Titration
E1638-94(2004)	Standard Terminology Relating to Sieve Analysis

* Available from <http://www.astm.org>.

described by temperature–composition diagrams (phase diagrams) and property–composition diagrams. It is convenient practice to use index values to describe composition requirements of a given process. Thorough discussions of the properties of metallurgical slags can be found in several references (Derge and Tenenbaum 1951; Rosenqvist 1974; Turkdogan 1983; Elliott 1984; Lankford et al. 1985; Mills and Keene 1987).

Properties of Slags

Melting Point

The melting point of pure lime is higher than process temperatures during smelting of iron ores or refining of steel; however, when lime is added to other components, such as silica, the melting point is lowered and a liquid phase forms. This phenomenon also is used in multicomponent systems. In most systems, there typically are more than two components, and interactions between components become complex. It is customary to represent these complex interactions on ternary, or 3-component, composition diagrams. Phase diagrams for many systems, including those in ironmaking, steelmaking, and nonferrous smelting and refining, can be found in a series of publications: *Phase Diagrams for Ceramists* (Levin et al. 1956–1969) or *Phase Equilibria among Oxides in Steelmaking* (Muan and Osborn 1965).

Iron blast furnace slags are represented in a $\text{CaO}\cdot\text{SiO}_2\cdot\text{Al}_2\text{O}_3$ ternary system. Typical iron blast furnace slag contains 32% to 42% SiO_2 ; 7% to 16% Al_2O_3 ; 32% to 45% calcia (CaO); and 5% to 15% MgO (Lankford et al. 1985). Slag compositions vary significantly from one country to another depending on the chemistries of the raw materials available (Blattner 1992).

Iron blast furnace slag is controlled to maintain a composition with about 10% Al_2O_3 (some practices contain greater amounts) to achieve a relatively constant melting point and to maintain slag liquid over a wide range of lime and silica combinations. The melting point is typically 1,400°C to 1,500°C. Ferrous iron reacts with silica at much lower temperatures than calcia and alumina, and local melting can occur in the lower part of an iron blast furnace shaft. One purpose of flux in fluxed pellets is to avoid early melting that results from the formation of iron silicate (Fe_2SiO_4 or fayalite) by preferentially reacting silica in the pellets with lime and magnesia (Taguchi, Hanaoka, and Ikeda 1980; Ranade 1992). In nonferrous smelting, iron silicate slags, which melt near 1,200°C, are formed.

Viscosity

Silica can form complex silicate networks in the molten state. These networks comprise chains of silica molecules that result in very viscous flow conditions. Because silica also melts at a high

temperature, separation and movement of silica is difficult. The addition of high-calcium lime breaks up the silicate networks, lowers the melting point, and decreases viscosity of the slag. Addition of the basic oxide magnesia has only a small effect on viscosity and is used to minimize the variability of viscosity over a range of slag compositions; however, if sufficient lime is present to precipitate dicalcium silicate (a solid phase), viscosity will increase rapidly (Rosenqvist 1974).

In steelmaking slags, lime is added as a flux to react with silicon and phosphorus oxidized from the steel bath. The reaction of lime is sometimes impeded by the formation of a dicalcium silicate or calcium ferrite coating on lime particles. Fluorspar is added to the steelmaking vessel to aid in dissolution of lime and to reduce the viscosity of the slag. Although the precise mechanism is not known, it is thought that fluorspar attacks the coatings on the lime (Peters 1982). Fluorspar melts at 1,386°C and dicalcium silicate melts at temperatures higher than 2,000°C, but when approximately equal portions of fluorspar and dicalcium silicate are mixed, the melting point decreases to lower than 1,200°C (Levin et al. 1956–1969).

Surface Tension

Although surface tension of slag is important, it is not used often to characterize slag because of the difficulty in measuring it. Surface tension affects the wetting of both metals and refractories by slags, and this in turn affects rates at which various components dissolve in the slag and the ease of separation of slag and metal. Foaming during blowing in basic oxygen steelmaking, and also in the EAF, is affected by surface tension. Surface tension decreases with increasing silica content, with the addition of alkali oxides, calcium sulfide, and phosphoric oxide, and with an increase in temperature. Lime, iron oxide, and alumina increase the surface tension of slag (Rosenqvist 1974).

Density

Density is controlled to achieve separation of metal and slag by adjusting the proportions of components. In ironmaking, the slag density increases with increasing lime and iron contents, but it is not controlled specifically. In copper smelting, where the product is a matte with a density lower than the metal, the separation of slag and matte is enhanced by decreasing the density of the iron-rich slag by the addition of lime (Rosenqvist 1974).

Activity

The activity of a chemical species in a slag is a function of both concentration and temperature. It also determines how a particular chemical species will react with other components in a given system. Values of thermodynamic activity can predict the equilibrium in the process. Activity (a_i) is related to the more familiar concentration term expressed as the mole fraction (X_i) through the activity coefficient (g_i) by:

$$a_i = g_i \cdot X_i$$

For ideal gases, the activity is the partial pressure (p_i).

A thorough discussion on the thermodynamics of slag can be found in Derge and Tenenbaum (1951), Turkdogan (1983), Elliott (1984), Coudurier, Hopkins, and Wilkormirsky (1985), and Lankford et al. (1985). In general, activity cannot be predicted and must be measured experimentally, or the activity coefficient is predicted from slag models. Values for particular systems can be found in the previous references.

Sulfide Capacity

Slags desulfurize metals by reacting sulfur with lime to form calcium sulfide, which dissolves in the slag. The ability of slag to dissolve sulfides is expressed as the sulfide capacity (C_s), which is:

$$C_s = (\%S)(p_{O_2}/p_{S_2})^{1/2}$$

where

p_i = the partial pressure of component i (e.g., O_2 is oxygen, S_2 is sulfur).

Sulfide capacity can be expressed in terms of optical basicity (B_{OB} ; see definition in next section) and temperature as follows:

$$\log C_s = [(22690 - 54640 B_{OB})/T] + (43.6 B_{OB}) - 25.2$$

where

T = the temperature in degrees Kelvin (K) over the range 1,400° to 1,700°C (Sosinsky and Sommerville 1986).

The sulfide capacity of a slag increases with added amounts of lime, and a low silica activity (a_{SiO_2}) is desirable.

Index Values

The desired composition of a slag in a metallurgical system often is defined by index values that express the acidity, basicity, or the capacity of a slag to perform a desired function. The composition of slag is adjusted so that the flux will combine with impurities and gangue to yield a desired index value. Common index values are basicity (B) or total basicity (B_T), V-ratio, and B_{OB} .

Basicity

Basicity is the ratio of basic oxide components to acid oxide components in the slag and is defined in several ways. Because lime and silica are the most prevalent species in basic slags, the definition of basicity is often given as the lime-to-silica ratio or binary basicity (B_2):

$$B_2 = CaO/SiO_2$$

where the weight percent of the chemical species is used to compute the ratio. This ratio also is called the C/S ratio (using the first initials of CaO and SiO_2) in the manufacture of fluxed pellets. The magnesia-to-silica ratio (M/S ratio) also may be specified for fluxed pellets.

The most often-used definition of basicity in blast furnace practice is the four-component basicity (B_4), or total basicity, defined as:

$$B_T = B_4 = (CaO + MgO)/(SiO_2 + Al_2O_3)$$

Total basicity sometimes is modified to include titanium or phosphorus (P_2O_5) as acids.

V-Ratio

In steelmaking, the basicity often is referred to as the *V-ratio*, which expresses the ability of a slag to desulfurize or dephosphorize the steel. The V-ratio usually is defined as one of the following:

$$V\text{-ratio} = CaO/SiO_2$$

$$V\text{-ratio} = (CaO + MgO)/SiO_2$$

$$V\text{-ratio} = (CaO - 4P_2O_5)/SiO_2$$

Sometimes the V-ratio is synonymous with total basicity.

Optical Basicity

Optical basicity is used sometimes to characterize a slag for correlation with desulfurization (Sosinsky and Sommerville 1986;

Blattner 1992). The optical basicity is defined as follows (all quantities in wt %):

$$B_{OB} = (\text{CaO} + 1.11 \text{ MgO} + 0.915 \text{ SiO}_2 + 1.03 \text{ Al}_2\text{O}_3) / (\text{CaO} + 1.42 \text{ MgO} + 1.910 \text{ SiO}_2 + 1.69 \text{ Al}_2\text{O}_3)$$

USES OF FLUXES

Ferrous Metallurgy

Fluxes are used at various stages in the production of iron and steel. Iron used for steel production traditionally is produced in the iron blast furnace as described by Lankford et al. (1985). Studies of iron-bearing raw materials and dissections of iron blast furnace burdens have improved the high-temperature performance of the iron-bearing burdens (Taguchi, Hanaoka, and Ikeda 1980; Yamooka et al. 1980). This led to modifications in fluxing practices wherein flux was introduced to the furnaces as fluxed sinter and fluxed pellets rather than by direct charging. Another result was an increase in the use of external desulfurization of hot metal prior to steelmaking that allows greater flexibility in selection of furnace burden materials with respect to sulfur content and greater flexibility in furnace operations for controlling other furnace parameters (Stubbles 1984).

Steelmaking is accomplished in BOFs and EAFs. Modern steelmaking includes the treatment of steel in ladles for improved cleanliness, greater throughput in the steelmaking vessels, and shape control of inclusions in the continuous casting process, which now dominates over ingot processing (Szekely, Carlsson, and Helle 1989). A variety of powder mixtures and prefused slags are used as molten fluxes in the continuous casting of steel (Branion 1987).

Iron Blast Furnace

The modern iron blast furnace uses iron-bearing agglomerates, coke, and flux to produce hot metal. Flux, which is largely limestone and dolomite, provides basic compounds (calcium oxide and magnesium oxide) to the furnace charge to form slag with acid flux compounds (silicon oxide and aluminum oxide) present in the iron-bearing agglomerates and coke. Slag provides a medium to remove silica and alumina gangue (introduced with the ore and coke) and sulfur (introduced with the coke). To reduce impurity levels, hot metal produced from blast furnaces is treated further in transport vessels and in subsequent steelmaking operations, which also require the formation of slag.

Limestone and dolomite flux used in the blast furnace is added as 25- to 75-mm-sized lumps or is added to iron-bearing agglomerates and charged to the furnaces as fluxed pellets or fluxed sinter. Agglomerates are large particles formed from smaller ones, which are either fused at high temperatures or bonded at low temperatures to form material that is handled easily and transported with minimal degradation. Limestone and dolomite are proportioned to the silica and alumina in the agglomerates; the ratio is expressed as the basicity. For fluxed pellets, basicity is calculated as the C/S and M/S ratios, which reflect only the major components. A comprehensive overview of raw materials used in blast furnaces was published by Ranade (1992).

To achieve a fluid slag with adequate capacity to remove sulfides, total basicity (or four-component basicity) of iron blast furnace slags is typically between 1.05 and 1.15, although ratios as low as 0.9 and as high as 1.4 are reported (AISI 1989). Typically, fluxed pellet basicities are between 0.7 and 1.7, and sinter basicities are between 1.7 and 4.0. When the basicity of agglomerates is higher than the basicity of the furnace, siliceous materials are added to match the required furnace slag basicity. Coke ash furnishes silica to the furnace, but an additional siliceous material may be required.

Basicity of agglomerates is selected for specific reducing and melting properties that improve furnace operation. Higher basicities are necessary for sinter when its primary function is to provide calcined flux to the furnace. Melting of the sinter because of very high basicities can be a problem when dicalcium silicate forms.

With the emphasis on consistent quality, lower-cost hot metal, and high productivity from blast furnaces, improvements have been made in the type of burden and in the characteristics of agglomerates. To minimize heat loss during slag removal from the furnaces (which requires the burning of expensive coke), the trend is to lower slag volumes (actually, slag mass per unit of hot metal produced). Lower slag volumes are a result of using agglomerates with low amounts of gangue and using low ash coke, thereby decreasing limestone and dolomite consumption. Slag removal cannot be independently controlled, because slag is removed with the hot metal during tapping; other factors such as furnace size and design can affect slag volumes. There are also some economic tradeoffs; for example, less expensive high-sulfur coals may be available for making coke, which may offset the cost of using more flux.

The amount of flux charged directly to blast furnaces varies widely depending on amounts charged in fluxed agglomerates. The majority of blast furnaces in the United States operating with fluxed pellets and/or fluxed sinter require an additional amount of flux of 10 to 50 kg/t of hot metal. Those not using any fluxed burden materials are charging 100 to 250 kg/t (AISI 1989). Typically, 225 to 275 kg/t is normal, but many modern furnaces approach 200 kg/t. Some furnaces have reached 150 kg/t under special circumstances, while some are much higher (AISI 1989; Blattner 1992). With increased use of external desulfurization (described in the next section), lowering flux levels become a function of furnace operation. A typical blast furnace skip charge, for example, could contain 900 kg of pellets, 650 kg of fluxed sinter, 25 to 100 kg of recycled steelmaking slag, and 50 kg of dolomite, depending on the chemistry of individual materials used (Lankford et al. 1985).

The presence of alkali metal oxides (e.g., sodium and potassium in particular) in the blast furnace can lead to operating problems such as coke degradation and the formation of scaffolds, or buildups, on furnace walls. Scaffolds can greatly reduce permeability, causing damage if they break loose. Alkali metal content in the furnace is regulated through the selection of raw materials and through the control of slag basicity (Sciulli 1992). Alkali removal is greatest with slags of low basicity; 60% to 80% of the alkali input is typically removed with the slag.

External Treatment of Hot Metal

In the United States, external treatment of hot metal, or pretreatment prior to steelmaking, is done most often for desulfurization. Performed in transfer cars or ladles, this treatment controls sulfur input and reduces slag requirements in steelmaking, allows the use of higher-sulfur raw materials in the blast furnace, and produces low-silicon hot metal (Stubbles 1984; Szekely, Carlsson, and Helle 1989). Magnesium, lime, and fluorspar are common reagents used for this. Limestone, calcium carbide, coke, sodium carbonate, salt-coated magnesium, and aluminum also are used sometimes; consumption is on the order of 4 to 7 kg/t except for salt-coated magnesium, which is added at 0.5 kg/t (Szekely, Carlsson, and Helle 1989; Cameron 1992). The thermodynamics of the process along with case studies are described by D'Orazio (1984), Dukelow (1984), and Pehlke (1984).

Simultaneous desphosphorization and desulfurization is accomplished with soda ash (sodium carbonate) or lime if the metal is low in silicon (Szekely, Carlsson, and Helle 1989). Sodium carbonate (Na_2CO_3) reacts with sulfur, silica, and phosphorus to form

sodium sulfide (Na_2S), sodium silicate ($\text{Na}_2\text{O}\cdot\text{SiO}_2$), and sodium phosphate ($3\text{Na}_2\text{O}\cdot\text{P}_2\text{O}_5$) in the slag. An advantage of this process is that sodium carbonate can be recovered and recycled; however, high refractory wear is typical (Yamamoto, Kajioka, and Nakamura 1980).

Oxygen Steelmaking

In blast furnace steelmaking, steel is produced from hot metal by oxidizing sulfur, phosphorus, carbon, silicon, and other impurities so that they will enter the slag or gas phases, thus separating from the metal phase. The basic oxygen process (BOP) oxidizes impurities in a BOF when the hot metal comes in contact with oxygen. Oxidized impurities rise to the top of the hot metal and are absorbed in a slag, which is formed from lime and dolomitic lime with the addition of other compounds such as fluorspar to improve fluidity. Fluorspar (calcium fluoride) is added in amounts of 2 to 10 kg/t (Peters 1982), either as lump or gravel-sized material, or as briquettes made with about 15% fluorspar fines combined with slag residues from the BOF. The amount of added flux usually is proportioned to the target silicon content by the V-ratio. The V-ratio typically is 2.5 to 4.0 (Peters 1982). The reader is referred to Boynton (1980) and Oates (1998) for the use of lime in steelmaking.

The amount of flux added depends on the silicon, sulfur, and phosphorus content of the metals, and the purity of the flux (Lankford et al. 1985). Typically, 40 to 100 kg of lime per ton of hot metal and 10 to 30 kg of dolomitic lime per ton of hot metal are added to the BOF (Peters 1982; Lankford et al. 1985). By decreasing the silicon content of the hot metal and by lowering the manganese content, the amount of lime required in steelmaking has steadily declined. Increased use of scrap, along with external desulfurization, resulted in lower flux consumption in steelmaking. Typical steelmaking slag now contains the following: 10% to 20% SiO_2 ; 40% to 50% CaO ; 10% MgO ; 15% to 20% iron (mixed oxides); 2% to 5% Al_2O_3 ; and 10% manganese oxide (MnO) and other oxides. Iron oxide content depends on carbon levels attained in the metal; it generally increases with lower carbon levels.

A second function of flux in steelmaking is to provide slag that is neutral with respect to the lining of the steelmaking vessel. The refractory lining in basic steelmaking typically is magnesia brick. To help prevent erosion and dissolution of magnesia brick, 5% to 12% magnesia is maintained in steelmaking slag (Boynton 1980; Peters 1982; Lankford et al. 1985). This also aids in controlling the slag viscosity. Solubility of magnesia is greater in acid slags as the V-ratio decreases. The effect of magnesia on phosphorus removal is questionable.

Electric-Arc Furnace Steelmaking

EAFs are used to make steel and ferroalloys from direct reduced iron, scrap, other ferroalloys, and alloying elements. Oxidation is accomplished by the injection or addition of iron oxide either as mill scale or iron ore. Carbon is added as coke, used carbon electrodes, or coal; and lime is added as flux. In the EAF, both oxidation and reduction processes are used to achieve the necessary purification of the metal and a high retention of alloying elements. In alloy steels, many components are oxidized readily and will report to the slag in an oxidizing environment, but they can be recovered in a subsequent reducing environment. Modern practice for carbon steels is primarily single stage followed by ladle metallurgy. In the past, double-slag, and so-called slag-and-a-half practices followed by ladle metallurgy were used (Reebel 1950; Sharp 1967; Peters 1982; Lankford et al. 1985). In single-slag practice, after the meltdown, oxidizing slag is held in the furnace, and steel is removed and further treated in a ladle. In double-slag practice, slag

and metal are held in the furnace while slag composition is adjusted. In either practice, alloy additions are made prior to the second stage. In slag-and-a-half practice, the first slag is removed, and a lime-fluorspar slag is added to the electric furnace (Lankford et al. 1985).

For oxidizing slags, limestone can be added, but calcined lime and dolomitic lime are used most often for slag formation. Using calcined materials reduces energy consumption compared to using uncalcined fluxes. To protect refractories and to improve power efficiency, limestone and coke are added in some practices to help create a foaming slag. Lime and dolomitic lime also are added to protect furnace refractories. Lime addition ranges from 15 to 50 kg/t (Boynton 1980). Other slag-forming ingredients are fluorspar, silica sand, crushed coke, and aluminum. During melting, oxidation of carbon to gas (CO_2) occurs, and the oxidation of phosphorus, silicon, manganese, and chromium allows their removal to the slag. The V-ratio is maintained over 2.5 in the meltdown state; a range of 2 to 4 is typical (Lankford et al. 1985). Basicity depends on the amount of silica in the charge and in the added flux. Iron oxide content in the slag is inversely related to the carbon content in the bath, as in oxygen steelmaking. An oxidizing meltdown slag might contain 40% to 50% CaO ; 12% to 20% SiO_2 ; 5% to 35% iron oxide (FeO); 3% to 10% Al_2O_3 ; 2% to 12% MgO ; and 5% to 15% MnO (Peters 1982; Lankford et al. 1985). Generally, 40% to 50% CaO is required for effective sulfur removal (Lankford et al. 1985).

Although not used often, the second stage in a two-stage furnace practice is accomplished in a mildly reducing slag in a ladle. There, a basic, nonoxidizing $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ slag is built up from additions of lime, dicalcium aluminate, and aluminum. During the second process stage, metal oxides in the slag are reduced and sulfur enters the slag as calcium sulfide (particularly in low iron-oxide slags). In the double-slag electric-furnace practice, a finishing or deoxidizing slag is formed by reacting coke with lime to form a calcium-carbide slag. High-purity coke and lime are desirable. Fluorspar equal to about 10% of the lime sometimes is added to increase reaction with lime and increase fluidity (Sharp 1967). Silica is added sometimes, and alumina can be added in place of fluorspar. The slag quantity is generally about 2% to 3% of the metal. Typical reducing slag might contain 55% to 70% CaO ; 15% to 25% SiO_2 ; 1% to 3% Al_2O_3 ; 3% to 12% MgO ; and 0.5% to 2% FeO and MnO (Peters 1982).

Ladle Metallurgy

Reagents are added to liquid steel in the transfer ladle for additional refining to remove sulfur, reduce metallic oxides, and condition the slag prior to casting. Additions also are made for alloying and for shape control of inclusions in the cast product. Reagents similar to those for hot metal desulfurization are used. The reagents are added at the top of the ladle or injected. Metallic elements can be added in the form of wire. Typical reagents are magnesium, lime, alumina, aluminum, fluorspar, calcium carbide, calcium-silicon alloy, and prefused dicalcium aluminate (calcium-aluminate). Magnesium is often added in combination with lime. Typical addition rates are 1 to 5 kg/t (Szekely, Carlsson, and Helle 1989). Calcium-aluminate increases deoxidation of steel and has a high capacity for sulfides (Turkdogan 1985). An exothermic synthetic calcium-aluminate mixture comprising 58% dry lime, 30% hematite, and 12% aluminum powder might be added at tap (Gilbert, Monos, and Turkdogan 1988).

Continuous Casting

Fluxes used during the continuous casting of steel and during bottom pouring of ingots often are referred to as *mold powders*. These

are either mix tures of co mpounds or fused synth etic slags formulated to do the following:

- Provide thermal insulation and prevent solidification in the mold
- Prevent oxidation
- Absorb oxide inclusions
- Lubricate at high temperature
- Maintain uniform heat transfer

Mold powders are important for the following physical properties: flowability, melting rate, viscosity, crystallization temperature, inclusion absorption capacity, and insulation characteristics. Mold powder selection is critical because the powders can interact with the metal (Bommaraju 1991).

Mold fluxes are largely silica-based with additions of lime, alumina, fluorspar, alkali metal oxides, and carbon, and are used both as raw mixtures (synthetic flux) and in premelted and sintered forms. More recently, mold powders are fused and spheroidized to form a well-behaved flowable powder to facilitate automatic feeding and uniform melting in the casting mold. Particle sizes range from granules finer than 10 mesh (1.5 mm) down to powders with 90% finer than 200 mesh (0.074 mm). Typical mold fluxes contain 17% to 56% SiO_2 ; 2% to 45% CaO ; up to 25% Al_2O_3 ; up to 15% fluorine (F_2); up to 10% iron Fe_2O_3 ; up to 20% borate (B_2O_3); up to 25% alkali metal oxides (Na_2O , K_2O , lithia [Li_2O]); and up to 30% carbon (C). Amounts vary widely in order to obtain the desired effect. Basicity (CaO/SiO_2) typically ranges from 0.65 to 1.67. Consumption of mold fluxes is 0.3 to 0.8 kg/t in continuous casting, and 1 to 3 kg/t in ingot casting (Branion 1987; McCauley and Koul 1987).

Nonferrous Metallurgy

The use of fluxes in nonferrous smelting is described in depth in Rosenqvist (1974), Moore (1981), Turkdogan (1983), and Habashi (1986). Nonferrous slags are based largely on the formation of iron silicate rather than calcium–aluminum silicate as in ironmaking and steelmaking. Typical nonferrous slag contains 30% to 55% FeO , 30% to 45% SiO_2 , and less than 10% CaO , although variations occur depending on the system. Rosenqvist (1974) and Coudurier, Hopkins, and Wilkomirsky (1985) present phase diagrams of typical nonferrous systems that show the compositional ranges of slags. In copper smelting, silica is the predominant flux, but lime also is added to modify slag viscosity and density.

Limestone is used in small amounts to aid in refining metallic copper, lead, zinc, tin, and antimony (Boynton 1980). Although limestone flux purity and particle size are similar to that used in ironmaking and steelmaking, high-calcium limestone is used most often. Both high-grade siliceous materials and lower-grade siliceous ores are used as fluxes along with limestone. An overview of the technology applied to smelting and refining copper, lead, nickel, and other nonferrous metals was published by Peacey (1989).

Copper

Copper occurs as oxide and sulfide minerals, and recovery of copper from sulfide ores is by smelting. Many copper–sulfide ores contain iron that must be fluxed, and typically silica is used to flux iron and form an iron–silicate slag (fayalite). During smelting, sulfur combines with copper and some iron to form a copper–iron sulfide matte, which is separated from the slag. The matte is converted to metallic copper by oxidation, consequently removing iron and sulfur; copper is further refined to remove impurities (Moore 1981; Turkdogan 1983).

Although copper smelting is done in bath processes and flash-smelting furnaces with oxygen enrichment, flash smelting is the predominant method practiced today (Peacey 1989). The older, reverberatory–furnace practice is described in Anderson (1961), Fowler (1961), and Nicholson, Lockridge, and Beals (1961). Electric-furnace smelting of copper sulfides is reported in detail along with other smelting processes by Barth (1961), Floyd, Grave, and Lightfoot (1980), and Phelps (1991). Slags in reverberatory–furnace smelting, flash smelting, and other processes are similar; however, the Mitsubishi continuous-smelting and refining process differs in that a calcium–ferrite slag is used in the converting furnace.

Copper-bearing concentrates often contain 5% to 10% silica. About 5% silica is added as either pure silica or ore; if additional silica is necessary, it is obtained from recycled converter slag that was used to make copper metal from the matte. Lime is added to break up silicates, take up excess silica from aluminosilicates, and reduce the viscosity of the silica-rich slag. Typically, 3% to 10% limestone or lime-bearing mix is added. A typical smelting slag contains about 30% to 45% FeO ; 30% to 40% SiO_2 ; 5% to 10% Al_2O_3 ; 2% to 6% CaO ; and 2% to 4% MgO (Watanabe, Okada, and Muto 1980). The ratio of slag to metal varies, but it is in the range of 0.6:1 to 1.5:1.

One problem in the recovery of copper is the tendency to form magnetite in the converters, although a certain amount of magnetite is required for high-copper recoveries. Magnetite melts at a temperature higher than either smelting or converting temperatures; has a low solubility in slags and matte; and does not form a silicate because much of the silica present is tied up in other forms. Some free silica is added to combine with magnetite as iron silicate, but the excess silica will react with basic furnace brick. The silica is often of very high purity—greater than 90% SiO_2 (Fowler 1961; Floyd, Grave, and Lightfoot 1980; Watanabe, Okada, and Muto 1980). Siliceous slags are normally used; however, Turkdogan (1983) and Chaubal et al. (1989) have reported that lime-based slags have a lower viscosity; have a higher solubility for magnetite; separate more easily from the matte; and remove arsenic, antimony, and bismuth more efficiently than siliceous slag.

In converters, flux particle size is in the 6 × 25 mm range. Although coarser flux is difficult to inject and to dissolve, finer flux tends to float on the bath and is also a source of dust (Anderson 1961). In the Siros melt process, limestone flux was 5 to 10 mm in size (Floyd, Grave, and Lightfoot 1980).

Lead

Lead is processed by a number of older techniques including sintering followed by smelting in the lead blast furnace, electric furnace, or Imperial Smelting Process (ISP). Several newer direct- and flash-smelting methods such as Kivcet, Outokumpu, and QSL are being utilized also (Castle et al. 1989; Pickard and Crawford 1989). In the blast furnace and ISP processes, lead–sulfide ores are roasted to form lead–oxide sinter, which is charged with limestone and coke to the lead blast furnace or the Imperial Smelting Furnace (Moore 1981). In the latter, lead is collected in the furnace bottom where it separates from slag, while zinc vapor exiting the top is condensed. In the direct- and flash-processing methods, lead is partially or totally oxidized into the slag, then the slag is treated in an electric furnace with carbon (coal or coke) to reduce oxidized lead into lead bullion (Turkdogan 1983). Copper is removed from lead by adding sulfur and by several other processes. Further refining is accomplished by oxidizing impurities with air, lead oxide, sodium hydroxide, or sodium–nitrate flux, and by electro-refining (Moore 1981; Peacey 1989).

These slags are complex. The following is a typical lead blast furnace slag composition (Grant 1980):

- 2% to 12% zinc oxide (ZnO)
- 20% to 25% FeO
- 1% to 2% ferrous iron (Fe_3O_4)
- Up to 2% litharge (PbO)
- 16% to 19% CaO
- 26% to 31% SiO_2
- 5% MnO
- 10% Al_2O_3
- 1% to 2% CaS
- 5% to 10% MgO

Nickel

Nickel ores occur as both sulfides and oxides. Sulfide ores often contain copper-iron sulfides in association with nickel-iron sulfides. Processing of sulfide ores is accomplished in reverberatory or flash-smelting furnaces and horizontal converters (Moore 1981; Pickard and Crawford 1989); flash converting also is used (Phelps 1991). Copper and nickel sulfides are separated from the matte by crystallization, grinding, and froth flotation; then copper and nickel sulfides are refined further. In some nickel ore smelting, slag formation is complex because of the presence of MgO in various silicate minerals. The slag is typically iron- and silica-rich, but with elevated MgO levels. MgO increases the melting point, allowing olivine, $(\text{Mg,Fe})_2\text{SiO}_4$, to crystallize out of the melt. This can be countered with silica and lime addition; lime decreases the viscosity of the melt (Davey, Segnit, and Boow 1980).

In New Caledonia, in the South Pacific, an oxide ore comprising a nickel-bearing hydrated silicate of iron and MgO contains 37% SiO_2 ; 2.2% Al_2O_3 ; 23% MgO; 20% Fe_2O_3 ; 2% Cr_2O_3 ; 0.3% CaO; and 2.2% nickel (Ni). It was sintered with gypsum and smelted in a blast furnace to an iron-nickel matte. This was treated further in a converter to remove iron (Thurneysen, Szczeniowski, and Michel 1961; Habashi 1986). At the now-closed smelter at Riddle, Oregon, garnierite, a magnesium silicate containing alumina, was smelted. The ore contained 25% to 38% MgO; 45% to 55% SiO_2 ; 1% to 3% Al_2O_3 ; 1% to 2% CaO; 8% to 15% Fe; and 1.5% Ni. In the Uginé process, silicon as ferrosilicon (FeSi) was used as the reductant, and the silica that formed was removed in the slag. Phosphorus was removed by oxidizing the bath with iron ore in the presence of a lime-rich slag. The metal was further refined with slag containing lime and fluorspar (Coleman and Vedensky 1961).

Tin

High-grade tin-oxide concentrate is smelted in reverberatory and electric furnaces, and low-grade concentrate is smelted in blast furnaces, kilns, and horizontal furnaces (Castle et al. 1989). In the first stage of a two-stage process, part of the oxide is reduced to metal with the formation of a ferrous-silicate slag containing a small amount of lime and unreduced tin as a tin silicate. First-stage slags typically contain 30% to 40% SiO_2 ; 15% to 25% FeO; 5% to 15% CaO; and 5% to 25% SnO_2 . In the second stage, tin silicate is reduced by iron metal to form iron silicate and an impure tin, which is recycled. Second-stage slags from Southeast Asia typically contain 24% to 28% SiO_2 ; 9% to 11% Al_2O_3 ; 20% to 22% CaO; 12% to 20% FeO; 2% to 6% MgO; and impurity metals (Habashi 1986).

ECONOMIC FACTORS

Because the iron and steel industry is a large consumer of flux, consumption of limestone and dolomite is influenced strongly by steel-

making. The USGS reports that the United States enjoyed a long economic expansion that lasted from 1991 until March of 2001, followed by a short recession of about eight months. Shipments of steel products grew for six consecutive years until 1998, increased slightly in 1999 and 2000, and then dropped during the recession of 2001. Steel consumption actually peaked at 120 Mt in 2000 and decreased to 107 t in 2002, the lowest consumption since 1995. Growth in U.S. economic output in 2002 was projected as 2.4% or less (Fenton 2002).

In the steel industry, low-priced imports continue to affect domestic steel production—amounting to 30% of U.S. consumption. During the period from 1998 to 2002, 35 steel companies filed for bankruptcy protection (Miller 2002b). The crisis in the steel industry continued in 2003 and was reflected in the fluxstone industry as well. In 2004, rising consumption in China and an upturn in the economy caused a significant increase in steel production.

The market for limestone and dolomite greatly influences the pricing of fluxstone because it is part of the much larger crushed stone industry; however, fluxstone purity is an important consideration that limits the selection of sources. According to the USGS, 71% of crushed stone was limestone and dolomite, but only 14% was for the chemical and metallurgical industries. About 20% of limestone and 7% of dolomite was used in the chemical and metallurgical industries. Because less than 5% of this is used as flux in the chemical and metallurgical industries, overall flux usage is less than 1% of the crushed stone industry. Consequently, fluxstone use is not followed closely as a separate commodity (Tepordei 2002a).

In 2002, imports of foreign pellets amounted to 17.4% of U.S. blast furnace consumption. Major sources of pellets were approximately one-half from Brazil and one-half from Canada (Kirk 2002). Greater importation of pellets into the United States from Brazil is limited at present only by the cost of transportation to inland steel mills. The proportion of fluxed pellets, if any, was not indicated.

Because limestone, dolomite, and silicate fluxes are plentiful, foreign trade is limited to the boundary regions between countries. Imports and exports are inconsequential in the overall usage patterns at present; however, fluorspar, which is used at a rate of up to 10 kg/t of steel, is almost entirely imported because of high domestic production and transportation costs (USBM 1991). Metallurgical fluorspar imports and domestic consumption were about 51,000 t in 1998, with 70% from China; 20% from South Africa; and 10% from Mexico; almost the reverse situation of 15 years ago when Mexico was the largest source (Hodge 1998; Miller 2002a). In 2002, the U.S. government placed various quantities up for sale from the National Defense Stockpile, but there were no buyers, a situation that continued into 2003. Demand for metallurgical-grade fluorspar is continually decreasing in steel and allied industries.

Because metal consumption per capita in industrialized nations is 30 times that of underdeveloped nations (USBM 1991), worldwide potential for increased metal production and complementary consumption of flux is very large. Future shortages in mineral commodities were not predicted 10 to 15 years ago. In a review of the state of the metals industry (Davis 1989), it was suggested that consumption of ferrous and nonferrous metals would cease growing around 1960. In fact, consumption trends turned negative in the late 1980s (Davis 1989), attributed to decreasing economic growth in industrialized countries and the lessening intensity of metal use in the service and manufacturing industries. Several economists also proposed that the demand for raw materials had become dissociated from economic growth (Davis 1989). This was particularly true in Japan and the United States, where the impact was greatest on the steel industry, the largest user of flux minerals.

The implication of this negative trend was that economic recovery would not necessarily result in increased demand for metals (and hence fluxes). To stimulate further growth, the suggestion was made that new demand needed to be created, driven by market development. This changed, however, with the modernization of China and the creation of a market-driven economy there. In 2003 China's economic growth became evident, and in 2004 it was so strong that shortages in all types of raw materials were apparent, driving up prices significantly worldwide (Fortner 2004). India also is on the verge of new economic growth. Although this rate of economic growth is not evident in the United States, raw materials prices still are affected. Fluxstone is not a likely participant in this growth because of the universal availability of many of the resources. China currently is trying to dampen its growth rate to more manageable levels.

Changes in South Africa and the Commonwealth of Independent States (CIS; formerly the U.S.S.R.) during the last decade and increased trade with China have altered the supply-and-demand situation of certain minerals and steel, which potentially can affect flux consumption. Greater imports of metals from these countries by the United States will impact domestic flux production and consumption. Even with increased imports of metals and other mineral commodities, it is unlikely that any large-scale trade in fluxstone or silica flux will occur because of their relative abundance, low unit values, and high transportation costs.

Other factors that could affect the flux industry are the introduction of the North American Free Trade Agreement (NAFTA); wider use of the Internet; closure of the U.S. Bureau of Mines (USBM) and assumption of some of its activities by the USGS; continued development of alternate ironmaking technologies; and foreign ownership of U.S. iron mines and steel companies.

GOVERNMENT, ENVIRONMENT, AND HEALTH CONSIDERATIONS

Government influences mineral and metal markets through labor laws, land use and environmental regulations, trade and energy policies, and funded programs and research. In the United States, the flux industry can be affected by actions of the Department of the Interior, the Department of Energy (DOE), the Environmental Protection Agency (EPA), the Occupational Safety and Health Administration (OSHA), the Mine Safety and Health Administration (MSHA), and the Bureau of Land Management (BLM), to name a few.

Mining and quarrying have effects on the environment, particularly land use. In some instances, the crushed stone industry has developed near populated areas, causing problems with dust, noise, blasting, trucking, and so forth with its closest neighbors. Although little emphasis was placed on the environment in years past, that has changed because of increased public awareness and as the result of state and federal regulations. Environmental regulations that affect mining and quarrying include reclamation of process water and solid waste, reduction of dust and noise, and control of air and ground shock from blasting.

For updates on minerals, land-use planning, and mining law, readers should contact the BLM (<http://www.blm.gov/nhp/index.htm>). For information on mineral statistics, minerals and the environment, recycling, or mining, readers should contact the USGS (<http://www.usgs.gov>).

In 2002, tariffs on steel imports became important. To temporarily slow steel imports by increasing prices, the U.S. government introduced three years of tariffs up to 30% on some imports, under Section 201 of the 1974 Trade Act. During this time the domestic steel industry began consolidating in an attempt to become more efficient and competitive. Foreign governments objected, and the

U.S. Department of Commerce exempted 727 special types of imported steel products. It also became apparent that support for the steel industry was waning, and foreign trade cases were settled in favor of importers. In 2003 the tariffs essentially were abandoned.

Environmental regulations continue to affect the steel industry. For industrial facilities built between 1962 and 1977, EPA is developing regulations that will require limitations on SO₂, NO_x, and particulate matter emissions. Lime plants, in particular, will be affected by these emissions requirements; some have been forced to close already. The lime industry has been identified as a source of a wide range of hazardous air pollutants (Miller 2002b). Some foreign steel mills have been exposed to radioactive materials from stolen radioactive sources, and there is additional potential exposure from scrap hospital equipment. Mercury is another element that has received increased attention lately. Potential point sources are lime kilns burning coal or oil, and copper smelters, among others (Fenton 2002).

Recycling is a good source of scrap in both the iron and aluminum industries; however, consumer recycling has reached equilibrium. Because of impurities such as copper in iron, many sources of scrap are limited in use. As a result, environmental and some industry groups suggest that products be designed for recycling.

In January 2002, the U.S. government passed the Small Business Liability Relief and Brownfields Revitalization Act, which incorporated both the Brownfields Revitalization and Environmental Restoration Act and the Small Business Liability Protection Act. (Brownfield sites are abandoned industrial sites requiring environmental cleanup prior to reuse.) This act authorized funding for assessment programs and subsequent cleanup, and made specific property owners exempt from liability under Superfund laws (Fenton 2002).

FUTURE TRENDS AND OPPORTUNITIES

In the United States, the consumption of fluxes largely depends on the state of the steel industry, which historically is cyclical. During the period from 2002 to 2004, the steel industry has recovered from a depressed market (1999 to 2002) into a growth industry fueled by an economy that supports higher steel prices even as the costs of raw materials increase. On a worldwide basis, growth in China and other developing countries is driving raw materials prices higher, particularly affecting coke and iron oxide pellets. Significant merging has occurred in the industry during these times. Consolidation of U.S. steel mills is nearly complete unless additional mergers of steel companies occur. Although the steel industry enjoyed high prices and strong demand resulting from moderate growth in the economy in 2004, future downturns can be expected.

Increasing fuel costs and demands for environmental compliance will help to increase steelmaking costs, making it more difficult for domestic steel to compete. Both metal production and flux consumption will be influenced by new process technologies, recycling, and substitution (Castle et al. 1989). Trends that will increase competition for steel include the use of composite and lightweight materials in transportation vehicles; more use of high-technology devices; and miniaturization. Substitution by plastics, composites, and lightweight alloys, including aluminum, will impact the use of steel and attendant flux consumption; however, increased use of aluminum will require more fluorspar consumption. Space requirements for slag disposal and the need to contain effluent from slag dumps (to prevent undesirable elements from entering the environment) led to the development of metallurgical processes that demanded less flux for slag production.

The current blast furnace practice of using domestic iron ore pellets with a silica content of only 5% requires a blast furnace slag practice that dictates the amount of flux consumption; therefore,

further reductions in flux consumed per ton of hot metal are unlikely. The continuing trend is to use fluxed pellets in blast furnaces, although the amount of flux used in pellets from different suppliers varies widely (1% to 11%). In 1990 fluxed pellets comprised 34% of domestic pellet production (Ranade 1992). In 1993 the proportion of fluxed pellets increased to 42%, and by 2002 it had reached 66% (Kirk 2002). Recycled steelmaking slag that contains lime presently provides the additional flux needed by many furnaces. Sinter plants are useful for recycling steel-plant wastes, but environmental pressures, particularly for smokestack emissions, may prevent such recycling. The potential of converting sinter plants to lime calcination plants is being investigated.

In steelmaking, new slag functions might redefine flux requirements. These include foaming to provide a blanket over the bath to achieve post-combustion of gases, allowing adequate heat transfer, or slag splashing, to protect vessel linings. For example, at times both limestone and lime could be used in the same smelting vessel. A decrease in the consumption of fluorspar in BOF steelmaking also is likely to continue. The practice of continuous casting, which affects consumption of mold powders, is now the dominant mode of casting steel (Fenton 2002).

High fuel prices, particularly for natural gas and coke, have renewed interest in direct ironmaking and direct steelmaking processes that can use coal. Direct ironmaking very likely will require a different slag practice than blast furnace ironmaking, so flux requirements could change. Direct ironmaking processes will use coal in preference to coke, which will increase the sulfur burden. Use of lower-grade coals also could require the alteration of flux practices because of higher ash contents.

In one direct ironmaking process, iron ore concentrate is mixed with flux and coal, pelletized at low temperature, and then reduced and melted on a rotary hearth furnace. The slag and metal separate from each other during melting. Subsequent cooling and magnetic separation result in a pig iron "nugget" that can be charged to electric furnaces. The process results in the production of pig iron nodules, which are desirable as electric furnace feed. One such process has operated successfully at pilot scale. Commercial scale could be reached within the next several years (Huskonen 2001; Negami 2001). Proprietary slag modifiers and fluidity enhancers are added to enhance slag-metal separation.

The rise of mini-mills, the desire by steel producers to decrease coke consumption in order to meet environmental regulations, and increased recycling of scrap are resulting in greater use of EAFs. Although mini-mills accounted for only 6% of U.S. steel production in 1992 (Ashby 1992), in 2002 mini-mill and specialty mill production of steel increased by 8% over 2001 levels, and total EAF production exceeded 50% of total steelmaking capacity (Fenton 2002). Consequently, production from the established BOF route was less than 50% of total steel production in 2002. One mini-mill producer became the third largest domestic steel producer and would have been ranked higher except for mergers of other steel companies. If major steel producers adopt mini-mill and EAF practices, the demand for lower-silica iron sources is likely to increase, and a further decrease in flux consumption is likely as well.

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Fluxes Used in Fusion Welding and Brazing

R. David Thomas Jr. and Dan Kay

INTRODUCTION

Brazing and welding are processes for bonding two metal surfaces. Both methods may use a fluxing material to prevent the oxidation of the surfaces to be joined and to facilitate melting of the bonding metal or the metallic surfaces that are being joined. Brazing involves the use of a brazing filler metal (BFM), which is melted to form the union. The brazing process is carried out at temperatures higher than 450°C (840°F) but lower than the melting temperature of the metal to be joined, whereas welding involves the melting of the actual metal surfaces to be joined. A third process, soldering, discussed in the 6th edition of *Industrial Minerals and Rocks*, is not included here because fluxes used in soldering are generally organic and not mineral based.

FUSION WELDING

Fusion welding processes use heat to melt two surfaces, usually the edges of the same material, joining them together to form one complete surface. A clean surface and intimate contact are required to assure a successful weld. Ideally, intimate contact is achieved when the atomic spacing at the interface of the welded surfaces is equal to that of the parent material (*Van Nostrand's Encyclopedia of Science* 1968). Gas welding, in which heat is supplied by a flame, and electric arc welding are the most common types of fusion welding. In arc welding, an arc struck between the welding electrode and the base metal melts both the electrode and the base metal to form the weld.

Arc welding processes fall into several categories:

- *Shielded metal arc*, utilizing an electrode with a flux covering and a metallic core, commonly 3.2 to 6.4 mm ($\frac{1}{8}$ to $\frac{1}{4}$ in.) in diameter and 225 to 450 mm (9 to 18 in.) in length, often called “stick electrode”
- *Submerged arc*, in which the electrode is a metallic wire of similar diameter fed from coils or drums and the arc is completely submerged by a granular flux
- *Flux cored arc*, a tubular continuous wire formed from a strip which surrounds the fluxing ingredients and is subsequently drawn to diameters ranging from 1.2 to 2.4 mm (0.045 to $\frac{3}{32}$ in.)
- *Electroslag*, in which the wires are continuously fed into a molten, electrically conductive slag that covers the weld pool and fuses the sides of the adjacent thick, vertically oriented, metal plates

Each of these four welding processes depends on the use of fluxes and is described in greater detail in the next section. Several other fusion welding processes are in use, all of which depend on a heat source sufficient to melt the materials to be welded. Commonly used heat sources are an oxy-acetylene (or other fuel) flame or an electric current in which the heat is generated by the resistance to the flow of current, as in spot or seam welding. These and two other arc welding processes, gas metal arc and gas tungsten arc, are not included in this chapter because they do not make use of fluxes.

Function of Fluxes

As the term is used in the welding industry, fluxes are materials used to promote the joining of metals by fusion welding. As used in this chapter, the term applies to mineral formulations used in welding procedures in which their primary and/or secondary function (Lawrence 1983; Griffiths 1985) may be the following:

- Shielding gas formers—volatile compounds and mineral substances that, when heated, give off gases that shield the arc and weld pool from the atmosphere
- Slag formers—minerals that protect the weld metals as they both solidify by forming a molten slag when operating temperatures are reached
- Slag modifiers—minerals that control the physical properties of the slag (melting point, freezing range, conductivity, wettability, fluidity)
- Arc stabilizers—mineral compounds that, with heat, evolve elements with low ionization potential that stabilize the arc
- Deposition rate augmenters—metallic additions that increase the rate of deposition of the weld metal
- Deoxidizers—metallic additions, including iron powder and ferroalloys, that are added to remove free or combined oxygen from the molten metal in the weld pool
- Alloying agents—metallic substances added to flux formulations to enhance the properties of the weld metal
- Fluxing agents—minerals that are active in the removal of impurities from the weld

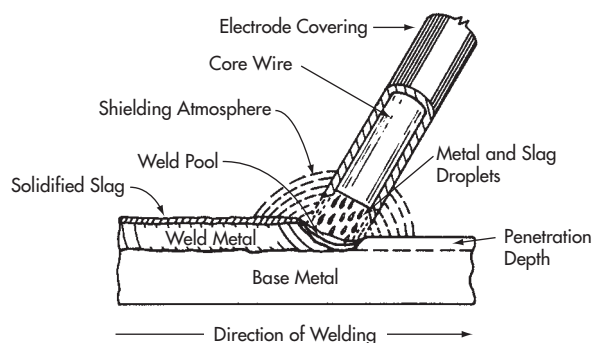
In addition, flux formulations may contain materials that serve as binders and extrusion aids in the manufacture of coated welding rods or promote agglomeration and extrusion processes in the manufacture of granular flux.

Table 1. Minerals and other materials used in arc welding fluxes

Arc Stabilizers	
Titania—Purified white mineral	
Potassium oxalate—Infrequently used	
Lithium carbonate—Infrequently used	
Gas-Forming Materials	
Cellulose—Purified wood pulp	
Wood flour—Raw wood pulp	
Limestone—Produces CO and CO ₂	
Fluxing Agents	
Cryolite—Strong fluxing agent	
Barium fluoride	
Lithium fluoride—Very effective flux	
Lithium chloride—Infrequently used	
Witherite (BaCO ₃)—Produces CO and CO ₂ as well as fluxing agent	
Fluorspar—Strong fluxing agent	
Slag-Forming Materials	
Bauxite (Al ₂ O ₃)—Raises melting temperature & viscosity	
Feldspar	
Fluorspar—Decreases viscosity of slag	
Ilmenite—Impure form of rutile (TiO ₂)	
Rutile—Unrefined TiO ₂	
Cristobalite (SiO ₂)—For strong acid slag	
Wollastonite (CaSiO ₃), Dolomite (CaMg(CO ₃) ₂)—Neutral slag formers	
Zirconia—Helps slag removal	
Magnetite (Fe ₃ O ₄)—Magnetic iron oxide	
Periclase (MgO)—Raises melting and viscosity	
Pyrolusite (MnO ₂)	
Slipping Agents	
Bentonite clay, Kaolin clay, Mica, Talc, Glycerin—Used in mineral-coated arc welding electrode manufacture to facilitate extrusion	
Binding Agents	
Sodium silicate, Potassium silicate—For extruded arc welding electrodes (potassium allows AC arc welding)	
Dextrin, Gum arabic, Sugar—Used occasionally for special situations	
Alloying and Deoxidizing Ingredients	
Ferrosilicon—Removes oxygen and oxides from weld and may add Si to weld	
Ferroaluminum—Strong deoxidizer	
Ferrotitanium—Deoxidizer and grain refiner in weld	
Ferro-aluminum-titanium—Combined deoxidizer sometimes used	
Zirconium alloy—Deoxidizer and sometimes improves slag removal	
Ferromanganese—Modest deoxidizer often used with ferrosilicon	
Electrolytic manganese—Commonly used to add Mn to weld metal	
Nickel powder, Chromium metal powder, Ferrovanadium, Ferrotungsten or tungsten powder, Other alloying ingredients—Alloying of steels and nonferrous weld metals and for surfacing weld overlays for hardness or corrosion-resisting properties	

Adapted from Linnert 1994.

Fluxes and flux formulations used in pyrometallurgical processes (and the slags produced from them) are generally referred to as acid, basic, or neutral. As with smelting fluxes (Kokal and Renade 1993; see also the Fluxes for Metallurgy chapter in this volume), acid fluxes (e.g., silica) generally form acids in water; basic fluxes (calcium carbonate and lime) form bases in water; and



Source: AWS 1991a.

Figure 1. Schematic illustration of the shielded arc welding process

fluorspar, or calcium fluoride, is a neutral substance because it is the reaction product of a base and an acid.

Minerals commonly used in welding fluxes are listed in Table 1.

Coverings of Shielded Metal Arc Electrodes

Covered electrodes are the most widely used fusion welding materials for joining metals (AWS 1991a). Because they are supplied in individual rods from 225 to 450 mm (9 to 18 in.) long, they are often referred to as “stick” welding rods. Shielded metal arc welding is often preferred for use in small welding shops because light-duty welding power sources, either transformers or rectifiers, are readily available and can be connected into 110- or 220-volt electrical outlets. Rural operators have portable, gasoline-powered generators to provide welding services where power may not be available. Improved electrode formulations and power sources allow operators to acquire the needed skills for sound welds in local training schools in a relatively short period of time. Although many newer processes have been developed over the years, the simplicity of the shielded metal arc welding process provides the primary means for small welding operations and for many maintenance functions in even the largest industries.

In the shielded arc process the arc is struck between the base metal and the filler metal exposed at the end of the self-shielded coated electrode. The heat from the arc melts both the electrode and the base metal, forming a weld pool that is protected from atmospheric contamination by a shield formed of the gases that evolve from the constituents of the electrode coating. The coating also includes appropriate slag-forming, arc-stabilizing, and alloying agents. The consumable electrode is hand-fed into the weld. The nature of the electrode covering and its function within the arc during the welding operation are illustrated in Figure 1.

The major components of the coating determine the four major types of covered electrodes: cellulosic, rutile, lime or lime-titanium, and iron powder. Some of these include two subclasses: one for use only with direct current and one that may be used with either direct or alternating current. Most arc welding with stick electrodes is done with direct current, so as to provide a steady current. Alternating current power sources are based on transformers that are adapted for welding voltages and are relatively inexpensive; however, it can be difficult to maintain the arc because of the polarity reversals of alternating currents.

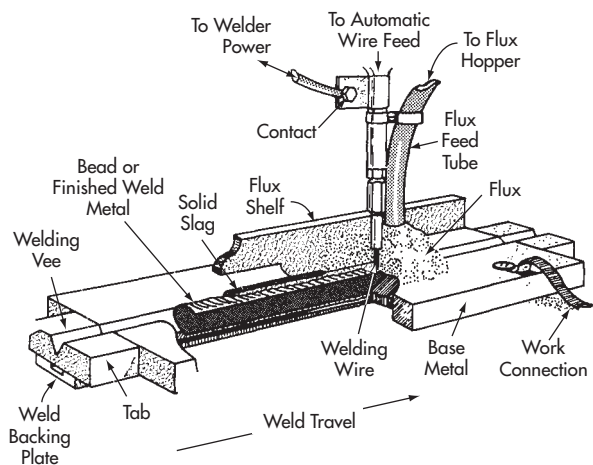
Cellulosic covered electrodes, as their name implies, incorporate considerable wood flour or other forms of refined cellulose. The combustion of the cellulose provides the shielding gas that surrounds the arc. Slag-forming materials are incorporated in the

coating to control the molten metal as it flows into the joint. For welding in other than the flat position, for example in pipeline welds where the operator must weld completely around the pipe, a fast-freezing slag is needed to hold the molten weld metal in the joint while the weld is solidifying. This is one of the principal uses of cellulosic electrodes. An operator may start the joint in the six-o'clock position (overhead) and progress upward to the three-o'clock position (vertical), thence to the twelve-o'clock position (flat); periclase is often used for increasing the fusion temperature of the siliceous slag. The deoxidizers are usually a combination of ferromanganese and ferrosilicon that contributes to the slag when the manganese and silicon combine with oxygen in the arc. Titania is present to stabilize the somewhat longer arc, allowing the operator greater flexibility when welding in all positions, either uphill or downhill. Cellulosic electrodes for use with alternating current contain potassium silicate, rather than sodium silicate, as a binder; the potassium ionizes the arc more readily, giving it stability as the current alternates between positive and negative polarity.

Rutile electrode coatings contain more than 50% rutile, providing a very stable arc. For gas shielding the electrode also contains some cellulose, along with deoxidizers, and arc stabilizers. As with the cellulosic electrodes, rutile types can be used in all positions, but the arc does not penetrate as deeply as does the cellulosic type. This allows the weld to bridge gaps more readily, and thus rutile-coated electrodes are preferred when poor fit-up conditions prevail. A dense slag that is easily removed forms uniformly over the weld surface. The se electrodes are preferred by less-skilled operators and consequently are used for a wide variety of maintenance operations. The rutile type made for use with alternating current has a very stable arc, and, with its low penetrating character, is especially suitable for sheet metal joining. Another variation of rutile electrodes contains a relatively large amount of iron powder, which fuses and adds to the weld metal.

Lime type electrodes are generally called basic type electrodes because they produce a basic slag formed largely from limestone and fluorspar. Decomposition of calcium carbonate forms carbon dioxide and carbon monoxide that shield the arc from atmospheric contamination. During manufacture with alkaline liquid silicates as binders, lime type electrodes are baked at much higher temperatures than those containing cellulose and thus produce welds characterized by low hydrogen contents. Such electrodes frequently are referred to as low-hydrogen electrodes, allowing them to be used on low-alloy steels where hydrogen cracking can be a problem. They are suitable for use on direct current with the electrode connected to the positive terminal. Unskilled operators may find it more difficult to maintain a steady arc with these electrodes; thus variations with up to 8% titania (lime-titania electrodes) have been developed to improve arc stability. With the addition of potassium silicate as the binder, this type of basic electrode can be used with alternating current, although the alternating current types are often used with direct current as well. Basic electrodes are usable in all positions, although their slags are somewhat more difficult to remove; the addition of titania and sometimes zirconia makes the slags more friable when cold and thus more readily removed. As with the cellulosic types, iron powder additions have improved the ease of operation and provide additional weld metal, and are now the most popular of the low-hydrogen types. They are used not only for carbon steels, but also for stainless steels, low-alloy steels, and even some nonferrous alloy electrodes.

Electrode coatings with very high amounts of iron powder, in which the thick coatings comprise as much as 50% of the electrode weight, are also available. The iron powder adds considerably to the amount of weld metal produced by the metallic core; thus these



Source: AWS 1991a.

Figure 2. Schematic illustration of the submerged arc welding process

electrodes sometimes are referred to as high-efficiency electrodes. The relatively thick covering and the conductivity provided by the iron powder allow the electrode to rest on the weld sea m to produce a flat groove weld. This sometimes is referred to as gravity welding.

Fluxes for Submerged Arc Welding

In some operations, submerged arc welding (SAW) is a fully automatic method performed with a continuous electrode and a layer of granular flux (Griffiths 1985; Althouse et al. 1997). The flux, composed of silicates, with or without deoxidizers and alloying agents, is fed automatically from a hopper. The arc, struck between bare filler metal wire and the base metal, melts some of the flux to form a protective layer of molten slag over the weld pool. Unmelted flux can be recovered by means of vacuum and recycled (see Figure 2).

SAW is most commonly used in large fabrication operations where the process is fully automatic. A machine supporting the wire and flux feeders is mounted on a device that travels over the weld groove, tended by an individual who positions the machine, starts the arc, and observes and monitors the operation. It may be employed to make a single weld pass in steel plates up to 2.5 cm (1 in.) thick or to make multiple passes for greater thicknesses. All welding is done in the flat or horizontal fillet position. For very thick welds or for fast travel rates, the speed of the operation is greatly augmented by the use of multiple wires fed into the joint, each energized with different electrical polarities. The fluxes selected for the operation are determined by the welding process requirements, including penetration of the weld with the base metal, the contour of the weld deposit, the ease of slag detachment, and the metallurgical properties of the weld metal.

SAW can also be done manually with a combination electrode and wire feed cable attached to an electrode holder with a small hopper for flux built into the holder (Althouse et al. 1997). The operator guides the electrode along the joint.

Submerged arc fluxes protect the depositing weld metal from the atmosphere primarily by the granular flux covering and the vapor and other gases formed during fusion in the arc. The y are supplied in three forms: prefused, bonded, and agglomerated.

Prefused Fluxes. Prefused fluxes are produced by melting the ingredients in a n electric furnace. After melting, the flux is

Table 2. Classification of submerged arc fluxes

Symbol	Chemical Constituents	Composition Limits, %
MS (manganese-silicate)	MnO + SiO ₂	50 minimum (min)
	CaO	15 maximum (max)
CS (calcium-silicate)	CaO + MgO + SiO ₂	55 min
	CaO + MgO	15 min
ZS (zirconium-silicate)	ZrO ₂ + SiO ₂ + MnO	45 min
	ZrO ₂	15 min
RS (rutile-silicate)	TiO ₂ + SiO ₂ 50	min
	TiO ₂	20 min
AR (aluminate-rutile)	Al ₂ O ₃ + TiO ₂ 40	min
AB (aluminate-basic)	Al ₂ O ₃ + CaO + MgO	40 min
	Al ₂ O ₃ 20	min
AS (aluminate-silicate)	CaF ₂	22 max
	Al ₂ O ₃ + SiO ₂ + ZrO ₂	40 min
	CaF ₂ + MgO	20 min
	ZrO ₂	22 max
AF (aluminate-fluoride-basic)	Al ₂ O ₃ + CaF ₂	70 min
FB (fluoride-basic)	CaO + MgO + CaF ₂ + MnO	50 min
	SiO ₂ 20	max
	CaF ₂	15 min

Adapted from ISO 14174:2004.

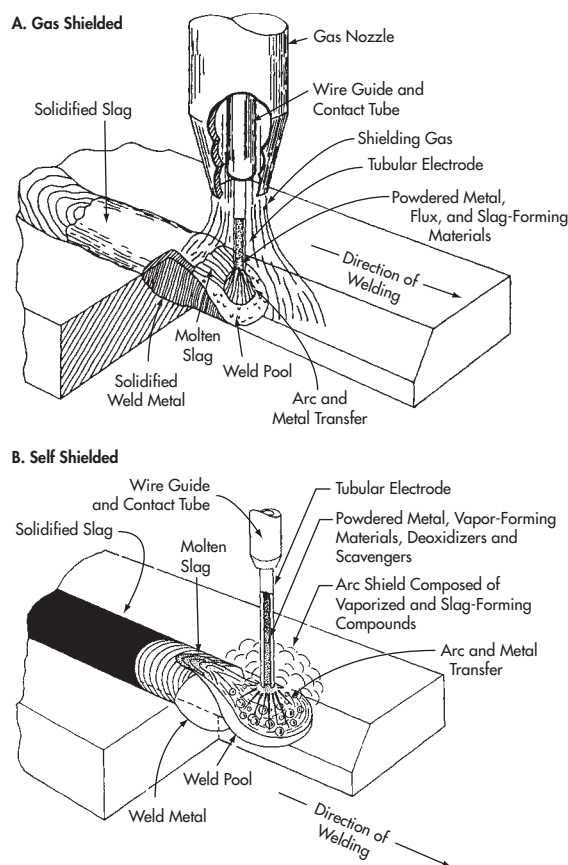
Table 3. Flux characteristics

Symbol	Type	Basicity Index	Application
CS	Bonded	0.5, strongly acid	Tolerates high current. Easy slag removal. High oxygen levels in weld.
CS	Fused	1.1, neutral	Moderately good toughness. Slag removal difficult in multiple-pass groove welds.
MS	Bonded	0.8, mildly acid	Fast weld travel speeds. Does not tolerate rusty steels.
AB	Bonded	1.1, neutral	Used only with DC power. Can tolerate rusty steels with suitable deoxidizers.
FB	Agglomerated	3.5, strongly basic fluoride	Excellent for mechanical properties, especially in multiple-pass welds. Slag removal difficult.

Adapted from Linnert 1994.

quenched and crushed. The resulting product is a glass that has good chemical homogeneity. Prefused fluxes are generally non-hygroscopic. Unfused portions of the flux can be reused without a change in the chemical composition of the flux and are suitable for high welding speeds. The greatest disadvantage of prefused fluxes is that alloy additions and deoxidizers cannot be incorporated into the flux because of the high-temperature prefusing operation.

Bonded Fluxes. Bonded fluxes are produced by binding the constituents together with potassium or sodium silicate, which results in the pelletization of the flux. The advantages over prefused flux are: the deoxidizers and ferroalloys are retained; a lower-density flux allows better protection from thicker flux blankets; and the resulting slag is removed more easily after welding. The disadvantages of bonded flux are that, during vacuuming, the composition may be altered, and they are more hygroscopic, making the welds subject to hydrogen cracking.



Source: AWS 1991a.

Figure 3. Schematic illustration of the two types of flux cored wires

Agglomerated Fluxes. Agglomerated fluxes are similar to bonded fluxes except that a ceramic binding agent is used and, thus, higher processing temperatures are required. Agglomerated fluxes tend to be slightly less hygroscopic than bonded fluxes, but their higher processing temperatures limit the recovery of deoxidizers and alloying ingredients.

Submerged arc fluxes are often classified by their principal ingredients, as shown in Table 2.

The mechanical properties of the welds produced by SAW are influenced greatly by the selection of the flux. Those fluxes that form acid slags (high in silica) generally are not used where stringent requirements for strength, ductility, or toughness are to be achieved. To characterize the nature of the slag-forming characteristics of various fluxes, the basicity index (BI) is determined using the following expression (Tuliani, Boniszewski and Eaton 1969):

$$BI = \frac{CaO + CaF_2 + MgO + K_2O + Na_2O + BaO + SrO + \frac{1}{2}(MnO + FeO)}{SiO_2 + \frac{1}{2}(Al_2O_3 + TiO_2 + ZrO_2)}$$

Fluxes with a BI less than 1.0 are called acid fluxes, those with a BI between 1.0 and 1.5 are neutral, and those with a BI greater than 1.5 are basic. Table 3 shows several types of commercially available fluxes with different characteristics and uses.

Flux Ingredients in Flux Cored Wires

There are two major types of flux cored wires: (1) those requiring an external shielding gas, usually carbon dioxide or a mixture of

Table 4. Typical flux formulations for steel flux cored electrodes

Type of Electrode	AWS Designation			
	EXXT-1, Gas Shielded	EXXT-3, Self Shielded	EXXT-5, Gas Shielded	EXXT-8, Self Shielded
Essential operating characteristics and application	Spray-transfer, direct-current electrode positive (DCEP), suitable for multiple-pass welding, medium slag	Spray-transfer, DCEP, suitable for single-pass welding of thin base metal	Globular transfer, single- and multiple-pass welding, thin slag blanket	All-position deposition, direct current electrode negative (DCEN), good low-temperature toughness
Core Ingredients	Percentage of Ingredients in Core by Weight			
Cryolite	5	5	15	5
Dolomite	15	NS*	NS	NS
Feldspar	7	10	15	5
Ferroaluminum	NS	20	NS	15
Ferromanganese	10	15	10	15
Ferrosilicon	5	10	5	10
Ferrotitanium	NS	5	NS	5
Fluorspar	10	25	25	25
Iron powder	10	NS	5	NS
Limestone	NS	5	NS	10
Magnetite	3	NS	NS	NS
Rutile	30	5	15	10
Silica	NS	NS	5	NS
Sodium silicate	5	NS	NS	NS

Adapted from Linnert 1994.

* NS = not significant.

carbon dioxide and argon; and (2) those not requiring an external shielding gas, called “self-shielded.” The schematic sketches in Figure 3 illustrate the two classes.

Two groups of mineral ingredients are used in gas-shielded electrodes: rutile and lime-fluoride. The self-shielded types generally utilize relatively large amounts of metallic aluminum powder, the aluminum providing a vapor that protects the metal deposition as well as serving as a deoxidizer. Table 4 shows the composition of the flux ingredients in four of the most common commercial types of flux cored wires.

Flux cored arc welding offers all-position capability in wire diameter under $3/32$ in.; larger sizes are generally used only in the flat or horizontal fillet position. For most welding out-of-position, the wire size most commonly used is 1.2 mm (0.045 in.). Some formulations are not readily produced in diameters that small, especially those that require large amounts of flux (which limits the diameter to that which the tubular material can be reduced). The ingredients largely determine the nature of the arc. Arc stabilizers promote spray type arc transfer and basic ingredients, such as fluorspar, promote a globular type of transfer. As in covered electrodes, flux cored wire can incorporate ferromanganese and other ferroalloys for deoxidation. The process allows core formulations with substantial additions of alloying ingredients for welding low-alloy steels. Stainless steel, nickel-, copper-, and cobalt-based alloy sheathed flux cored wires are produced for joining stainless steel, nonferrous alloys; for weld surfacing; and for a wide variety of other applications.

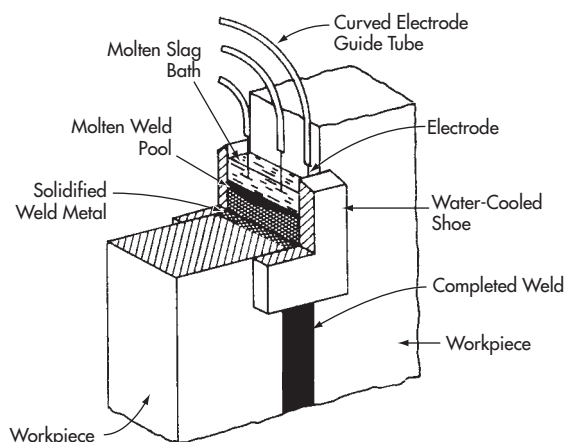
Fluxes for Electroslag Welding

Electroslag welding (ESW) is used to weld butt joints on thick metal (Griffiths 1985; Althouse et al. 1997). The weld is performed vertically, moving upward. Before the weld is started, a conductive flux material 50 to 75 mm (2 to 3 in.) thick is laid down between the two pieces to be joined. An arc is struck between one or more continuous, consumable electrodes, either solid wire or flux-cored,

and the base metal. When the flux becomes molten, the arc is stopped, but the electricity continues to flow from the electrodes, through the electrically conductive slag, to the base metal. The flux (slag) remains molten because of its resistance to the flow of electricity. The molten flux melts the base metal and the continuously fed filler to form the weld. Movable water-cooled copper shoes, one on each side of the joint, confine the molten flux, filler metal, and weld metal to the gap and are moved up as the weld progresses upward. The electrode can be oscillated automatically when very thick plates are welded. Figure 4 illustrates the ESW process.

The process depends on a molten flux that continuously fuses both sides of the welded joint and the filler wires that project into the flux bath. As with fluxes used in electric furnace refining of alloy steels, the components of the flux must have melting temperatures in a range well below that of the steel and remain fluid with minimal vapor formation at temperatures above those of the steel being welded. At these temperatures the slag must be chemically stable and electrically conductive in order to provide the thermal energy to melt both the edges of the base metal and the filler metal. If the slag becomes too conductive during the operation, an arc will form above the slag pool, thus melting the electrode wires but failing to fuse the side walls of the joint. Most commonly, fluxes are formulated with combinations of lime, alumina, and silica. Fluorspar increases the fluidity and the electrical resistivity of the molten slag; titanium and manganese oxides tend to increase the conductivity. Highly basic flux combinations are thought to give exceptionally low oxide inclusions that, as in the welded state, will have large grain sizes and relatively slow solidification rate. Post-weld heat treatment will improve greatly the weld properties of these coarse-grain welds, both in the weld metal and the heat-affected zones.

For ESW of thick stainless steels, a basic flux with less silica and more lime and fluorspar generally is preferred in order to reduce the loss of chromium in the weld metal. Alumina is needed



Source: AWS 1991a.

Figure 4. Schematic illustration of the electroslag welding process

in such fluxes to provide the desired fusion temperature range and conductivity. One typical flux composition contains 5% lime, 15% fluorspar, 5% magnesia, 20% pyrolusite, 20% alumina, and 35% silica (Linnert 1994).

On the exterior weld surfaces on both sides of the joint, the slag solidifies against the copper shoes as the weld progresses upward. The amount of slag depends on the thickness of the plates being welded and is considerably less in very thick welds. For example, flux consumption may be as much as 0.5 kg per 10 kg (1 lb per 20 lb) of deposited metal for welding 38 mm (1½-in.) thick plates, decreasing to 0.5 kg per 35 kg (1 lb per 80 lb) of weld for thicknesses of 100 mm (4 in.) or more. To maintain a constant depth of the slag bath as the weld progresses, incremental additions of dry flux must be provided.

Most ESW is accomplished with solid wire electrodes. Tubular composite wires, similar in construction to the flux cored wires previously described, sometimes are found useful for providing the needed flux additions. More often, tubular filler metals are used for welding of low-alloy steels, the alloying ingredients being incorporated as ferroalloys in the core.

Fluxes for Electrogas Welding

Electrogas welding (EGW) resembles ESW in that the weld is done vertically and moves upward, confined by movable copper shoes (Althouse et al. 1997). It differs from ESW in that a shielding gas is used, either a solid or a flux cored wire is fed automatically into the weld joint, and an electric arc is maintained continuously between the electrode and the weld pool. The flux cored wires are similar in construction to those previously described and use the same minerals to protect the arc and to form a slag. They differ principally in the amount of core ingredients because only a very small amount of slag is needed to protect the solidifying metal that forms on the exterior surfaces of the weld joint.

Specification Requirements for Minerals used in Welding Fluxes

Producers of covered electrodes, SAW fluxes, and flux cored wires for carbon and low-alloy steels are constrained by industry specifications that, in particular, limit the sulfur and phosphorus content of the weld metal. For nickel alloys, sulfur is especially harmful, and care is required in the selection of minerals used in electrode coverings and fluxes. Table 5 lists the specifications for many of

the ingredients used in welding fluxes, with particular attention given to specifications commonly imposed on sulfur and phosphorus contents.

Prospective Usage of Minerals for Welding Fluxes

The shielded metal arc welding process has dominated arc welding filler metal production for most of the past century. In terms of minerals use, coverings for electrodes represent the greatest proportion of total minerals used in all arc welding processes. Until the advent of the gas metal arc process in the 1950s (which uses no minerals and thus is not covered in this chapter) and the flux cored arc process in the 1960s, arc welding by covered electrodes represented well more than 60% of all arc welding filler metals. The growth of gas metal arc welding and flux cored arc welding processes, operated both automatically and manually, provided the flexibility that manual welding with covered electrodes had previously. Because both processes use electrodes supplied as coils, they can operate continuously, eliminating the need to interrupt the arc to change individual, separate electrode rods. In recent decades, covered electrodes have declined in volume of welding filler metals to less than 40% in the United States. This is offset, in part, by the growth of arc welding processes worldwide. Even though SAW and other flux-shielding processes use as large an amount of mineral ingredients for each unit of weld as covered electrode welding, their total proportion of the filler metal world market is less than 15%.

Health and Safety

Although arc welding is considered to be a safe occupation, it has potential harmful effects. Welders and operators must wear helmets with eye protection and guard against skin damage from radiation. The welder must be aware of the safe use of electrical equipment and also must avoid fumes evolving from the arc for some metals. This last item has been given considerable emphasis in the last 30 years as a result of litigation and efforts of industrial hygienists and government safety enforcement agencies. The evolution of manganese fumes from welding ordinary steels and certain alloys containing high manganese are of particular concern. Welding stainless steels results in the evolution of chromium fumes, especially the hexavalent form, and to a lesser extent, nickel fumes. Employers in the United States are instructed to provide protection by taking cognizance of the American National Standards Institute (ANSI) Standard Z49.1 (ANSI 1999), and the American Welding Society (AWS) Safety and Health Fact Sheets (AWS 2003).

FLUXES USED IN BRAZING

Brazing is a high-temperature joining process that takes place above 450°C (840°F) but below the melting point of either of the two parent materials that are being joined. A permanent metallurgical bond results when a molten BFM flows, by capillary action, into the closely fitting space between the two metals (brazing joint or gap) and then alloys with (i.e., diffuses into) each of the parent metals, to form a strong, leak-tight, permanent joint. A properly brazed joint will be as strong as, or stronger than, either of the parent materials being joined. In the twenty-first century, both metals and ceramics commonly are brazed. Brazing of ceramics is done primarily in either a vacuum or in inert gas atmospheres and is not discussed here because fluxes are not used in those processes.

Brazing is distinguished from other metallurgical methods of joining. If the temperature is lower than 450°C (840°F), the joining process is known as soldering, and if the temperatures are high enough to melt the parent materials, the process is known as welding.

Table 5. Specifications for welding flux components*

Minerals	Specification		
	Sulfur, % max [†]	Phosphorus, % max	Others, %
Aluminum oxide			Al ₂ O ₃ , 85 min [‡] ; TiO ₂ , 6 max; SiO ₂ , 8 max
Barium fluoride	0.10	0.01	BaF ₂ , 98 min
Cryolite	0.10	0.09	Na ₃ AlF ₆ , 96 min
Fluorspar	0.10	0.02	CaF ₂ , 96 min
Ilmenite	0.10	0.10	TiO ₂ , 65; Fe ₂ O ₃ , 30; SiO ₂ , 0.4 (typical)
Iron oxide (magnetite)	0.10	0.05	Fe, 65 min; Mn, 1.0 max; SiO ₂ , 1.0 max
Limestone			CaCO ₃ , 90; MgCO ₃ , 6; Other 4 (typical)
Lithium fluoride	0.15		LiF, 97 min; Fe, 1 max
Magnesium carbonate	0.02	0.02	MgCO ₃ , 92 min; SiO ₂ , 4 max; CaO, 1.5 max
Magnesium oxide	0.03	0.03	MgO, 96 min; Fe ₂ O ₃ , 1.5 max; Al ₂ O ₃ , 1 max; CaO, 1.5 max; SiO ₂ , 1 max
Manganese oxide	0.10	0.15	MnO, 79 min; SiO ₂ , 8 max; Al ₂ O ₃ , 8 max
Manganese carbonate	0.25		MnCO ₃ , 90 min
Nepheline syenite			Na ₂ O, 15 min; TiO ₂ , 34 min; MnO, 20 min; SiO ₂ , 15 min
Potassium manganese titanate			TiO ₂ , 35; K ₂ O, 26; MnO, 18; SiO ₂ , 15 (typical)
Potassium titanate	0.10	0.10	TiO ₂ , 66; K ₂ O, 25; SiO ₂ , 6 (typical)
Rutile	0.02	0.03	TiO ₂ , 92 min; ZrO ₂ , 2.5 max; SiO ₂ , 2.5 max
Silica sand	0.03	0.03	SiO ₂ , 98 min
Sodium fluoride			NaF, 97 min
Sodium manganese titanate			Na ₂ O, 15 min; TiO ₂ , 34 min; MnO, 20 min; SiO ₂ , 15 min
Sodium silica titanate			Na ₂ O, 20; SiO ₂ , 20; TiO ₂ , 60 (typical)
Strontium carbonate	0.10		SrCO ₃ , 96 min; BaCO ₃ , 2 max; CaCO ₃ , 1 max
Strontium fluoride	0.20	0.03	SrF ₂ , 96 min; BaF ₂ , 2.5 max
Zircon	0.06	0.07	ZrO ₂ , 65 min; SiO ₂ , 34 max

* Blank cells indicate that the mineral is not normally specified by users because commercial supplies rarely contain significant amounts.

[†] max = maximum.

[‡] min = minimum.

As metals are heated, they tend to react more readily with oxygen, forming oxides on the surfaces to be joined; this can prevent complete brazing from occurring. Two ways to prevent the occurrence of such surface oxidation during brazing are: (1) to heat the parts in an atmosphere in which there is no oxygen (such as in a vacuum, or in dry hydrogen, nitrogen, or argon); (2) to coat the surfaces to be brazed with a flux.

Role of Minerals in Brazing Fluxes

For the BFM to spread completely over the surfaces to be brazed, the surfaces must be cleaned completely and free of oil, dirt, grease, or oxides before the flux is applied. A flux is designed to keep the brazing surfaces clean and free of oxides during the brazing process. Fluxes react with any oxides formed on the metal surface during heating to remove those oxides and free up the metal surface to receive and alloy with a molten BFM. When surfaces to be brazed are cleaned properly, the BFM is said to “wet” (i.e., alloy with) and flow over those surfaces effectively. A good flux helps to make that happen whenever the brazing process occurs in an atmosphere that contains oxygen (e.g., torch brazing in air).

BFMs range widely in composition. They can be pure copper; complex alloys of aluminum; precious metals (silver, gold, or platinum); or nickel-based alloy systems. Each requires a different type of flux because the temperature at which the fluxes need to be active depends on the BFM system being used. Fluxes for aluminum brazing need to become active in the 475°C (900°F) range and fully active by 540°C (1,000°F), whereas some of the nickel-based

Table 6. Requirements for commercial brazing fluxes

AWS Class	Base Metal Used on	Temperature Range
FB1	Aluminum	540–615°C (1,000–1,140°F)
FB2	Magnesium	480–620°C (900–1,150°F)
FB3	Steel, copper, stainless steel	565–1,200°C (1,050–2,200°F)
FB4	Base metals with some Al, Ti	600–870°C (1,100–1,600°F)

Adapted from AWS 1992.

BFMs require fluxes that are most active at temperatures higher than 1,100°C (2,000°F). Brazing done with silver-based BFMs requires fluxes that are most active in the 500° to 900°C (1,000° to 1,600°F) range. See the *Brazing Handbook* (AWS 1991b) for a more thorough discussion of brazing, brazing filler metals, and brazing techniques.

Constituents of Brazing Fluxes

As mixtures of various minerals, flux formulations vary considerably because, as mentioned, they are designed to become “active” within different temperature ranges, depending on the type of BFM used. The AWS *Specification for Fluxes for Brazing and Braze Welding* (A5.31), which is used widely in industry, has changed completely the previous AWS flux designations (AWS 1992). Most commercial brazing fluxes in present use meet the current requirements of this specification (Table 6).

The minerals and compounds used in making the fluxes listed in Table 6 usually include one or more of the following (AWS 1991a):

- Borates (sodium, potassium, lithium, etc.)
- Fused borax
- Elemental boron
- Fluorides (sodium, potassium, lithium, etc.)
- Chlorides (sodium, potassium, lithium, etc.)
- Alkalis (sodium hydroxide, potassium hydroxide)

Borates

Borates, such as potassium tetraborate ($K_2B_4O_7 \cdot 4H_2O$), are used in high-temperature fluxes because they effectively can reduce oxides at temperatures around 760°C (1,400°F) and higher. Because they are quite viscous when molten, they usually are mixed with other mineral salts to lower their viscosity so that they will flow easier into the brazing joints.

Fluoborates flow well on metal surfaces and have excellent oxide-dissolving properties.

Fused Borax

Fused borax ($Na_2B_4O_7$) is used in high-temperature fluxes because it will also reduce oxides at higher temperatures.

Elemental Boron

Finely powdered boron is added to other flux chemistries to give them greater fluxing ability for higher-temperature applications and to last over longer periods.

Fluorides

Fluorides, such as potassium fluoride (KF), very aggressively reduce metal oxides and so are used in fluxes for metals containing refractory oxides of chromium and aluminum. They also increase the fluidity of the fluxes in the molten state.

Chlorides

Chlorides, such as potassium chloride (KCl), are similar to fluoride fluxes in their use, but are more effective at lower temperatures.

Alkalis

Alkalis are used sparingly because of their water-absorbing properties; however, alkali compounds, such as potassium hydroxide ($K(OH)_2$) and sodium hydroxide ($Na(OH)_2$), help to elevate the useful working temperature of the flux. Because of the tenacious nature of the oxides of aluminum, titanium, and zirconium, and because of the lower temperatures used in brazing aluminum, specialized fluxes consisting of mixtures of alkali metal chlorides and potassium or lithium fluoride are used in brazing these metals. A reaction flux containing 7% to 12% by weight of zinc chloride is helpful in brazing aluminum because of the difficulty in removing the aluminum oxide layer between the brazing surfaces.

Sources of Minerals for Use in Brazing Fluxes

Boron minerals and compounds, such as borax ($Na_2B_4O_7 \cdot 10H_2O$), boric acid (H_3BO_3), and potassium borate, are produced mainly in Southern California (primarily in the Death Valley region), Turkey (the world's largest producer), Chile, and Russia. Industrial boron compounds are recovered from both crude and refined sodium borates, from anhydrous derivatives, and from anhydrous boric acid. The largest domestic boron minerals producer operates open pit mines for tinical (crude borax) and kernite ($Na_2B_4O_7 \cdot 4H_2O$). Other producers in the same area recover potash in addition to boric acid

and other boron products by differential evaporation and solvent extraction methods from saline brines. Total U.S. production of boric oxide in 2003 amounted to approximately 536,000 t, valued at about \$275 million (Lyday 2004a).

Fluorides

The primary fluorine compounds used in fluxes for brazing include aluminum fluorides, potassium fluoride, and lithium fluoride. Major sources of fluorine are fluorite (CaF_2) in fluorspar deposits and the mineral fluorapatite, which occurs in natural phosphate rock (Fulton and Montgomery 1994). China is the world's most important producer of fluorspar (Lyday 2004b). At the present time no fluorspar is being mined in the United States, although the United States is a major producer of phosphate rock and thus of fluoro-silicic acid.

Hydrofluoric acid (HF) is made when acid grade fluorite (97% CaF_2) is reacted with sulfuric acid in a heated kiln or retort. Elemental fluorine, prepared from anhydrous hydrofluoric acid by electrolysis, reacts with all metals to form fluorides, including artificial cryolite (Na_3AlF_6), aluminum fluoride, potassium fluoride, and other inorganic fluorine compounds. Fluorosilicic acid is produced during the processing of phosphate rock, and some is converted to aluminum fluoride and cryolite.

A rapidly growing part of the aerospace/brazing industry involves the high-temperature cleaning of aerospace jet engine components in special furnaces using anhydrous hydrogen fluoride gas.

Chlorides

Practically all of the chlorine and chlorine compounds made in the United States are produced by electrolysis from sodium chloride solutions. Sodium chloride, salt or the mineral halite ($NaCl$), occurs in sea water, salt lakes, and in extensive beds of rock salt. A common mineral, halite is produced by either mining salt beds or by solar evaporation of brines in many domestic locations, including New York, Michigan, Louisiana, Utah, and other states. Potassium chloride, the mineral sylvite, occurs in salt deposits in New Mexico and Saskatchewan, and in several European and Asiatic locations.

Chlorine reacts readily with hydrogen to form hydrochloric acid; both chlorine and hydrochloric acid react with most metals to form chlorides. Hydrated aluminum chloride ($AlCl_3 \cdot 6H_2O$) is formed when aluminum hydroxide reacts with hydrochloric acid. Ammonium chloride (NH_4Cl) is formed as a byproduct from the reaction of gaseous ammonia with hydrogen chloride gas or by the reaction of ammonium hydroxide with hydrochloric acid.

In the United States, spodumene deposits in North Carolina and geothermal brines in Nevada supply the raw materials for the manufacture of lithium compounds, such as lithium chloride ($LiCl$). Lithium carbonate is the primary product of lithium chemical plants and is the compound from which all other downstream lithium products are obtained.

Cesium-based Flux Compounds

Cesium, in the forms of cesium chloride, cesium fluoride, or cesium aluminum fluoride, has been used on an experimental basis as a component of some general purpose fluxes, but such use has not met with widespread acceptance because of the high cost of cesium compounds.

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Foundry Sands

Stanley T. Krukowski

INTRODUCTION

Foundry sands, which are used to make molds and cores, have been very important to foundry workers since metal casting began hundreds of years ago. They now are used in two basic ways, either in a natural state bonded with clay or in a chemically cured state achieved with sand that, mixed with chemical resin or oil, is cured by baking or by chemical reaction.

The term *sand*, as used in foundry applications, can best be defined as material composed of granular particles of mineral matter ranging from 0.5 to 2.0 mm in diameter. Based on their origin, raw materials for foundry sand vary in grain shape, grain composition, relative surface, grain size, and grain distribution patterns. These properties, in addition to chemical analyses, sinter point, and expansion characteristics, play an important part in the choice of sand used as the base molding or core aggregate in metal casting. Different types of sand may be blended to produce specific compositions and grain size distributions.

Early raw material requirements based on silica sand were simple, but as sand/core/mold technology became more sophisticated and binder technology developed further, the physical properties of foundry sand became more critical. Silica sand is mainly quartz and, in most cases, small amounts of feldspar, mica, clay, and other common minerals. Although silica sand is still by far the most widely used base material in production of molds and cores used in metal casting, other natural mineral sands have their own unique characteristics and fill an important niche in special applications. As a result, the term *sand*, when applied to raw materials used in metal casting, logically has been extended to include granular materials composed of a group of minerals other than quartz. With increased use in advanced foundry technology, natural sands composed predominantly of zircon, chromite, staurolite, or olivine have become more than just alternate materials and now are classified commonly as sands. Therefore, foundry sands can be divided into two categories: silica sands and non-silica sands.

SILICA SANDS

Silica is the common term applied to silicon dioxide (SiO_2); the mineral name is quartz. The term *sand* has two different meanings, depending on the context in which it is used. In context of mineral composition or rock type, the term usually is understood to refer to unconsolidated quartz grains within a certain range of grain size.

In ancient rocks, granular particles (sand grains) have become cemented together to form a consolidated sedimentary rock referred to as sandstone. The term sand also is included in a continuum of particle sizes that includes other terms denoting size classification from finest to coarsest (in diameter): clay (< 0.0039 or $1/256$ mm), silt (0.0039 to 0.0625 or $1/16$ mm), sand (0.0625 to 2.0 mm), granule (2.0 to 4.0 mm), pebble (4.0 to 64.0 mm), cobble (64.0 to 256.0 mm), and boulder (> 256.0 mm).

The most common foundry sand used over the years has been silica sand. It is common, abundant, and easily mined, occurring at or very near the earth's surface. Silica sands are produced from rocks that formed under a variety of geologic conditions and are used in a number of industrial applications other than foundry sands: sand blast abrasives, fillers, glass manufacture, oil and gas proppants, refractories, and as a source of silicon.

Modes of Occurrence

Silica sand deposits occur naturally as a result of weathering and erosion of quartz-bearing igneous, metamorphic, and sedimentary rocks. The products generated from these processes are subsequently transported to the site of deposition. Disaggregated rock and mineral particles may be carried hundreds of kilometers from their source(s) by fluvial, glacial, glacioluvial, marine, and eolian processes. The composition of deposits depends on the nature of the original rocks that were eroded, the intensity and duration of weathering, the distance and agents of transportation, the manner of deposition, and postdepositional history. Deposits may be reworked by natural processes and redeposited under similar or entirely different conditions.

Silica sands accumulate along stream channels and floodplains, in lake and lakeshore deposits, and under marine conditions in seacoast environments. Geologically young deposits tend to be unconsolidated or poorly consolidated. Ancient sand bodies, which were buried under great thicknesses of younger sediments and later consolidated, are termed *sandstone*. Subsequent uplift from tectonic forces can stop sedimentation and begin widespread erosion and exhumation of previously deeply buried formations. Those that are exposed at the surface, or that have only a thin layer of overburden, can readily be mined. Cycles of repeated weathering, erosion, transportation, sorting, and deposition result in well-sorted, high-purity, quartz sandstone from which practically all heavy minerals have been eliminated.

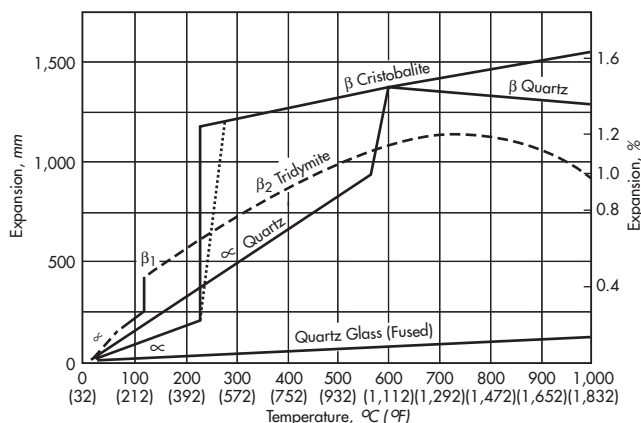


Figure 1. Thermal expansion of silica materials

Advantages and Disadvantages

Silica sand has the advantages of common occurrence and abundance, ease of bonding with organic or inorganic binders, low cost, and the ability to be reclaimed for reuse by wet, dry, or thermal methods. It also possesses certain disadvantages when used in the production of metal castings. The major disadvantage of silica sand is its characteristic high thermal expansion. This expansion causes casting quality problems and contributes to other expansion-related defects. Figure 1 illustrates the typical thermal expansion of various silica materials and depicts alpha quartz, the characteristic polymorph of silica sand, expanding at a constant rate until it reaches a temperature of approximately 573°C. As the temperature increases beyond this point, a sudden expansion takes place because of the change from alpha quartz to beta quartz. High thermal expansion requires carefully controlled additions of cushioning materials (e.g., cellulose additives) to minimize the deformation and rupture of mold surfaces in contact with molten metal. Another disadvantage is that silica sand is unable to resist metal penetration and reactions that occur in quartz when in contact with casting surfaces. These problems arise where there are reentrant angles in hot-spot areas of large iron and steel castings and, in Hadfield's austenitic manganese steel castings, when the steel contains high amounts of manganese that attack (or wet) the silica sand mold surfaces.

Classification of Silica Sands

Silica sands used in foundry practice vary in grain size distribution (Table 1), purity, structure, grain shape, and refractoriness.

Unbonded sands, which often are referred to as washed and dried silica sands, are found in many areas of the United States. Analyses of typical silica sands are shown in the top rows in Table 1. Major production in the Midwest and midcontinent comes from the St. Peter Sandstone and its stratigraphic equivalents. Medium- and fine-grade washed sands are produced in the East, particularly in Cumberland County, New Jersey. Silica sands from Nevada have been shipped to West Coast foundries. For additional sources of silica sand, refer to the chapter on industrial sand and sandstone in this volume.

Processing

Washed, graded, and dried (clay-free) silica sands are prepared for use in casting production by bonding them with required amounts of binders, additives, and necessary amounts of temper water. The

total sand mixture is prepared in the sand muller to achieve uniform distribution and dispersion of clay and additives over and around individual sand grains.

Foundry Use

Medium-grade sands are used predominantly for casting steel and heavy, gray, ductile iron; fine-grade eastern silica sand is used in making precision castings (Henderson 1983). The St. Peter Sandstone is a popular product when washed and dried because its round grain shape promotes flow and its smooth grains require less bonding material.

Bank Sands

Unconsolidated deposits with relatively small clay content (less than 5%), requiring little processing beyond drying and scalping, still are referred to as *bank sands*, although they usually are subjected to considerable processing and blending before shipment. These bank sands are sedimentary in origin and vary in purity depending on the amount of minerals and foreign materials that they contain. In many areas they have high purity and are suitable for foundry use. Table 1 shows a typical analysis of fine bank sand from New York.

Processing. Bank sands are hauled to the plant after stripping. A front-end loader dumps the sand into a hopper, and then it is conveyed to a rotary screen with 12.7-mm openings to remove roots and other organic debris. Some screened sand is dried and shipped without further processing because it meets the specifications for a system sand addition and for synthetic sand base; some is washed to produce a cleaner, more consistent product.

The sand is dropped into a surge bin to ensure a uniform feed and for subsequent washing. It is then conveyed to a tank where it is mixed with water and pumped to a scalping screen where fine roots and other organic materials are removed. Scalped sand is pumped to a deslimer to remove clay and silt, fresh water is added, and the sand slurry is either pumped to a second deslimer before going to ground storage or fed to banks of screens and separated further into fine and coarse particle sizes. Each sand grade is collected in a sump, mixed with water, pumped to a deslimer and dewatering cyclone, and stockpiled for drainage and storage. Then the sand is dried, cooled, and passed over a final scalping screen before it is conveyed to storage bins before shipment.

Foundry Use. Fine bank sand is used as a base for molding sand in medium- to small-sized, gray iron castings typical of those used in casting hardware and hand tools and for casting aluminum and copper-based alloys (Henderson 1983).

Lake Sands

The term *lake sands* refers to sands dredged from Lake Michigan or dug from dunes bordering its shore; although the dune sands were shifted by wind, they still are considered a part of the lake-sand deposit. During deposition, some natural sorting by grain size, grain composition, and specific gravity can occur. Table 1 shows a typical size analysis of lake sand. The degree of purity is the result of geologic processes and history.

Processing. In a typical lake-sand operation, overburden is stripped and a front-end loader mines the sand and feeds a hopper that discharges to a portable screen where deleterious material is removed. The hopper and screen can be moved along a field conveyor as required. Conveyor belts transport sand to the plant site for further processing or blending.

Foundry Use. Lake sands in large quantities are used in the production of automotive and farm machinery castings (Henderson 1983).

Table 1. Typical analyses of various foundry sands

Medium-Grade Washed Eastern Silica Sand		Fine-Grade Washed Eastern Silica Sand		Midwestern Rounded-Grain Silica Sand, St. Peter's Sandstone		Silica Sand from Nevada	
U.S. Standard Sieve Size	% Retained	U.S. Standard Sieve Size	% Retained	U.S. Standard Sieve Size	% Retained	U.S. Standard Sieve Size	% Retained
20	0.4	50	0.4	40	2.0	30	0.5
30	1.6	70	5.2	50	24.0	40	7.5
40	6.4	100	14.6	70	40.0	50	19.5
50	22.6	140	23.4	100	22.0	70	42.0
70	40.4	200	25.8	140	8.0	100	18.5
100	23.6	270	16.2	200	3.0	140	10.0
140	4.6	Pan	14.4	270	1.0	200	1.5
200	0.6			Pan	0.0	270	0.5
270	0.0					Pan	0.0
Pan	0.0						
AFS* fineness #53		AFS fineness #148		AFS fineness #60		AFS fineness #57	
Fine Bank Sand—New York State		Fine-Grade Naturally Bonded Albany Sand		Naturally Bonded Molding Gravel		Lake Sand	
U.S. Standard Sieve Size	% Retained	U.S. Standard Sieve Size	% Retained	U.S. Standard Sieve Size	% Retained	U.S. Standard Sieve Size	% Retained
30	0.2	12	Trace	6	3.0	30	Trace
40	0.2	20	Trace	12	8.8	40	2.4
50	1.0	30	0.2	20	16.0	50	22.6
70	4.4	40	0.2	30	13.8	70	44.4
100	12.4	50	1.0	40	17.6	100	24.0
140	20.6	70	3.4	50	10.8	140	6.0
200	24.8	100	10.2	70	5.6	200	0.6
270	18.2	140	12.0	100	2.0	270	0.0
Pan	18.0	200	13.6	140	0.8	Pan	0.0
		270	13.0	200	0.4		
		Pan	33.4	270	0.2		
				Pan	1.0		
AFS fineness #157		AFS clay 13.4 AFS fineness #191		AFS clay 20.0 AFS fineness #29		AFS fineness #55	

Source: Henderson 1983.

* AFS = American Foundry Society.

Consumption of Silica Sands

About 27.5 Mt of industrial sand and gravel were sold or used in the United States in 2003 (Dolley 2003). Of this total, more than 19% (5.225 Mt) was molding and core sand and refractory sand. Refractory sand accounted for only 3.25% of the total foundry sand sold or used. About 83% of the foundry sand was produced in the Midwest.

NONSILICA SANDS (AGGREGATES)

Continued demand for improved cast surfaces and closer dimensional tolerances has revealed some of the physical and chemical limitations of silica sands. Specialty sands composed of materials other than silica possess properties that make them superior to silica sand for certain applications.

Nonsilica aggregates (zircon sand, chromite sand, and olivine sand) have gained wide acceptance and are used throughout the metal-casting industry for their desirable properties. Nonsilica molding media such as aluminum silicate sand and staurolite sand also possess unique properties, but their use in casting production has been on a smaller scale. Table 2 shows some of the typical properties of the nonsilica sands compared to silica sand.

Nonsilica aggregates have much lower rates of thermal expansion than silica sand (Figure 2), and their rates of expansion on heating are not affected by phase-change relationships like

those exhibited by quartz. Expansion-type defects are greatly reduced or, in many cases, eliminated when major nonsilica minerals are used.

Zircon Sand

Sources

Major sources of zircon ($ZrSiO_4$) sand are heavy mineral sands in Australia (east and west coasts), Brazil, India, Sierra Leone, Republic of South Africa, and the United States (north-central Florida). Heavy mineral suites commonly consist of ilmenite, leucosine, tourmaline, spine l, kyanite, sillimanite, corundum, topaz, zircon, and staurolite. The primary products mined from these heavy mineral sands are titanium-bearing minerals. Zircon, staurolite, and aluminum silicate minerals are valuable by-products for use in foundry practices.

Mining and Concentration

The following describes a typical mining operation in a marine, dunal shoreline deposit in the southeastern United States. After stripping, a suction dredge recovers sand at up to 1,000 t or more per hour. The sand, which contains about 4% heavy minerals, is pumped to a floating wet mill where it undergoes three stages of gravity concentration using spiral separators. The wet mill produces

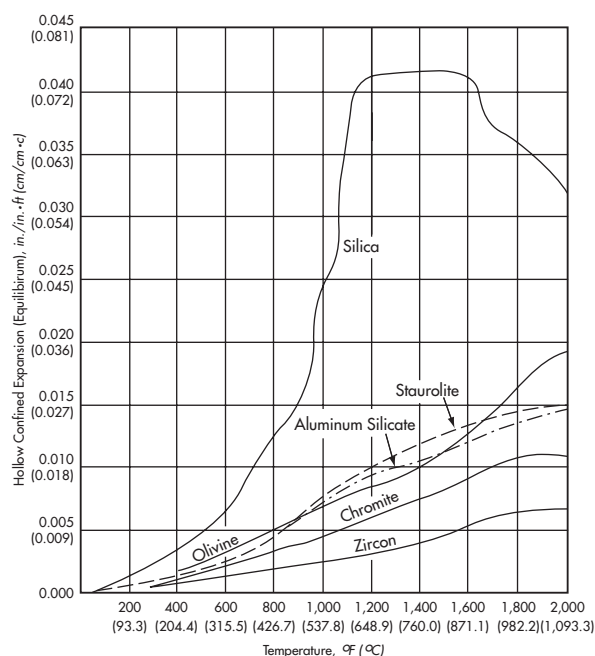
Table 2. A comparison of silica and nonsilica sand properties

	Silica	Olivine	Chromite	Zircon	Zircon-Aluminum Silicate	Staurolite
Origin	United States	United States (Washington, North Carolina), Norway	Republic of South Africa	United States, Australia	United States (Florida)	United States (Florida)
Color	White-light brown	Greenish gray	Black	White-brown	Salt and pepper	Dark brown
Hardness	6.0–7.0	6.5–7.0	5.5–7.0	7.0–7.5	6.5–7.0	6.5–7.0
Dry bulk density, kg/m ³	1,362–1,602	1,602–2,002	2,483–2,643	2,563–2,964	2,483–2,691	2,291–2,339
Specific gravity	2.2–2.6	3.2–3.6	4.3–4.5	4.4–4.7	3.2–4.0	3.1–3.8
Grain shape	Angular/rounded	Angular	Angular	Rounded/angular	Rounded	Rounded
Thermal expansion, cm/cm	0.018	0.0083	0.005	0.003	0.005*	0.007*
Apparent heat transfer	Average	Low	Very high	High	High	High
Fusion point	1,427°–1,760°C	1,538°–1,760°C	1,760°–1,982°C	2,038°–2,204°C	1,815°–1,982°C	1,371°–1,538°C
High-temperature reaction	Acid	Basic	Basic	Acid	Slightly acid	Slightly acid
Wettability with molten metal	Easily	Not generally	Resistant	Resistant	Resistant	Resistant
Chemical reaction	Acid-neutral	Basic	Neutral-basic	Acid-neutral	Neutral	Neutral
Grain distribution†	2–5 screens	3–4 screens	4–5 screens	2–3 screens	3 screens	3–4 screens
AFS grain fineness number ranges	25–180	40–160	50–90	95–160	~80	~70

Source: Kotzin 1989.

* Clay-bonded sand mixture.

† 10% or more retained on U.S. standard sieve sizes.

**Figure 2. Typical thermal expansion data of nonsilica aggregates compared with silica sand**

a concentrate averaging 85% heavy minerals with an 80% recovery. The concentrate is pumped to a land-based dry mill where the scrubbed ore is dried before undergoing various magnetic and electrostatic separations that remove titanium-bearing minerals. Tailings from the titanium separations are fed to high-intensity magnetic separators to produce a variety of by-products; zircon is the major constituent of the nonmagnetic, nonconductive fraction.

Properties

Zircon sand possesses most of the desirable properties for foundry sand, including chemical and thermal stability. The major advantages of zircon sand are

- Lowest thermal expansion of any foundry sand
- High thermal conductivity and high bulk density, which are responsible for a cooling rate approximately four times that of quartz
- Completely unwetted by molten metal
- Chemically nonreactive
- Less binder required than any other foundry sand when using chemical binders
- Compatible with all known binder systems (organic or inorganic)
- Excellent dimensional and thermal stability characteristics at elevated temperature
- pH neutral or only slightly acid

Foundry Use

Zircon sand is used as a molding medium and as core sand. When finely ground and combined with a suspending agent and a binder, zircon is employed widely as a refractory in the manufacture of core and mold washes.

Chromite Sand

Sources

The element chromium (Cr) combines with iron (Fe), magnesium (Mg), calcium (Ca), lead (Pb), copper (Cu), phosphorus (P), and sulfur (S) to form a variety of minerals. Of these, chromite (FeCr_2O_4) is the only metallic ore mineral of chromium and the only source of chromium compounds, chemicals, and foundry sand. In 2003, the International Chromium Development Association (ICDA) reported that 91.2% of the world production of chromite

ore (14.868 Mt) was consumed in metallurgy, 5.2% in chemicals, 2.8% in foundry sand, and 0.8% in refractories (Papp 2003).

Most of the world's production of chromite ore comes from South Africa, which accounts for 48%. Kazakhstan and India account for 19% and 15%, respectively. Brazil, Finland, Turkey, and Zimbabwe represent 12% of world production, and 12 other countries produce the remaining 6% (ICDA 2005). The United States has a small amount of chromite ore reserves, but more than 92% of the material has relatively high Fe and low Cr content. The reader is referred to the chapter on chromium in this volume for more detailed information.

Mining and Milling

Chromite deposits are associated with the basic igneous rocks peridotite and pyroxenite, or with serpentine resulting from the alteration of the se rocks. Most South African mines extend underground. Ore is drilled, blasted, loaded onto conveyors or mine cars, and hauled to a processing plant. Hand sorting or mechanical screening separates lumps and chips from the sand, followed in some cases by bar or rod milling to reduce the sand to American Foundry Society grain fineness number (AFS GFN) 80, and to release the gangue minerals (primarily serpentine and talc). The natural grain size of approximately AFS GFN 55 is preferred for metal casting. Chromite sand is beneficiated further by auger-type washers to remove slimes and by gravity concentration using riffling tables or spiral separators. Then the sand is stored on concrete pads where it is allowed to drain. The sand, which must contain a minimum of 45% Cr₂O₃, is assayed at this point. A turbidity test has been developed to control washing processes and to ensure production of clean sand. The sand is hauled by truck or rail before it is shipped to the United States or other places.

Finishing

At finishing plants in the United States, chromite sand is beneficiated by drying, cooling, and screening to produce grades ranging from AFS GFN 55 to 80. The sand may be washed further to less than 150 ppm turbidity for certain core operations. Quality control tests include turbidity, acid demand values (ADV), and sieve and chemical analyses.

Properties

Chromite sand was introduced to the foundry industry in the early 1960s when zircon sand was in short supply. Later, when zircon sand prices were rising, foundry workers adapted chromite sand as a substitute for zircon sand. Chromite sand is successful as nonsilica foundry sand because of its following properties:

- Excellent thermal stability
- Good heat-diffusivity characteristics
- Not easily wetted by molten metals
- Highly refractory
- Chemically nonreactive
- Low thermal-expansion coefficient

One of the major disadvantages in using chromite sand is the presence of hydrous impurities that can contribute to pinholing and blows.

Foundry Use

Properties of chromite sand, shown in Table 2, specifically fulfill some of the extreme thermal requirements of heavy, sectioned, ferrous castings. In addition, the basic nature of chromite sand makes it highly desirable when producing castings of Hadfield's austenitic manganese steel.

Olivine Sand

Sources

Olivine is a magnesium-iron silicate mineral, (MgFe)₂SiO₄. Olivine sand is produced from dunite, a rock composed predominantly of olivine. Large deposits of dunite are found in Norway, Sweden, the Commonwealth of Independent States (CIS), Austria, Zimbabwe, South Africa, and the United States. Norway is the principal producer and supplier of olivine. Additional producers include Australia, Austria, Brazil, China, Italy, Japan, the Republic of Korea, Mexico, Spain, Taiwan, Turkey, and the United States. Deposits in Washington and North Carolina furnish major amounts of olivine sand for foundry use in the United States; processing plants are located in Indiana, North Carolina, and Washington (Kramer 2004).

Mining and Milling

Olivine mining is by open-pit methods in the United States. After blasting, a drop ball breaks large lumps into particles 2 ft or smaller. Ore passes through a primary jaw crusher where it is reduced to 15 cm or smaller before it is fed to the processing plant. At the mill, the rock is reduced further to 12.7-mm particles by jaw and gyratory crushers. It then passes through a screw classifier that washes out clays and slimes. A rod mill then reduces the olivine to sand size before it is pumped to scalping screens. Oversized material returns to the rod mill and undersized material is fed to riffling tables for gravity separation of olivine from gangue, which is predominantly serpentine and talc. Tables are fed slurry of 25% solids and more water is added. Product quality is controlled by the amount of water used, the tilt of the tables, and reciprocating speeds. Olivine concentrate, representing 60% of the table feed, is pumped to a dewatering screen and then to dewatering tanks. The sand is dried before screening to produce a variety of size grades.

Properties

Olivine sand is less stable under thermal shock conditions than zircon sand or chromite sand, but its thermal expansion is much less than silica sand. The presence of hydrous magnesium silicates (serpentine) may contribute to pinholing or pock marking when olivine sand (uncalcined) is used in the production of low carbon steel castings. Olivine sand particles are less durable than other nonsilica sands, although it has comparable hardness. This may be attributed to olivine's cleavages and other physical or chemical characteristics. Olivine still has good refractory properties plus lower free silica content and strong resistance to metal attack.

Foundry Use

Olivine sand has been very successful in nonferrous casting as well as ferrous casting production where high thermal requirements are not necessary. Olivine sand is an excellent substitute for silica foundry sand, particularly for molding sand for aluminum, bronze, copper, manganese steel, gray iron, and alloy steel. Additionally, olivine's low basicity enhances bentonite's bonding properties so that clay demand is reduced (Harben 2002). The basic characteristics of olivine also make it an ideal aggregate for the production of castings of Hadfield's austenitic manganese steel.

Aluminum Silicate Sand

Sources

Along with zircon sand, aluminum silicate is a by-product of mining titaniferous, heavy mineral, beach sands. Those mined in Florida contain significant quantities of kyanite, sillimanite, and andalusite. The Republic of South Africa, the United States, France, and India account for up to 98% of worldwide sillimanite

production; andalusite production is dominated by the Republic of South Africa, France, and Spain; kyanite production comes mainly from the United States and India (Harben 2002).

Mining and Concentration

Mining and concentrating Florida beach sands and processing the various heavy mineral products were discussed briefly in the section on zircon sands. To concentrate the aluminum silicates, additional processing is required, removing contaminants, dust, and other fines by scrubbing and washing the heavy mineral sand. Intensive magnetic and electrostatic separation produces rounded-grain sand.

Properties

In terms of mineralogy, the aluminum silicate minerals, kyanite, sillimanite, and andalusite, are similar; all have the same chemical composition (Al_2SiO_5). In addition, all three are thermally stable up to $1,810^\circ\text{C}$. At that temperature they break down to yield 88% mullite ($\sim\text{Al}_6\text{Si}_3\text{O}_{15}$) and 12% free silica (cristobalite). Mullite has the following desirable characteristics:

- High refractoriness
- Low thermal expansion
- Resistance to thermal shock
- Intermediate thermal conductivity
- Resistance to chemical erosion

Foundry Use

Because of its neutral character, aluminum silicate sands have been successful in producing Hadfield's austenitic manganese steel and other ferrous castings. These nonsilica sands are also compatible with all known binder systems.

Staurolite Sand

Sources

Staurolite occurs naturally as a mineral with the general formula $(\text{FeAl}_5\text{Si}_2\text{O}_{12})(\text{OH})$. Staurolite sand is produced in the southeastern United States as a by-product of heavy mineral operations that also yield zircon sand and aluminum silicate sands.

Mining and Concentration

Staurolite and other heavy minerals are removed from heavy mineral sand after dredging by concentrating them in three stages of spiral separators on a floating wet mill. Then the heavy mineral concentrates are pumped to a conditioning unit where they are scrubbed with caustic to remove organic and clay coatings from grain surfaces. The heavy mineral sands are rinsed and dried; electrostatic and magnetic separation concentrates the staurolite. This magnetic, nonconductive product used for foundry sand consists principally of staurolite with small percentages of tourmaline, spinel, and silicates with magnetic inclusions as impurities.

Properties

Staurolite sand for casting production possesses the following favorable properties:

- Low thermal expansion
- High melting temperature
- Low silica content
- High thermal conductivity
- Suitable refractoriness

- Durability
- Compatibility with various binder systems

Although staurolite sand's thermal expansion is slightly greater than that of zircon sand or chromite sand, it is approximately equal to that of aluminum silicate sand and olivine sand (depicted in Figure 2).

Foundry Use

Staurolite sand has been used as base aggregate or blended with silica sands in the production of nonferrous castings and ferrous castings of light to medium section thickness. Because of its lower melting point at approximately $1,538^\circ\text{C}$, staurolite is not recommended for use in steel casting production.

Overall Benefits from Nonsilica Sands

Increasingly complex castings present the foundry worker with problems of design and geometry, so it is becoming more critical that workers plan to use special aggregates for molds and cores. Judicious use of various nonsilica sands can minimize problems in casting quality. Their use results in costs savings in finishing, which improves quality of the casting surface.

ECONOMIC FACTORS

Most economic factors related to production and processing of foundry sands raw materials are covered in the commodity chapters of this volume; some of these factors are discussed here. Most of this discussion involves silica sand.

Consumption

In 2003, industrial sand and gravel (silica sand) in the United States amounted to 27.5 Mt sold or used; 19% of that production was accounted for by the foundry industry. In the United States, minable resources are relatively common and abundant so that mining companies can easily locate their operations near their markets. Manufacturers traditionally locate their operations close to the source of raw materials. The U.S. automotive industry is an example. Factories originally were located in the Midwest where abundant clay, coal, iron, limestone, and silica resources occur. Consequently, foundry sands have been produced widely in Illinois, Indiana, Michigan, Ohio, and other midwestern states. In 2003, more than 83% of foundry sand was produced in the Midwest (Dolley 2003).

Consumption of foundry sand is closely tied into the manufacturing sector of the economy. It stands to reason, therefore, that when the economy is healthy, the consumption of foundry sand should increase; likewise, during economic downturns, consumption of foundry sand would decrease. Demand, production, and use of silica sand reflect the overall economic trend, but to some extent the substitution of nonsilica foundry sand also may play a role in silica foundry sand consumption.

In 1984, the U.S. foundry industry comprised 3,400 foundries; in 2004, there were just 2,380, which meant a loss of more than 1,000 businesses and a contraction of almost 30%. More than 50 foundries have been lost every year for the past 20 years. Despite some new and expanded facilities, it was estimated, based on 2001 production, that a loss of casting supply of 225,000 t was to occur in 2004 (AFS 2005).

Price

In 2003, ground sand for foundry molding and core had the highest average price of industrial sand and gravel at \$85.29/t. The average value of refractory-grade silica sand was \$39.16/t. The total value of

foundry sands sold or used in 2003 was approximately \$81.8 million; less than 3.25% of that value was attributed to refractory sands.

Transportation

Transportation costs to point of first sale or use have a pronounced effect on the pricing structure of sand products and the viability of deposits. As previously noted by Henderson (1983), because of higher shipping costs, the market price of zircon sand from Florida heavy mineral deposits, in which zircon concentration runs about 1.5%, is comparable to that from Australian sands, some of which run up to 15% zircon.

Of the total industrial sand and gravel produced in 2003, 64% was moved by truck, 35% was moved by rail, and 1.4% was transported by waterway (Dolley 2003). Such statistics for foundry silica sand would, perhaps, be similar. The trend was toward truck haulage and use of pressurized tank trucks when the sixth edition of this volume was written, and indeed that is reflected in the 10% increase from 1990 as reported by Kotzin (1994); oil prices are at near-record highs (greater than \$60 per barrel) at the time of this writing, however, and the trend is to increase shipments by rail.

REGULATORY CONSIDERATIONS

Zoning and Land Uses

Certain permits are required for the installation and operation of sand pits and dredging operations. Provisions for land use and mining permits vary from state to state and differ with respect to private and public land ownership. The following requirements are generic and may be more closely related to silica sand operations in states in the midwestern United States.

Special Use Permit

Many pits and quarries operate in lands zoned for agriculture under a special use permit issued by local zoning agencies. State agencies may not necessarily be involved in this permitting process. Applications submitted to and reviewed by a zoning board may then be referred to the county board of supervisors or similar agency for approval. Some counties require that a copy of the application also be submitted to the local soil and water conservation district, from which a response may be required before the application can proceed.

Mining Permit

A mining permit may be required if the planned operation will disturb more than a prescribed acreage annually, or involve the removal of a specific thickness of overburden. The application ordinarily goes to the state regulatory agency with jurisdiction over mining. An environmental assessment (EA) or environmental impact statement (EIS) usually is required. In some states the application for a mining permit must be filed with the appropriate county clerk concurrently. The county, in some cases, may have a specified length of time in which to respond. If no timely objections are lodged, the permit is issued within some specified time interval. The time period can be extended indefinitely if there are objections and a call for public hearings. Permits usually are for periods of a few years. In some jurisdictions, if no development has occurred during the original life of the permit, an extension may be limited to a fraction of the original acreage.

Construction and Operating Permits

Construction and operating permits generally are necessary. Applications typically are submitted to the state environmental protection

agency or department of environmental quality and may require an EA or EIS.

Dredging Permits

Dredging operations require a permit from the U.S. Army Corps of Engineers and also may require filing with the environmental agency responsible for water quality.

ENVIRONMENTAL CONSIDERATIONS

In 1987, the International Agency for Research on Cancer (IARC) expressed the opinion that crystalline silica (quartz) is probably carcinogenic to humans. This subject is covered in the Industrial Sand and Sandstone chapter in this volume and is not duplicated here.

Water Pollution

Many sand pits and other sources of foundry sand are located in riparian areas, or, in dredging operations, the materials may be derived directly from a wetland area or water body. The mine operator may require large amounts of water for washing or classification of sand products. Sand producers in some western and southwestern states rely on water wells.

Process water often becomes laden with fines and must eventually be discharged back into water courses. Because such operations usually do not use process chemicals, process waters are not affected; water turbidity, however, may be a matter of regulatory scrutiny. Different water clarification methods can be used to restore water quality, and in some cases effluent waters may leave a plant in better condition than when first obtained for processing.

Air Pollution

Stockpiles, roadways, and sand dryers may pose challenges to dust control. Watering roadways, dampening stockpiles, using dust collectors, and using other dust-control measures are common practice in suppressing dust in the mining industry.

FUTURE PROSPECTS

Supply-and-Demand Considerations

The future for molding sand is tied to metals. It has been suggested that consumption of both ferrous and nonferrous metals ceased to grow in about 1960 because of decreasing economic growth rates in the industrialized countries (Davis 1989). Conventional wisdom may indicate that economic recovery at the beginning of the 21st century means better days are ahead; Drucker (1986), however, proposed that U.S. demand for raw materials has been uncoupled from economic growth, implying that economic recovery may not, of itself, result in increased demand for cast metal products and molding sand.

The normal foundry procedure of constructing a mold of sand, clay and other binders, and additives for a single casting can be viewed as extremely inefficient. Burst (1991) proposed that using permanent ceramic molds, with cordierite or other refractory material, could reduce molding sand use in some applications; maintenance of precise dimensions, however, may be a problem as the permanent mold is used.

Future U.S. auto production, augmented by plants being constructed in the United States by foreign automakers, may outweigh such negative factors as increasing use of composites and the development of other lightweight, nonmetallic materials. The nature of the final resolution of the environmental safety issue with respect to crystalline silica will have an immense effect on the future supply-and-demand picture for the various types of foundry sands.

Despite environmental pressures, silica sand will continue to dominate foundry sand practice in the foreseeable future, but it is anticipated that advancements in metallurgy, increased use of light metals, and requirements for more uniform and higher finishes will require increased use of nonsilica sands and the implementation of new technology, some not yet discovered.

The U.S. Geological Survey had forecast that consumption of foundry sand in 2004 would fall within a range of 5 to 6 Mt and probably would be about 5.5 Mt (Dolley 2003). An overall trend toward decreasing production of silica foundry sands is due to increased recycling of foundry sand, additional increases in developing nonsilica substitutes both natural and synthetic, and the decline in casting for automobiles and light-truck production.

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Nanomaterials

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INTRODUCTION

Nanotechnology is engineering aimed at creating structures and materials (with at least one dimension) 1–100 nm long, having unique and potentially useful properties. These nanomaterials have been applied in the aerospace, electronics, and biomedical fields. When the sample size, grain size, or domain size becomes comparable with a specific physical length scale such as the mean free path or the coherence length of phonons, the corresponding physical phenomenon will be strongly affected. Although such changes in behavior can be dominant, their practical implications, except for electronic systems, are not yet realized significantly in industrial scales. Apart from the electronics industry, the only other large-scale application of nanotechnology has been the use of nanoclay as filler material in polymer systems. The combined physical, chemical, and biological aspects of nanoscale systems effectively form a new discipline with its own set of physical principles, experimental techniques, and environmental considerations. The recent advancement witnessed in technology is just a glimpse into the future of nanotechnology.

HISTORY AND BACKGROUND

Nature has been using nanomaterials for millions of years. Examples include DNA and proteins that help in proper functioning of cells (Alberts et al. 2002). Although humankind has been obliviously creating nanoparticles as by-products of combustion for thousands of years, the use of nanomaterials can be found as early as the ninth century in luster potteries (Padovani et al. 2004). The physicist Richard Feynman first laid out the conceptual framework of nanotechnology in 1959, in his lecture titled “There’s Plenty of Room at the Bottom” (Feynman 1960). Feynman explored the possibility of manipulating material at the scale of individual atoms and molecules, foreseeing the increasing ability to examine and control matter at the nanoscale. Norio Taniguchi first coined the term *nanotechnology* in 1974 to refer to the ability to engineer materials precisely at the nanometer level (Taniguchi 1974). The driving force for miniaturization at that time came from the electronics industry, which aimed to produce smaller and thereby faster electronic devices. Nanotechnology has been used to create the tiny features on computer chips for the past 20 years. Many chemical processes have nanoscale features—for example, researchers have been synthesizing nanoparticles, microemulsions, and micelles for decades. It is only in recent years, though, that

sophisticated tools have become available to investigate and manipulate matter at the nanoscale. A major step in this direction was the invention of the scanning tunneling microscope (STM) in 1982 and the atomic force microscope (AFM) in 1986. These tools use nanoscale probes to characterize a surface with atomic resolution. Development of characterization tools not only enhanced the understanding of the nanoscale world but also increased application of nanostructures. The research interest in nanotechnology is increasing worldwide, and is rapidly producing knowledge in this field. In turn, there is a hope that this will lead to dramatic changes in the way that materials, devices, and systems are created, resulting in improved quality of life.

CONCEPTS

Nanotechnology is concerned with materials and systems whose structures and components exhibit novel physical, chemical, or biological properties because of their nanosize. The control of structures at atomic, molecular, and supramolecular scales is desired for efficient fabrication and application of nanostructures. Nanotechnology can broadly be classified into two main areas: (1) particle nanotechnology, where particles are in nanodimensions and exhibit unique properties compared to the bulk, and (2) nanoengineering, where surfaces or devices are engineered in nanodimensions, resulting in unique properties. Nanotechnology emerges from the exploitation of the new properties, phenomena, processes, and functionalities that matter exhibits at intermediate sizes between molecules (~1 nm) and bulk materials (more than 100 nm). As opposed to the microscale, the nanoscale is not just another step toward miniaturization; it results in a qualitatively new material. At nanoscale, material properties are a manifestation of either quantum phenomena or a combination of quantum and classical phenomena.

At nanoscale, increase in surface to bulk ratio of atoms and size confinement produce qualitatively new behavior. When the size of a nanoscale structure becomes less than the characteristic length scale for scattering of electrons or phonons (the mean free path), qualitatively new modes of transport for electrical current and heat are observed (Link and El-Sayed 1999; Prasher 2004). For example, the ballistic transport of electrons is observed in carbon nanotubes (Frank et al. 1998), and other novel electronic properties are manifested by quantum dots (Timp 1999). Recently, electronic property aspects of materials, driven primarily by their vital importance to information technology, have dominated the scientific

interest and industrial application of nanotechnology. Many other novel combinations of properties can be expected to emerge for a wide range of materials as the nanoworld is explored.

Mechanical Properties

The grain size and grain boundary in polycrystalline materials or the concentration of strain fields significantly affects the mechanical properties as the dimensions approach the nanometer scale (Sternitzke 1997; Olemskoi, Valiev, and Khomenko 1999; Kumar, Van Swygenhoven, and Suresh 2003; Moussaif and Groeninckx 2003; Fratzl et al. 2004; Hierold 2004; Kothapalli et al. 2004). For example, grain size dependence is observed for properties related to plastic deformation along with decreased effective strain rate sensitivity (Jia, Ramesh, and Ma 2003). Modes of failure change as the scale of materials and structures shrink toward the nanoscale because of different mechanical and nonmechanical properties, such as the enhanced role of diffusion, which can modify fracture characteristics. Changes in the strength of nanoscale structural elements, the nature of friction, and other tribological properties will require new design strategies in the nanoscale regime (Adams et al. 2001).

Electronic/Optical/Magnetic Properties

Research on the electronic, optical, and magnetic properties of semiconductors at the nanoscale is growing at an astonishing pace. The fundamental properties of nanoscale semiconductor structures can be dramatically altered by controlling the size and shape of the structures without any change in their composition (Shipway, Katz, and Willner 2000; Qin et al. 2002; Wallace and Innis 2002; Wang 2002; Bonnell 2003; Bence 2004; Florey and Escobas 2004; Hao, Schatz, and Hupp 2004). When the electrons and holes in semiconductors are confined to dimensions less than their de Broglie wavelength (typically 1–30 nm), quantum mechanical size effects appear (Henglein 1995; Sun and Riggs 1999; Hao, Schatz, and Hupp 2004). Some of the observed effects of size are oscillatory behavior of the superconducting transition temperature with change in one atomic layer thickness (Guo et al. 2004), and resistivity enhancement and positive magnetoresistance with the diameter of nano wire (Liu and Chien 1998). The effect of shape on optical and electronic properties has also been recently observed (Xia et al. 2003; Hao, Schatz, and Hupp 2004). This gives impetus to future investigations of the effects of shape on other properties.

Thermal Properties

Thermal transport properties of nanostructured materials have received relatively little attention in the past decade (Che, Cagin, and Goddard 2000; Liu et al. 2002; Utracki and Kamal 2002; Adushkin, Andreev, and Popel 2004; Kikura et al. 2004; Liu and Kirchheim 2004). Several investigators have reported that nanoscale could result in significantly reduced thermal conductivities in nanostructured materials such as yttria-stabilized zirconia (YSZ), which could lead to improvements for applications such as thermal barrier coatings (Raghavan et al. 1998; Matsumoto and Matsubara 2004; Wang et al. 2004a). Reduced thermal conductivities are observed because of a reduction in the phonon mean free path that results from grain boundary scattering (Eastman et al. 1999). In contrast to the reduced thermal conductivity expected for nanostructured thin films or coatings, the thermal transport rates increase for fluids containing suspended nanoparticles. These nanofluids have recently been shown to exhibit substantially increased thermal conductivities and heat transfer rates compared to fluids that do not contain suspended particles (Patel et al. 2003; Eastman et al. 2004; Wen and Ding 2004).

Table 1. Classification of nanomaterials

Dimension	Nanomaterials
1 dimension <100 nm	Films, coatings, multilayers, nanopores
2 dimensions <100 nm	Tubes, fibers, wires, rods
3 dimensions <100 nm	Particles, hollow spheres, core-shells

CLASSIFICATION

All conventional materials such as metals, semiconductors, glass, ceramic, or polymers can, in principle, be synthesized in nanoscale dimensions. The spectrum of nanomaterials ranges from soft particles like microemulsions and liposomes to hard particles; they can be inorganic or organic, and crystalline or amorphous. Table 1 lists the nanomaterials classified according to shape.

Nanoparticles

Nanoparticles comprise several hundreds of atoms or molecules and can have a variety of sizes and morphologies (Kittel 1998; Pataki, Oszko, and Dekany 2003; Aslan et al. 2004). Some kinds of nanoparticles are already available commercially as dry powders or liquid dispersions in either primary size or aggregated states. With further processing steps, nanostructured powders and dispersions can be used to fabricate coatings, components, or devices. Industrial-scale production of some nanoparticulate materials like carbon black and titanium dioxide for polymer composites has been established for decades.

Some of the commercially important nanoparticles are silica (SiO_2), titania (TiO_2), alumina (Al_2O_3), iron oxide (Fe_3O_4), and microemulsions. Recently, nanoparticles of compound semiconductors (e.g., CdTe, GaAs, CdSe), metals (especially precious metals such as silver and gold), and alloys are finding increasing application (Pal et al. 2001).

Linear Nanostructures

Linear nanostructures include nanowires, nanotubes, and nanorods, which can be generated from different material classes (e.g., metals, semiconductors, and polymers) by various production techniques (Lieber 1998; Camerel et al. 2002; Xia et al. 2003). Carbon nanotubes are one of the most promising linear nanostructures, and they can be produced in different forms (e.g., single or multiwalled, filled, or surface modified). Carbon nanotubes are finding significant applications in nanoelectronics (data storage, flat-panel displays) and batteries, and as fillers for polymer nanocomposites.

Nanolayers

Nanolayers such as films, coatings, and multilayers are one of the most important aspects of nanotechnology, as they are extensively used in the microelectronic industry. The current Information Technology Age is the result of reproducible fabrication of these nanolayers. Nanoscale engineering of surfaces and layers produces a vast range of functionalities and new physical effects (e.g., magnetoelectronic or optical) (Chakravarti and Vetter 1998; Campbell 2001). Furthermore, nanoscale design of surfaces and layers is often necessary to optimize the interfaces between different materials (e.g., compound semiconductors on silicon wafers) to lower the lattice mismatch strain and to obtain the desired special properties. Materials with defined pore size in the nanometer range are of special interest for a broad range of industrial applications because of their outstanding properties with regard to thermal insulation and controllable material separation and release, and their applicability as templates for chemistry (Polarz and Smarsly 2002).

PRODUCTION TECHNIQUES

The two main routes of entry into the nanoworld are ultra-miniaturization resulting in smaller and smaller devices (working from the top down) and molecular manufacturing involving the manipulation of individual atoms or molecules (building from the bottom up). The former approach involves reducing the size of bulk material using mechanical, chemical, or other forms of energy. The latter approach deals with synthesizing nanomaterials from atomic or molecular species via self-assembly or chemical reactions, allowing the precursor particles to increase in size. Both production techniques can be employed in gas, liquid, or solid media, or in a vacuum.

Top-Down Approaches

The top-down methods of fabricating nanoparticles from bulk materials include high-energy ball milling, mechanochemical processing, etching, electroexplosion, sonication, sputtering, and laser ablation. Immediately after processing, nanoparticles are reactive owing to high surface energy, which is lowered by either agglomeration or adsorption of foreign species. If a reactive species is present, some additional reactions may occur. Nanoparticles can be coated during synthesis with a material that would prevent further interaction with other particles or the environment.

High-energy mechanical milling is widely used and is a very effective process for synthesizing metal-ceramic composite powders, because it allows incorporation of the metal and the ceramic phases in the same particle (Balaz et al. 2004). To produce nanoparticles of a specific material, a suitable precursor is chosen. Often a particular nanoparticle can be produced from a range of precursors, allowing the process to be optimized for industry. Oxides, carbonates, sulfates, chlorides, fluorides, hydroxides, and other compounds are all candidates for the precursor material. The chosen precursor is then milled with appropriate reactants.

Mechanical attrition, which produces a large amount of material, often contaminates the material. These industrial processes are mostly restricted to relatively hard, brittle materials, which deform, fracture, and cold-weld during the milling operation (Edelstein and Cammarata 1996). Typical objectives of the milling process include particle-size reduction (comminution), blending, solid-state alloying, and particle shape changes. The technique also produces a variety of nonequilibrium structures that include amorphous, quasicrystalline, and nanocrystalline materials. The mechanical attrition of multicomponent powder mixtures generally results in the formation of solid solutions extended in composition far beyond their equilibrium solubility limit (Shang, Bououdina, and Guo 2003). The potential of mechanical attrition to synthesize new materials under nonequilibrium conditions makes it a potential nanoparticle processing choice. For all nanocrystalline materials prepared, surface and interface contamination is a major concern. In particular, contamination by the milling tools and atmosphere can be a problem.

Bottom-Up Approaches

The methods to produce nanoparticles or nanoengineered surfaces from atoms and molecules are mainly sol-gel processing, chemical vapor deposition, plasma or flame spray synthesis, laser pyrolysis, atomic or molecular condensation, and self-assembly. Sol-gel processing differs from other chemical processes because of the relatively low processing temperature, making it cost-effective and versatile. In spraying processes, the reactants (gas or liquid as aerosols or mixtures of both) are introduced to a high-energy flame produced, for example, by plasma spray. The reactants decompose and particles are formed in a flame by homogeneous nucleation and growth. Rapid cooling results in formation of nanoparticles, and the cooling rate controls the crystallization.

Chemical Synthesis

Chemical synthesis permits the manipulation of matter at the atomic or molecular level. Chemical techniques are very versatile in that they can be adapted to nearly all materials (ceramics, semiconductors, and metals) and can be used for large-scale production. Most chemical routes rely on the availability of appropriate metal-organic molecules as precursors. Among the various precursors of metal oxides, metal β -diketonates, metal carboxylates, and metal alkoxides are versatile and available for most metals (Edelstein and Cammarata 1996). The challenges for chemical processing are finding the proper chemical reactions and processing conditions for each material. In the chemical synthesis of nanoparticles with desired properties, structural (crystalline or amorphous structure, size, shape, morphology, porosity) and chemical properties (composition of the bulk, interface, and surface) are important factors. Chemical homogeneity can be achieved because of mixing at the molecular level. To benefit from the advantages of chemical processing, an understanding of the principles of material chemistry, thermodynamics, and reaction kinetics is required. Formation and growth of the nanoparticles can be controlled by arrested precipitation and physical restriction. The former technique depends either on exhaustion of one of the reactants or on the introduction of a chemical that would block the reaction. The latter technique relies on physical restriction of the volume available for the growth of the individual nanoparticles using templates (Jain and Lakshmikumar 2002).

There are also potential difficulties in chemical processing. In some cases, the chemistry is complex and can be hazardous. Entrapment of impurities in the final product must be avoided or minimized to obtain desired properties. Scaling up for economical production of a large quantity of material may not be feasible for all systems. Another problem is that undesirable agglomeration at any stage of the synthesis process can change the properties of the desired nanoparticles.

With the advent of advanced thin-film processing methods like electron beam lithography, it has become possible to produce multilayered materials with precise control of the composition and thickness of the layers. In contrast to conventional bulk laminate composites, the individual layer thickness in multilayered thin films can be reduced to atomic or molecular dimensions by techniques such as dip-pen lithography (Ginger, Zhang, and Mirkin 2004).

Synthesis Using Organized Membrane

Using self-assembled membranes is an alternative approach to synthesizing stabilized, size-controlled nanoscale particles (Inglesten et al. 2001; Capek 2004). For example, Kumar et al. (1993) synthesized superconducting nanoparticles using water-in-oil microemulsion. Other examples of particles produced using this method include CdSe, silica, and silver. The self-organized organic and biological membrane assemblies include micelles, microemulsions, liposomes, and vesicles. The molecules of these assemblies have a polar head group with a nonpolar hydrocarbon tail, which self-assembles into membrane structures in an aqueous or nonaqueous environment. Aqueous and reverse micelles have diameters in the range of 3 to 6 nm and microemulsions in the range of 10 to 100 nm. Liposomes and vesicles are closed bilayer aggregates formed from phospholipids and surfactants, respectively. The membrane structures serve as reaction chambers controlling nucleation, growth, size, and shape of the particle. They also act as agglomeration barriers.

The main challenge for the top-down approach is the creation of increasingly small structures economically with sufficient reproducibility; whereas for the bottom-up approach the challenge is to make structures large enough and of sufficient quality economically. Current nanotechnology generally uses a combination

of both top-down and bottom-up approaches to produce a desired product.

Stabilization of Nanoparticles

The industrial-scale production and utilization of nanoparticles necessitates the ability to control particle size, shape, composition, particle-size distribution, and degree of agglomeration. But owing to their high surface area, and hence reactivity, nanoparticles tend to agglomerate, leading to loss of their unique properties. Commercial success or failure of nanoparticles in a particular application usually depends on the ability to prepare stable dispersions in fluids with controllable rheology. Therefore, it is often necessary to stabilize the nanoparticles with additional treatments. The common method to stabilize or modify the reactivity of the nanoparticles is encapsulation with a molecular or polymeric layer (Sun and Riggs 1999; Adler et al. 2000). A thin barrier shell enables compatibility of the particles with a wide variety of fluids. In this way, the nanoparticles retain their original chemical and physical properties, and the coating can be tailored for a wide variety of applications and environments ranging from extremely nonpolar (hydrophobic) to very polar systems. Coating nanoparticles with another material of nanoscale thickness can also alter the surface properties of nanoparticles. These core-shell structured nanoparticles display unique optical, mechanical, and magnetic properties (Caruso 2001). For example, Santra et al. (2004) recently developed nanoparticle composites for bioimaging.

CHARACTERIZATION

The wide range of potential applications makes nanotechnology truly multidisciplinary. Materials scientists, mechanical and electronic engineers, and medical researchers team up with biologists, physicists, and chemists to share their expertise on the nanoscale interactions in living and nonliving systems. One essential prerequisite for the development, manufacturing, and commercialization of nanomaterials is the availability of techniques for characterizing their physical, chemical, and biological properties. Powerful analytical detection and characterization methods also form the basis of risk assessment of nanomaterials in different environments such as water, soil, and air, and how they interact with the ecosystem.

The considerable wealth of detection and characterization methods for nanomaterials includes using AFM, STM, high-resolution transmission electron microscope, x-ray diffraction (XRD), and nanoindentation. These methods are used in research laboratories to study nanomaterial properties; however, most of them are not suitable for adoption into industry for on-line measurement because of their requirement for ultrahigh vacuum, sample preparation, and prolonged analysis.

INDUSTRIAL APPLICATIONS

Some nanomaterials had found a place in industrial markets before the current emphasis on nanotechnology. Now industries are more willing to incorporate nanomaterials into their processes to attract more customers, as long as they are economical. The major nanoparticles used are silica, titania, alumina, iron oxide, carbon black, nanoclay, and microemulsions. Research on nanotechnology in recent years has led to a significant increase in everyday applications. Some of the examples are

- Ever-increasing availability of new and high-performance electronic gadgets (e.g., flat-panel-display resolution enhancement by using nanocrystalline phosphors [Nanomats, undated])
- Antireflective, ultrathin polymer coatings with embedded nanoparticles used in sunglasses for durability and scratch resistance

- Clothes with stain-repellence and wrinkle-free, windproof, and waterproof properties. Clothes with additional electronic functionalities to monitor body conditions, facilitate drug release, and provide Internet access, etc., are anticipated.
- High-performance ski wax, which produces a hard and fast-gliding surface
- Tennis rackets with carbon nanotubes with increased torsion and flex resistance. The rackets are more rigid than current carbon rackets and pack more power (Nanocor 2004). Long-lasting tennis balls are made by coating the inner core with polymer-clay nanocomposites. These tennis balls have twice the lifetime of conventional balls.
- Sunscreens based on mineral nanoparticles such as titanium dioxide. Titanium dioxide nanoparticles have comparable UV protection as the bulk material, in combination with cosmetically desirable transparency.
- Nanoparticles in automotive parts and paints. The virtue of using nanocomposites for automotive applications is that less filler material is required to give better performance characteristics when compared to conventional materials (Kellar, Herpfer, and Moudgil 2003).
- In the area of health care, benefits from targeted and improved drug delivery systems. Nanoparticles are also used in developing new materials for bi implants and as sensors for bioimaging early detection of disease.

But all that has been achieved pales in the face of far greater opportunities that still need to be explored. Table 2 outlines the broad application of nanotechnology in various fields, and Table 3 lists some of the commercialized nanoparticles and their applications.

Table 2. Applications of nanotechnology in various fields

Industry	Application
Automotive	Lightweight construction, paints, catalysis, tires (fillers), coatings for windscreen and car bodies, etc.
Electronics	Data memory, displays, laser diodes, optical switches, conductive and antistatic coatings, etc.
Medicine	Drug delivery systems, bioimaging contrast medium, bioimplants, antimicrobial agents, coatings, etc.
Other	Flame retardants, construction materials, surface-processed textiles, "smart" clothes, food and drink packaging materials, wear protection of tools and machines (scratch-resistant coatings), ski wax, antifogging of glasses and goggles, antifouling coatings on ships, reinforced tennis rackets and balls, self-cleaning surfaces, sunscreen lotion

Table 3. Commercialized nanoparticles

Nanomaterial	Applications
Alumina	Ceramics, polishing slurries, coatings, catalysis
Carbon black	Fillers, pigments, inks, paper, building products
Carbon nanotubes	Electronic devices, structural elements, drug delivery
Fullerene	Paints, lubricants, coatings, electronic devices, nanocomposites
Iron oxide	Cosmetics, paints, pigments, ferrofluids
Nanoclays	Nanocomposites, packaging, construction materials
Silica	Catalyst support, "soft" silica-paints, foundry facings, polishing slurries, filtration media
Titania	Photocatalyst, paints, paper, self-cleaning surfaces
Zirconia	Catalysis, fuel cells, bioimplants
Zinc oxide	Cosmetics, catalyst, coatings, textiles

TRENDS AND OPPORTUNITIES

Modeling and Simulation

The emergence of unique phenomena at nanoscale creates a great need for theoretical and modeling efforts to understand the phenomena. Interactions between nanoscale structures and their surroundings can lead to many complex, collective properties. Theory and simulation tools are needed that can help predict these complex properties to design and produce better nanostructures for the future (Tsuchiya and Miyoshi 1999; Rafii-Taber 2000).

Inspiration from Nature

Living organisms are composed of structures that are indeed a part of the nanoworld. Proteins, enzymes, and DNA are in the nanometer range. The functioning of biological structures strongly depends on the nanoarchitecture of various components involved. Significant insight into nanoscale phenomena can be gained from nature's perfect biological systems. The limitations in everyday applications can be overcome by implementing acquired knowledge through human-made nanostructures. In addition, biological and artificial nanosystems can be coupled for application in both living and nonliving systems. Forming proteins with hierarchical complexity is an exquisite example of synthesizing nanomaterials through self-assembly.

ENVIRONMENTAL AND HEALTH CONSIDERATIONS

Nanotechnology promises huge benefits in wide areas of application ranging from superior lightweight materials, electronics, and biomedical applications to consumer goods. With the proliferation of nanotechnology as with any new technology, it is imperative to consider the other side of the coin—unintended impacts on human health and the environment. Studies on biological and environmental effects of nanotechnology lag far behind its exploration and implementation. Nanoparticles are on the same length scale as proteins and other bioactive molecules. The possibility of nanoparticles evading the natural defense system in bio- and ecosystems is a major concern. When considering the ill effects of nanoparticles, one should be aware that humans have been exposed to nanoparticles from natural sources like volcanoes, fires, and weathering of minerals, and to pollutant nanoparticles from power plants, incinerators, and vehicle emissions.

Environment

Nanoparticles can be released into the immediate environment in various ways such as from products in which they are not immobilized, by slow degradation of nanoparticles containing products, or by some mechanical action that releases nanoparticles. Nanoparticles can introduce new toxins or pose different unforeseen environmental hazards. Most of the research on nanoparticles produced by emission has focused on air pollution and its effect on ozone layer depletion. Currently, the focus of research is on the toxic aspects of nanoparticles. Nanoparticles can enter the biosystem via different environmental routes and travel up the food chain. Nanoparticles can be released to the environment by different means, such as industrial wastes, which can be taken up by organisms present in soil and water. Depending on their state of dispersion and surface activity, nanoparticles either can be toxic to the organism or can be accumulated in tissues, bones, or cells of organisms. Accumulated nanoparticles can then move up in the food chain to higher organisms. Recent studies show that carbon nanotubes can be toxic in a different way than common micrometer-scale fibers (Oberdorster et al. 2004; Warheit et al. 2004). In a separate study, when juvenile largemouth bass were exposed to 0.5 ppm of uncoated fullerenes

for 48 hours (Oberdorster 2004), the fullerenes accumulated in lipids of cell membranes and caused oxidative damage. Experiments also showed translocation of fullerenes to the brain. Further studies are required to determine the extent of damage, dependence on the fullerene modification process, and the dose. Persistence, accumulation, and toxicity are important factors determining the extent of damage to the environment posed by the nanoparticles (The Royal Academy of Engineering and The Royal Society 2004). Ease of recovery of nanoparticles from the environment in order to reduce their concentration to below acceptance levels is another important issue. Disposal of nanoparticles, in their primary size, to the environment should be treated as hazardous until further environmental and health risk data are available (Royal Academy of Engineering and the Royal Society 2004).

Health

With the advancement of nanotechnology, large-scale production and commercial use of nanoparticles are inevitable. For nanoparticles to have harmful effects on human health, they would have to come in contact with cells and cause adverse reactions. Nanoparticles released into the environment can enter the human body via three major routes—inhale, ingest, and dermal penetration. All three routes are commonly exposed to micrometer-sized particles and microorganisms. The human body has its own defense mechanism for protection against microorganisms, which act in a similar way for micrometer-sized particles (Alberts et al. 2002). Depending on the route, nanoparticles can evade the body's defense system and enter the living tissues.

Inhalation

Thousands of particles enter the airway during inhalation. The air pipe, or trachea, is lined with hair-like structures called cilia that restrict the passage of particles into the lungs. The epithelial, or surface, cells of the trachea are covered with mucous and macrophages. If the particles or microorganisms reach the epithelial cells, they are engulfed by macrophages and carried to lymph nodes, where they are discarded. If particles are present in a sufficiently high dose, they can cause inflammation and scarring of lung tissue, as in pneumonia or silicosis (Gehr and Heyder 2000). High proportions of inhaled nanoparticles are deposited in tracheobronchial and alveolar regions of the lung (Oberdorster 2001; Oberdorster et al. 2004). Nanoparticles, because of their small size, can enter the cell directly through the cell membrane. They are also known to diffuse into the lungs through epithelial cell lining. Inhaled nanoparticles can translocate to the liver, brain, and other organs through blood vessels and the central nervous system (Oberdorster 2001; Oberdorster et al. 2004).

Dermal Exposure

The skin acts as a protective barrier against microorganisms. The outermost layer of skin, called the epidermis, is composed of cells that keep replenishing every few weeks. Below the epidermis lies the dermis, which consists of living cells, nerve endings, sweat glands, and blood vessels. Macrophages are present in abundance in the dermis and provide a defense against entry of particles and microorganisms. Excessive exposure to particles or microorganisms can produce inflammatory reactions, and prolonged inflammation can also result in skin damage and diseases. Particles and microorganisms, though restricted by the epidermis, can reach the dermis if the epidermis is damaged by cuts or wounds. But the small size of nanoparticles helps them penetrate the epidermis and enter the bloodstream. Aerosolized beryllium nanoparticles were shown to penetrate epidermis (Tinkle et al. 2003). Agglomeration of airborne

nanoparticles can reduce the risk of dermal penetration. Titanium dioxide, zinc oxide, and iron oxide nanoparticles are commercially used in cosmetics (sunscreens and lipsticks), and current dermal exposure is limited to these nanoparticles (Royal Academy 2004).

Ingestion

Ingested particles first encounter a low-pH environment in the stomach. Acidic juices secreted by the stomach's cells help digest food, dissolve toxins, and inactivate microorganisms. The food broken down by the stomach enters the intestine, where it is absorbed. The epithelium of the intestine is impermeable to many large molecules and particles but absorbs small molecules. The epithelium also secretes mucus and digestive fluids that can dissolve particles and toxins and degrade microorganisms. Recently, it has been shown that intestinal epithelial cells can absorb nanoparticles of drugs (Pamujula et al. 2004; Russell-Jones 2004). Although the tests were performed for oral drug delivery, possibility of entry and accumulation of other nanoparticles through the gastrointestinal tract cannot be neglected.

Nanoparticle exposure to industrial workers depends on production techniques, storage, and disposal systems. Nanoparticles stored in a liquid medium or in an agglomerated state are less prone to dermal penetration. The toxic effect of nanoparticles depends not only on its surface area but also on dosage, clearance mechanism, surface chemistry, and state of dispersion. Combined interdisciplinary and international efforts are reevaluating the risks posed by nanotechnology to make it safe and beneficial.

NANOCLAYS

Introduction

Clays have played an immense role in the development of humankind from the earliest use for building shelters and pottery dating back to the Neolithic stage of civilization. The reason lies in their plasticity and abundance. Clays are typically hydrous aluminosilicates with a particle size of usually less than 4 μm . The layer structure of clays imparts moldability in a wet state and rigidity in a dry state.

Clay nanoparticles or nanoclays have come into focus in the last decade because of their ability to enhance mechanical, thermal, and optical properties of polymers in which they are used as fillers. Nanoclay-filled polymers have a weight advantage because the filler does not significantly change the density of a nanocomposite and the nanosize of clay maintains the optical transparency. Polymer-clay nanocomposites have found extensive applications in packaging and in the automobile and aerospace industries. Since enhanced mechanical and thermal properties can be achieved at a lower cost using a smaller quantity of nanoclay, many polymer industries incorporate nanoclays to improve their products.

Structure

Clay minerals are part of the larger class of silicate minerals called phyllosilicates. The layer structure of clays is composed of silica tetrahedral and alumina octahedral sheets. The silica tetrahedral sheet consists of individual SiO_4 tetrahedrons that share three of four oxygen atoms. The tetrahedrons are linked to form a hexagonal network with a composition of Si_4O_{10} . The apical oxygen atoms are shared with the octahedral sheet. The alumina octahedral sheet consists of individual octahedrons that share oxygen or hydroxyl edges. These octahedrons are also linked in a hexagonal network. The tetrahedral and octahedral sheets are stacked in different ratios, as summarized in Table 4. Depending on the ratio of tetrahedral and octahedral sheets, the layer thickness varies from 0.7 nm for 1:1 phyllosilicates to 2 nm for 2:1 phyllosilicates. Weak van der Waals forces hold the layers together to form stacks. The gap between the layers is called the interlayer or the gallery. The interlayer distance

Table 4. Classification of clay minerals

Structure	Group	Minerals
1:1	Kaolin-Serpentine	Kaolinite, halloysite, dickite, nacrite, chrysotile, antigorite, lizardite
2:1	Talc-Pyrophyllite	Talc, pyrophyllite
	True mica	Phlogopite, biotite, muscovite, phengite, celadonite
	Brittle micas	Margarite, clintonite, anandite
	Chlorites	Clinochlore, chamosite, donbassite, sudoite, cookeite
	Illite	Illite, glauconite
	Smectite	Montmorillonite, beidellite, saponite, nontronite, hectorite
	Vermiculite	Vermiculite

is 0.95 nm in the absence of any counterions or water of hydration (Otterstedt and Brandreth 1998). The clay layer can have substitutional defects like Al^{3+} substituting Si^{4+} and Mg^{2+} or Fe^{3+} substituting Al^{3+} . The net negative charge acquired by clay layers from substitution is counterbalanced by the presence of cations like Ca^{2+} and Na^+ in the interlayer spacing.

The most commonly used layered silicates for nanocomposite applications are montmorillonite, hectorite, and saponite, which belong to the 2:1 phyllosilicates family (Ahmadi, Huang, and Li 2004). The 2:1 phyllosilicates have two silica tetrahedral layers sandwiching one alumina octahedral layer, as shown in Figure 1.

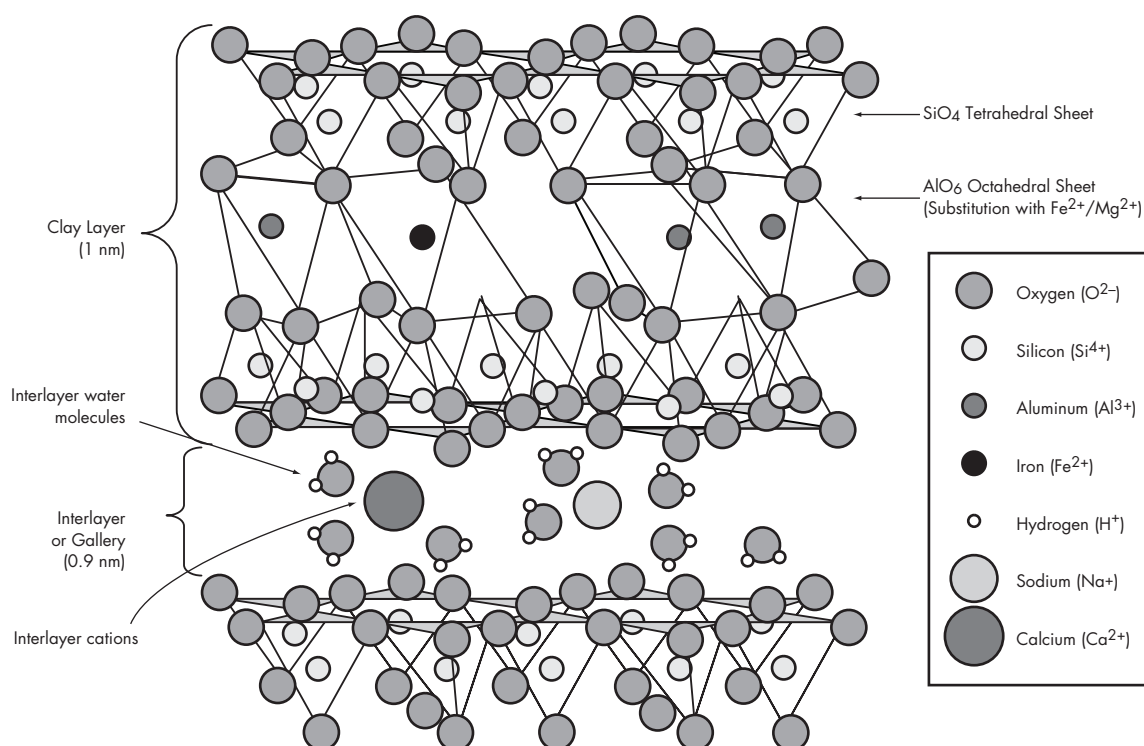
Polymer-Clay Nanocomposites

Toyota Central Research and Development Laboratories first synthesized the polymer-clay nanocomposite with polyamide 6 and montmorillonite cation exchanged with 12-aminolauric acid (Usuki et al. 1993a; 1993b). The polyamide 6-clay nanocomposites have enhanced mechanical and thermal properties compared to conventional clay composites. Since then, various other thermoplastic and thermosetting polymers such as epoxies (Xu, Bao, and He 2002), cellulose acetate (Park et al. 2004), polyester (Chang and Kim 2004), polyvinyl chloride (Gong et al. 2004), polystyrene (Wang et al. 2004c), polyimide (Yu et al. 2004), polypropylene (Ding et al. 2005), and polyurethane (Solarski et al. 2005) have been used for synthesizing nanocomposites with significantly improved properties.

Intercalation and Exfoliation

In polymer-clay nanocomposites, the clay should be dispersed in nanosize range to achieve the superior properties. The state of dispersion is often characterized using XRD and transmission electron microscopy (TEM) (Eckel et al. 2004; Wang 2004b; Wei, Tang, and Huang 2004) and recently using techniques such as small-angle neutron scattering (Malwitz et al. 2004), AFM (Park et al. 2004) and laser-induced fluorescence spectroscopy with optical probes (Maupin et al. 2004).

Intercalation and exfoliation are the two major steps involved in clay particle dispersion in polymers, as shown in Figure 2. The polar nature of clay sheets is not always compatible with polymers, which are usually hydrophobic. Modifications via cation-exchange reactions with various organics, including cationic surfactants (alkyl ammonium/phosphonium), are commonly used to render the hydrophilic clay layers partially hydrophobic. Cationic surfactants adsorb between the clay layers with their hydrophilic heads oriented toward the clay sheet and hydrophobic chains acting as spacers between the clay layers. Thus, the organically modified clays have larger interlayer spacing, which helps in intercalation or exfoliation during further processing with polymers.



Adapted from EUBA, undated.

Figure 1. Layer structure of 2:1 phyllosilicate

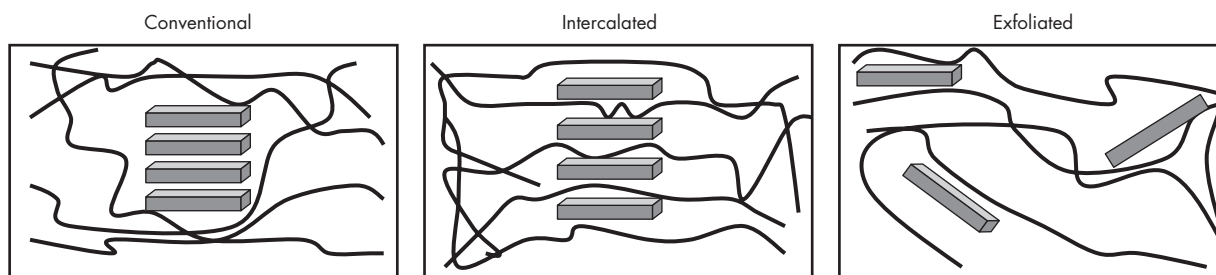


Figure 2. Clay dispersion in polymer nanocomposites

In intercalation, the polymer chains or molecules diffuse into the interlayer, increasing the spacing. The layer–layer interaction still exists through weak van der Waals forces. The clay layers remain parallel to each other; this can also be characterized by XRD, which shows increase in d-spacing. Dilution of clay or peak broadening, however, could be misinterpreted for exfoliation (Eckel et al. 2004).

Exfoliation separates the clay layers and randomly disperses them in a polymer matrix. The interlayer spacing is very large and there is no layer–layer interaction with van der Waals attraction forces. Since the clay layers are randomly dispersed, XRD cannot provide any information on the extent of dispersion because of any absence of peaks; hence, TEM is used. Initial interlayer spacing of cation-exchanged clay is required for exfoliation. For exfoliation of clay, Eckel et al. (2004) calculated the theoretical mean linear intercept distance between clay layers to be about 50 to 80 nm, in agreement with the experimental measurements. Exfoliation has been experimentally and theoretically shown to be strongly dependent on

the shear rate and viscosity of the matrix during processing, the Hamaker constant, interlayer spacing, layer–polymer interactions, and organic modifier–polymer interactions (Cho and Kamal 2004; Fornes, Hunter, and Paul 2004).

Production Techniques

Polymer-clay nanocomposite production techniques can be grouped into three categories: in-situ polymerization, solution polymerization, and melt intercalation.

In-situ Polymerization

The first polymer-clay nanocomposite developed by Usuki was synthesized by in-situ polymerization (Usuki et al. 1993a; 1993b). In this technique, the organically modified clay is added to a polar monomer solution. The monomer diffuses into the high surface energy interlayer of clay. Polymerization initiator is added after the monomer–interlayer equilibrium is reached. The monomers present

in the interlayer polymerize, shifting the equilibrium. More monomers are driven into the interlayer, further increasing the interlayer spacing, and in some cases resulting in exfoliation (Ahmadi, Huang, and Li 2004). Since clay can act as a catalyst, the presence of impurities can change the polymerization reaction. This method is commonly used for thermosetting polymer nanocomposites such as epoxy organo-clay nanocomposite.

Solution Polymerization

In solution polymerization, the organically modified clay and polymer are added in a polar or organic solvent. Hence the first requirement is that polymer should be soluble in the solvent. The polymer diffuses into the interlayer, resulting in intercalation. The solvent is subsequently evaporated, leaving behind intercalated nanocomposite. The nature and polarity of the solvent are critical factors in determining the intercalation process. The major drawbacks of this technique are the large amount of solvent needed and the solvent compatibility with organically modified clay as well as polymer.

Melt Intercalation

In melt intercalation, polymer is mechanically mixed with organically modified clay at a temperature above the softening or melting point of the polymer. The polymer diffuses into the interlayer, resulting in intercalation. Although this method is applicable to only thermoplastic polymers, it has the advantage of using conventional polymer-processing equipment. Because this method also does not need any solvent, there is no need for postsynthesis recovery.

Properties

Polymer-clay nanocomposites are superior to conventional clay-filled or pristine polymers because of enhanced thermal endurance, flame resistance, tensile strength and modulus, biodegradability, reduced shrinkage, and pristine polymer optical properties.

Thermal Properties

The thermal properties of polymer-clay nanocomposites are studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Blumstein first reported the high thermal endurance of polymer-clay nanocomposite in 1965 (Blumstein 1965). Using nanoclay, the heat distortion temperature and crystallization temperature of the polymer composite can be increased by 20°C (Ke 2003; Gong et al. 2004). Increased thermal decomposition temperature by 30°C is also reported (Chiu et al. 2004; Solarski et al. 2005).

Flame resistance of polymer-clay nanocomposites is studied by cone calorimetry and radioactive gasification experiments. The heat release rate and flammability have been shown to be 30% to 35% lower for polymer-clay nanocomposites compared to conventional polymer-clay composites (Song and Yao 2004; Wang 2004c).

Mechanical Properties

Conventional clays are being used as filler in polymer mainly to improve, marginally, its mechanical properties. Nanoclays, on the other hand, can increase the tensile strength and modulus by 100% to 400% (Chang and Kim 2004; Chen 2004; Wei, Tang, and Huang 2004). Since the filler content is usually less than 5% for nanoclays, the processing is easier and the products are lighter.

Chemical Properties

Polymer-clay nanocomposites reduce gas and liquid permeabilities, including reduced solvent uptake. Nanoclays can decrease the gas permeability coefficient by 35% (Chen 2004). The increased resistance is attributed to tortuosity and higher modulus of clay nanopar-

ticles (Ahmadi, Huang, and Li 2004). Osman et al. (2004) showed that intercalation can decrease the permeability coefficient by 20%, whereas exfoliation increased the permeability coefficient by 10%. Polymer nanocomposites can also be used in anticorrosion applications (Yu et al. 2004).

Optical Properties

The optical properties of polymer-clay nanocomposites are studied using UV-visible transmission spectroscopy. Although nanoclay is known to scatter light in the ultraviolet region, nanoclays with dimensions of less than one quarter of visible light wavelength are optically transparent (Ahmadi, Huang, and Li 2004; Yeh et al. 2004). Thus polymer-clay nanocomposites have optical properties similar to pristine polymer.

Improvement in the previously mentioned properties, combined with ease of processing and low volume of clay needed, promises widespread application of polymer-clay nanocomposites.

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Pigments

George Podolsky and Austin H. Reid Jr.

The pigments industry represents one of the most demanding and technology-intensive applications of industrial minerals. Pigments are used in all major materials known to man. The building products, polymers, glass, paper, and paint and coating industries are major users of inorganic mineral pigments. Various clay minerals and titania are more widely used as white pigments than, for example, silica, alumina, calcium carbonate, and zinc oxide. Similarly, iron oxides and chromates are representative of the important colored pigments. In this chapter, discussion focuses primarily on natural and synthetic iron oxides typifying the colored pigments, and on titanium dioxide exemplifying the white pigments, as these find the predominate use in the industry. To familiarize the reader with the various terminologies and definitions specific to the pigments industry, these two important pigments are discussed in a single chapter.

IRON OXIDE

Iron oxides are unique in that they are the only significant colored mineral found in a natural state suitable for use as a pigment after being pulverized to pigmentary size (typically, less than 1 μm). The global production of iron oxide pigments in 2000 was estimated to be 1.5 Mt (Will 2004). In addition to their abundance (about 7% of the earth's crust), iron oxides have the advantage of low cost, permanency, and nontoxicity. The amazing durability of iron oxides is reflected in the numerous examples of beautiful prehistoric art found in cave paintings in many regions of the world. Through the centuries, succeeding civilizations have used iron oxides as a major source for decoration and protection when these properties were desired. In the last century, the chemical industry improved on nature by developing a complete range of synthetic iron oxide pigments that surpass the pigments produced from natural iron ores in uniformity, color quality, and chemical purity. Globally, the combined annual production of natural and synthetic iron oxide pigments is valued at approximately \$2 billion (Will 2004).

Terms and Definitions

As with other pigmentary minerals, it is necessary to make a distinction between the natural or mineral pigments and the synthetic pigments. Natural pigments are products derived from selected ores and should not be confused with iron ores mined for steel production. Iron ores that are mined for steel must be capable of being mined and reduced to iron on a competitive commercial basis. These ores are selected on the basis of iron content and processing

economics. It is therefore unusual when iron ores for steel production are suitable for use as mineral pigments. Natural pigment ore sources are selected for their special physicochemical properties and are able to command a premium price over the iron ores used for steel manufacturing.

Synthetic pigments, and in this instance iron oxides, are pigments produced from basic chemicals. Chemical synthesis produces pigmentary particles directly, as opposed to the use of comminution, the procedure common to preparing all natural iron oxide pigments.

Classification

An important characteristic of a pigment is its color. Therefore, a logical separation can be made on this basis.

- Yellow iron oxide pigments
 - Natural mineral origin
 - Goethite
 - Lepidocrocite
 - Ochres
 - Siennas
 - Limonite
 - Synthetic pigments
 - Goethite (αFeOOH)
 - Lepidocrocite (γFeOOH)
 - Akagenite (βFeOOH)
- Red iron oxide pigments
 - Natural mineral origin
 - Hematite
 - Siderite (calcined)
 - Pyrites (calcined)
 - Synthetic pigments
 - Hematite ($\alpha\text{Fe}_2\text{O}_3$)
- Brown iron oxide pigments
 - Natural mineral origin
 - Umbers
 - Limonite (calcined)
 - Siderite (calcined)
 - Goethite (bog ore or sulfur mud)

- Synthetic pigments
 - Blends of hematite, goethite, and magnetite
 - Coprecipitated hematite–magnetite
 - Maghemite (γ -Fe₂O₃)
- Black iron oxide pigments
 - Natural mineral pigments
 - Magnetite
 - Slate (mixed minerals)
 - Synthetic pigments
 - Magnetite (Fe₃O₄)

Pigmentary minerals, natural or synthetic, have important physicochemical properties that distinguish them from metallurgical, cementitious, construction, agricultural, and other types of industrial minerals.

The iron oxide content of natural minerals is critically important. Also important are the amount, the type, and the form of any companion minerals. For example, an iron ore possessing good pigmentary qualities but associated with appreciable quantities of quartz would be undesirable because of the difficulty in grinding quartz and the regulatory issues surrounding crystalline quartz. High percentages of organic matter in the ore would require calcination to decompose the organics, and then grinding. Synthetic oxides, on the other hand, exhibit a high iron content because of chemical synthesis. They also contain minimal impurities, the degree to which depends on the synthetic route.

Chemical Properties

Most of the pigmentary iron ores are relatively nonreactive (Mellor 1953; Casey 1966) and contain only traces of heavy metals and toxic elements; these are usually chemically bound in the form of complex silicates. Synthetic pigments produced from basic raw materials have the advantage that purification steps can reduce the heavy metal content (e.g., lead, antimony, arsenic, cadmium, mercury, selenium) of the starting raw materials. If subsequent precautions are followed to avoid processing contamination, the heavy metal impurities in synthetic oxides can be about one tenth that of the best naturals.

Iron oxide pigments have a high degree of lightfastness. This term refers to the ability of a pigmented film to resist color changes and other physicochemical degradation caused by exposure to radiant energy.

Physical Properties

The physical properties of iron oxide pigments are usually more important than the chemical properties in view of their inertness. Several physical properties require definition to provide a clear understanding of the merit of a pigment and to distinguish between naturals and synthetics or pigments of other families.

Oil Absorption. Oil absorption is that weight of vehicle required to wet a definite weight of pigment to form a paste. Numerous methods (Stewart 1942; Von Fisher 1948; Anon. 1972b, 1983) and devices can determine oil absorption. The values in this chapter are from standards of the American Society for Testing and Materials (ASTM) spatula rub-up procedure. Oil absorption, or binder demand, is an important property because it relates to particle size, shape, and surface characteristics and places certain limitations on paint formulation or other end uses where solid–liquid interactions are important.

Surface Area. Two pigments of essentially the same mean particle size may have quite different surface areas. This may be due to shape or surface characteristics such as porosity, pore size distribution, smoothness, and convolutions. Because spectral and

surface energy properties depend on the particle surface, surface area becomes an important factor. The surface area of a material is the area of the total external surfaces, including pores but excluding *internal* (isolated) pores. When external pores are smaller than the molecule of the media being absorbed, they are not measured. The most widely accepted and fundamental method for calculating surface area is by measuring the adsorption of a gas, usually nitrogen (Brunauer et al. 1938; Herdan 1953) and is designated as the BET method. The value obtained expresses specific surface area in square meters per gram.

Particle Size. No single method or instrument can adequately measure particle sizes in the range from 100 to 0.01 μ m. Significant improvements have been and continue to be made, however, in the range and accuracy of the wide variety of instrumentation available. For example, laser diffraction-based instrumentation is available for ranges of 0.02 μ m to more than 2,000 μ m. A key is to completely disperse the particles and minimize the measurement time. Otherwise, various stages of reagglomeration of the primary particles will be measured. Complete books have been devoted to this subject, which is probably the most important physical property of pigments. It is not sufficient to state an average particle size since the size distribution of particles is equally important. Generally, electron microscopy is still used to most accurately measure the primary particle size of iron oxides. Terms that are often confused in particle technology are as follows:

- *Primary particle:* Sometimes may be referred to as *discrete particle*; a single unit of matter that can change in size only by the breakdown or fracture of chemical bonds within its structure.
- *Crystallite:* A minute single crystalline unit, i.e., that part of a particle that has its atoms and molecules arranged in a perfect crystal lattice. A discrete particle comprises an assemblage of many crystallites.
- *Aggregate:* A group of discrete particles bound together by strong chemical bonds.
- *Agglomerate:* A group of discrete particles or aggregates bound together by weak physical bonds.
- *Flocculate:* Groups of aggregates or particles usually formed in suspensions and readily dispersed with minimal forces.

Shape. In some applications, particle shape can have a more profound effect than size. Micaceous iron oxide (lamellar platelets) and acicular particles contribute completely different characteristics to a pigmented system than their equivalent spherical counterpart. Various techniques have been devised to apply numerical values for shape factors (Herdan 1953; Cadle 1955). Pigments are classified into five categories according to shape: (1) spheroidal, (2) cubical, (3) nodular, (4) acicular, and (5) lamellar.

Optical Properties. The optical properties of pigments depend on the molecular and crystal structure and are influenced by the size and shape of the primary particles. Because pigments are rarely used in their powder state, the ultimate effect depends on the entire system. Light entering a pigmented system may be absorbed, reflected, or refracted through particle-to-particle interactions. The manner and intensity of the light reflected results in spectral reflectance, which can be measured with a spectrophotometer.

Magnetic Properties. Iron oxides are usually antiferromagnetic (Schieber 1967), but they can also be ferromagnetic when produced synthetically as well as in certain natural mineral species. The magnetic properties of ferromagnetic materials can be determined by various techniques; a few of the more common are magnetic moment balance, vibrating sample magnetometer (VSM), and B–H (magnetic flux–magnetic field) meter.

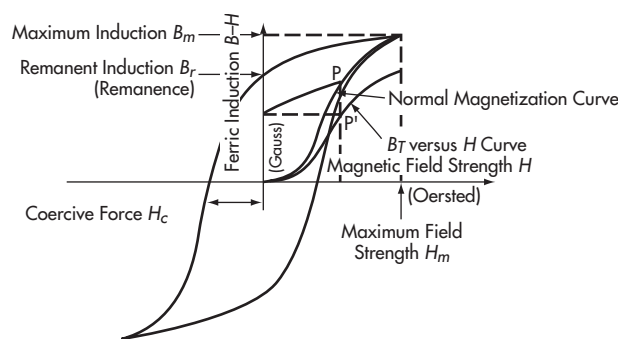


Figure 1. Hysteresis loop used to characterize magnetic iron oxides

Magnetic materials are best described by measuring the response to a magnetic field of varying intensity. This produces a magnetization, or BH curve, as shown in Figure 1. Ferromagnetic materials may then be characterized with values of coercivity (H_c), remanence (B_r), and saturation (B_m) at a specified field strength in Oersteds (H).

Natural Iron Oxide

Natural iron oxide minerals mined for pigment applications normally require more than simple grinding to attain commercial status. The major minerals are discussed along with their chemical and physical properties. The chemical compositions, especially those of goethite and hematite, do not represent the pure mineral but rather the range as received by the pigment manufacturer.

Hematite

This important iron-bearing mineral, besides providing a source for steel manufacture, is a major source for mineral pigments. Table 1 gives the physicochemical properties of hematite.

Major iron ore sources are sedimentary, as exemplified by the Lake Superior deposits in the United States. Hematite also occurs as igneous, volcanic, hydrothermal, metamorphic, and weathered deposits. Several deposits are unique for their high color value, such as those on the Island of Ormuz in the Persian Gulf or Spanish deposits near Malaga. Micaceous hematite, unique for its lamellar structure, is mined in Austria and Australia. Synthetic processes for the manufacture of micaceous iron oxide have been developed.

Goethite

The second most common iron-bearing mineral is goethite. This includes other hydrated mineral iron oxides such as the limonites, ochres, and siennas. Table 2 gives the physicochemical properties of goethite.

Goethite is typically formed under oxidizing conditions as a weathering product of ferrous minerals, siderite, pyrite, and magnetite, and is widespread as deposits in bogs. It is commonly associated with hematite, pyrolusite, manganite, calcite, quartz, lepidocrocite, clay minerals, and limonite. Hydrated iron oxide is also called limonite. By x-ray examination, most limonites are actually cryptocrystalline goethite with absorbed or capillary water (Palache, Berman, and Frondel 1944). Several excellent pigment ore sources are found in India. Domestic ochre is mined in Georgia and Virginia.

Lepidocrocite

This natural mineral has essentially the same chemical composition as goethite but different crystallographic constants. Table 3 gives the physicochemical properties of lepidocrocite.

Table 1. Physicochemical properties of hematite

Chemical formula	Fe_2O_3
Chemical composition of ore	50% to 95% Fe_2O_3 , associated with other iron or silicate minerals
Crystal class	Hexagonal; scalenohedral
Habit	Thick to thin tabular, as rosettes, rhombohedral, sometimes platy; also earthy
Physical	No cleavage, fracture subconchoidal to uneven, hardness of 5–6
Reaction mechanism	Will form, by solid-state reactions, a wide variety of ferrites of the composition $M \cdot \text{Fe}_2\text{O}_4$ where M represents one or more metals such as manganese, zinc, magnesium, nickel, barium, strontium, and yttrium. These ferrites have important electrical and magnetic properties and to a lesser extent pigmentary properties. Zinc ferrite (tan), magnesium ferrite (brown), and manganese ferrite (black), however, are important pigments in applications requiring heat stability.
Other properties	
Melting point	1,475°C–1,565°C
Boiling point	Decomposes
Solubility	Insoluble in water and common organic solvents
Index of refraction	3.042
Specific gravity	5.26
Magnetic	Usually antiferromagnetic, exists as ferromagnetic synthetically and naturally

Table 2. Physicochemical properties of goethite

Chemical formula	$\alpha\text{FeOOH} \cdot x\text{H}_2\text{O}$
Chemical composition of ore	50% to 88% Fe_2O_3 , 9% to 10% H_2O , balance silicate or clay minerals
Crystal class	Orthorhombic; dipyrnidal
Habit	Prismatic and striated; also in tablets or scales, grading into acicular and long prismatic forms; also earthy
Physical	Cleavage [010] perfect, [100] less so, fracture uneven, hardness of 5.0–5.5
Reaction mechanisms	Will form ferrites through solid-state reactions as noted under hematite. Can also be converted from $\alpha\text{FeOOH} \cdot x\text{H}_2\text{O}$ to $\alpha\text{Fe}_2\text{O}_3$ by heat and to ferromagnetic $\gamma\text{Fe}_2\text{O}_3$ by reduction and oxidation.
Other properties	
Melting point	Decomposes; naturals (finely ground) start to dehydroxylate at 190°C and is essentially dehydroxylated at 320°C; synthetics start at 180°C and are completely dehydroxylated at 300°C.
Boiling point	Decomposes
Solubility	Considered insoluble in water and common organic solvents, 0.0015 gpl cold water
Index of refraction	2.26–2.27
Specific gravity	3.3–4.0
Magnetic	Antiferromagnetic

Lepidocrocite is formed under similar circumstances as goethite and is often associated with it.

Magnetite

The mineral magnetite occurs abundantly and is found worldwide in many locations. The magnetic nature of this mineral gives it considerable historical interest going back to antiquity. Table 4 lists its physicochemical properties.

Magnetite deposits are found as magmatic segregation deposits, as an accessory mineral in igneous rocks, in metamorphic

Table 3. Physicochemical properties of lepidocrocite

Chemical formula	$\gamma\text{FeOOH}\cdot x\text{H}_2\text{O}$
Chemical composition	50% to 89% Fe_2O_3 , 10% to 11% H_2O ; minor amounts of silicates
Crystal class	Orthorhombic; dipyramidal
Habit	As flattened elongated scales sometimes striated; usually as isolated crystals or plumose groups on a matrix
Physical	Cleavage [010] perfect, [100] less perfect, [001] good; hardness of 5.0
Reaction mechanisms	Lepidocrocite converts to ferromagnetic $\gamma\text{Fe}_2\text{O}_3$ on heating at low temperature and to $\alpha\text{Fe}_2\text{O}_3$ at high temperature; will enter into other reactions similar to goethite
Other properties	
Melting point	Decomposes, similar to goethite
Boiling point	Decomposes
Solubility	Considered insoluble in water and common organic solvents
Index of refraction	1.94
Specific gravity	4.05–4.10
Magnetic	Antiferromagnetic

Table 4. Physicochemical properties of magnetite

Chemical formula	Fe_3O_4 (also $\text{FeO}\cdot\text{Fe}_2\text{O}_3$)
Chemical composition	84% to 99% Fe_3O_4 associated with minor amounts of silicate minerals; purity can be high for a natural mineral
Crystal class	Isometric (cubic); hexoctahedral
Habit	Usually octahedral; well-formed, nearly perfect crystals are common; occurs in coarse to fine-grained masses
Physical	Octahedral parting on [111] especially good; conchoidal to uneven fracture; [001], [011], [138] also reported as parting planes in magnetite; hardness of 5.5–6.5
Reaction mechanisms	Synthetic magnetites start to decompose in air to $\gamma\text{Fe}_2\text{O}_3$ at 105°C and are completely oxidized at 385°C. Natural magnetite, if finely ground, will start to decompose at 124°C and be completely oxidized at 550°C. It will form spinel compounds of the general formula $M\cdot\text{Fe}_2\text{O}_4$, where <i>M</i> represents metals such as manganese, zinc, and barium.
Other properties	
Melting point	Decomposes
Boiling point	Decomposes
Solubility	Insoluble in water and common organic solvents
Index of refraction	2.42
Specific gravity	5.16–5.17
Magnetic	Ferromagnetic

deposits in limestones, in chlorite schists with pyrite, in sulfide vein deposits, and in meteorites. Commercial deposits are found in the United States, Norway, and Sweden.

Pyrites and Siderites

These minerals do not fall into the class of iron oxides because they require transformation by heat to convert to the oxide. As such, they are potential raw materials rather than end products.

Manufacturing

The manufacturing procedures for the naturals must be designed around the starting ore base. For example, siderite (FeCO_3) requires

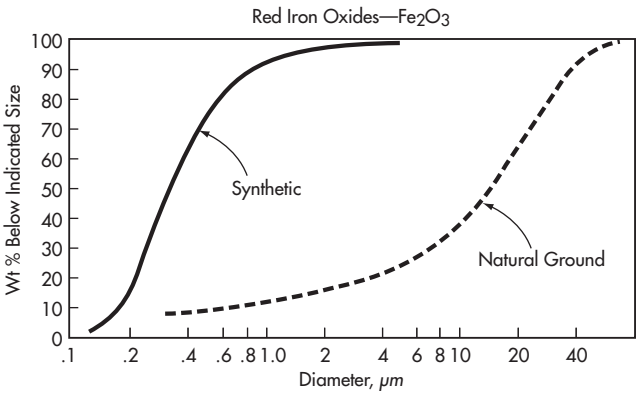


Figure 2. Particle-size distribution comparing a fine particle synthetic with a natural iron oxide

calcination to convert to the oxide, whereas pyrites cinder (calcined pyrite), although essentially Fe_2O_3 , must be freed of its acidic residues. Also, certain ores, although suitable for use by simple grinding, develop more desirable colors if calcined. Other natural ores, siennas, and umbers are produced in raw and calcined form.

Some of the hematites and the magnetites are magnetically beneficiated to increase the chemical purity and remove undesirable siliceous minerals. This is particularly true if the end use has chemical purity requirements such as do ferrites (Anon. 1965). Magnetic beneficiation is most efficient if the mesh size is controlled within fairly narrow limits. Therefore, wet magnetic beneficiation usually follows the crushing and screening operation and precedes fine grinding or calcination. The critical variables are magnetic field strength, pole and plate design, solids concentration and feed rate, demagnetizing field strength, and wash-water feed rate. The process produces a superconcentrate with purities of greater than 99.5% Fe_2O_3 or Fe_3O_4 from lower-grade concentrates.

Fluid energy mills, micronizers, and improved methods of classification have enabled manufacturers to produce natural iron oxide pigments for many applications where chemical purity and the ultimate discrete particle size are not factors.

Products

The broad selection of manufacturing procedures, coupled with the wide variety of natural ore, results in about 100 different products being marketed in the United States alone. Selling price and end-use considerations result in a range of products being produced from a single ore body. For example, a natural iron oxide for a paint primer must be finely ground but has wide latitude in its color specifications. Concrete coloring pigments, however, have stringent color requirements but moderate fineness requirements.

All natural products, without exception, are subjected to some type of final grinding. Comminution, as opposed to particle synthesis, produces characteristic fragmented particles covering a wide size distribution. Figure 2 compares a synthetic iron oxide with a natural ground iron ore, showing a major difference in size and fragmented nature of the natural ore.

Generally, natural iron oxide pigments have weaker tinting strengths because of the larger particle size and lower color purity.

Uses

Many of the applications for natural iron oxides are based on low cost and permanency (Anon. 1991a). There is some overlap in use

of the naturals and synthetics; both, for example, are used extensively in paint and coatings.

Paint and Coatings. The variety and types of industrial coatings are too numerous to mention individually. There are several general types of paints in which natural iron oxides provide excellent properties and represent major uses. *Primers* vary in the degree of pigment loading and function as a base for various topcoats. The primer pigments are usually hematites and can be highly loaded because of high density, fairly large particle size, and low oil absorption.

Industrial maintenance finishes for railway equipment and metal structures largely employ hematites. Micaceous iron oxide (Anon. 1972b), because of its platelike structure, has found extensive use in Europe in railway maintenance coatings, bridge paints, industrial maintenance finishes, and other exterior applications.

Micaceous iron oxide is not a primer or a rust-inhibiting pigment but is used as part of a corrosion control system. To capitalize on its platelike structure, the paint formulator must grind the paint properly to secure a lamellar film structure (Anon. 1971a).

Natural umbers and siennas have unique color characteristics that are not easily matched with synthetics and hence they are the major pigments in stains. With the increased use of prestained wall panels, this is an important application.

The naturals are also used in general interior and exterior house paints, but to a lesser extent than synthetics.

Electronic. Natural iron oxides are used to some extent in preparing barium ferrite ($\text{BaFe}_{12}\text{O}_{19}$) and to a lesser extent in preparing manganese zinc ferrite ($\text{Mn}_x\text{Zn}_y\text{Fe}_2\text{O}_4$). The magnetic properties of manganese zinc ferrites are very sensitive to impurities, and hence the use of naturals has been limited. Highly beneficiated magnetite or hematite can be used to prepare barium ferrites. Beneficiated magnetite when finely ground is used in magnetic inks (Love 1961). The magnetic energy (remanence) of an ink is proportional to the volume of iron oxide in the ink. Because of the low binder demand of the dense natural magnetites, high loadings of 60% to 70% by weight of magnetite pigment can be obtained.

Rubber, Plastics, and Related Compounds. Natural pigments are used to a limited extent in rubber and many of the more common plastics such as vinyls, phenolics, polyurethanes, and epoxies (Woernle 1967). Umbers contain a high percentage of manganese, which can cause undesirable effects such as accelerating the aging of rubber and retarding the curing of polyesters. Generally, these markets favor using the synthetic pigments because of their improved purity, dispersibility, and color value. The cost advantage of natural pigments, however, remains a key factor in their continued use.

Concrete Products and Building Materials. Natural oxides are suitable for coloring concrete, mortar, concrete roof tile, concrete pavers, and similar building materials. In coloring concrete, the tint is the important characteristic and synthetic pigments have replaced most of the naturals because of their higher tinting strength. In some cases, blends of synthetic and natural pigments may be used for a cost advantage.

Rouge. Before the introduction of the float glass process, large tonnages of natural iron oxides were used in polishing plate (flat) glass. This use has declined dramatically because of the float glass process. Ophthalmic rouge and metal-polishing rouge represent a small market. Specially processed grit-free hematites having high glass removal rates are required. Another market is in coloring glass and is referred to as a *batch rouge*.

Miscellaneous. Natural iron oxides are used in numerous other industrial applications such as foundry-core washes, ceramics, paper, and fertilizer, and as the iron source in glassmaking.

Synthetic Iron Oxides

The four major types of synthetic iron oxides are reds, yellows, browns, and blacks. All can be prepared from basic chemicals, usually iron salts and alkalis. The advantage of chemical synthesis is that it gives precise control over three important pigment parameters: particle size, particle shape, and chemical purity.

Raw Materials

Iron Salts. Only two iron salts of commercial significance—ferrous sulfate and ferrous chloride—are used to manufacture synthetic iron oxides. Ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), or *copperas*, as it is commonly called, was the historical base for red oxides produced by calcination. Subsequently, ferrous sulfate was used as the iron salt to produce yellows, reds, browns, and blacks by precipitation. The increased use of hydrochloric acid to pickle steel resulted in an abundance of by-product ferrous chloride.

Ferrous sulfate for pigment production is available from three sources. The first consists of neutralizing scrap iron with H_2SO_4 . A second is by-product sulfate pickle liquor from steel mills. This is a mixture of about 15% FeSO_4 (ferrous sulfate) and 10% H_2SO_4 , the balance being water. The excess acid is converted to FeSO_4 by neutralization with iron. The third major source is the titanium pigment industry, which produces by-product $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. This iron salt must be redissolved and purified. The subsequent processing is the same as steel mill pickle liquor.

Domestic pigment manufacturers rarely use ferrous chloride to produce color pigments. Its use limitations are more fully discussed in the following section on by-products.

Iron. The iron source is generally stampings and punchings of light gauge, soft black steel. Pigment producers avoid scrap that is plated (galvanized) or contains alloying elements because of the adverse effect of these impurities.

Alkalis. The major alkali used in the United States is sodium hydroxide (NaOH) followed by ammonium hydroxide (NH_4OH). Environmental regulations, however, have significantly reduced the use of ammonium hydroxide. Lime (CaO) is used to a limited extent but could become more important with increased regulation of the use of ammonium hydroxide. Both sodium hydroxide and liquid ammonia (NH_3) with a high degree of chemical purity can be purchased, which is less true of commercial limes. Sodium carbonate is sometimes used as well.

By-products. Most of the by-products require further processing either as raw materials or as end products. Spray roasting ferrous chloride pickle liquor produces Fe_2O_3 and HCl . The spray-roasted oxides can be returned to the steelmaking process but usually are landfilled. Some steelmakers, however, divert a portion of the Fe_2O_3 to other applications where color is not important. The spray-roasted oxides are generally poor in color quality but can exhibit good chemical purity. Even poorer in quality are the dust collector-recovered oxides produced from the basic oxygen steelmaking process. The thousands of tons of these two waste products have depressed pigment prices in markets where color quality is not a major consideration.

Mill scale, although abundant, has found only very minor usage in the iron oxide industry. One of the major contaminants of this product is refractory material from spalling of furnaces and linings. Also, mill scale is not a completely oxidized product and cannot be used for pigmentary purposes without further processing.

Other waste products that have attracted attention over the years but have not proven suitable for commercial pigments are red mud from bauxite processing, sponge iron from cement copper mining operations, and sulfur mud or *yellow boy*, a precipitate

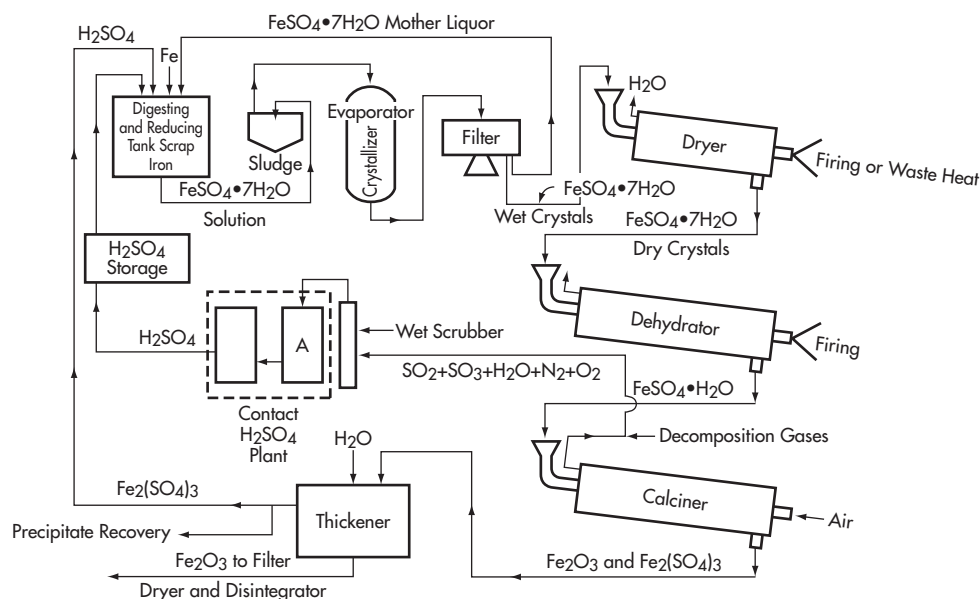


Figure 3. Simplified flow diagram for synthetic iron oxide (copperas red type)

formed from acid coal mine waters. Failure was generally caused by unacceptable color purity.

Manufacturing Processes

The three major methods for manufacturing synthetic iron oxides are thermal decomposition of iron salts or iron compounds, precipitation of iron salts usually accompanied by oxidation, and organic reduction processes using iron. The last route has become less significant as new processes have replaced iron as the reductant.

Thermal Decomposition of Iron Salts. There are numerous combinations of processing techniques, depending on the starting basis. Only one flow sheet (Figure 3) is outlined, starting with scrap iron and sulfuric acid (Ayers 1946). If the starting base is steel mill pickle liquor or titanium copperas, the process is essentially the same with the exception that steps may be introduced to remove undesirable impurities.

Figure 3 illustrates the production of iron oxides by the calcination of ferrous sulfate. These products are commonly known as copperas reds. One major advantage of this thermal decomposition process is that the products of combustion are reclaimed and reused.

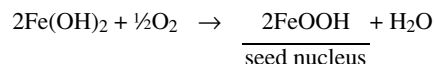
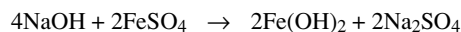
One of the earliest synthetic iron oxides and a variation of the calcination of ferrous sulfate is the Venetian reds. These oxides were produced by calcining an intimate mixture of ferrous sulfate and lime or preferably hydrated lime ($\text{Ca}(\text{OH})_2$). The calcination product must be ground to be suitable for pigmentary applications. The process has one advantage in that the kiln product does not require washing. Venetian reds have been supplanted by other synthetic reds.

Most steel mills have converted from sulfuric acid to hydrochloric acid in their pickling lines. This facilitates the recovery of the acid and generates iron oxide as a by-product. The amount of by-product iron oxide generated exceeds the total present production of iron oxide pigments. The by-product oxide may be pelletized and recycled into the steel process. Some of the oxide is also used as a raw material for the ferrite industry.

Precipitation Reactions. Precipitation processes were developed in the early 1900s (Penniman and Zoph 1921) but did not

achieve commercial importance until the 1930s to 1940s. Since that time, the major growth in synthetic iron oxide manufacture has been by precipitation technology. The precipitation process produces yellows, reds, browns, and blacks. Additional products can be produced by subsequent procedures such as calcination and reduction, among others.

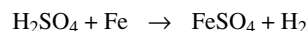
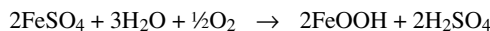
In the manufacture of yellow oxides by the Penniman–Zoph process (often referred to as the scrap iron process), the initial reaction is one of nucleation, wherein the reaction of an iron salt and an alkali forms a seed nucleus. The nucleation reaction is normally conducted in an excess of FeSO_4 and can be described by the following equations:



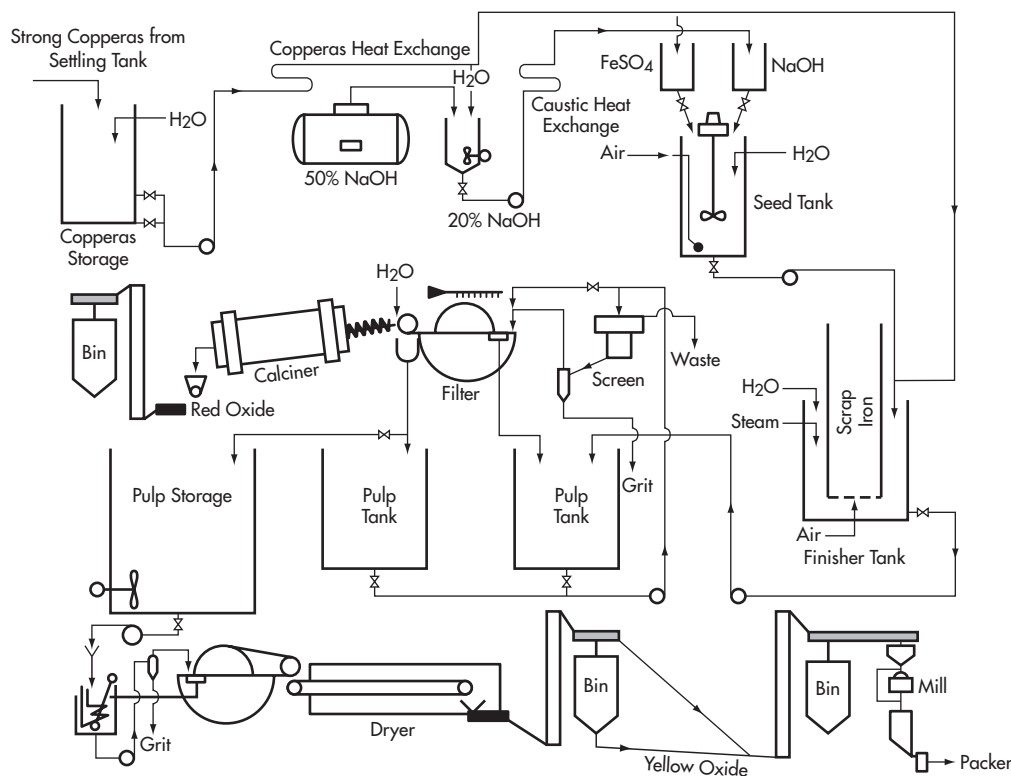
The nucleus is transferred to a precipitator containing FeSO_4 , H_2O , and iron, usually in the form of thin-gage stampings. The seed particles are continuously circulated over the bed of iron in an oxidizing environment at elevated temperatures (60°C to 88°C), and, as the iron oxidizes or dissolves, the reaction products precipitate on the nuclei, causing the particles to grow. The chemical reactions involved are



also



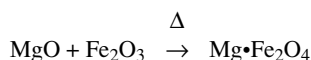
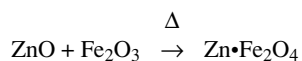
From the simplified chemical reactions, the precipitation process would not appear to be complex, but the actual gas–liquid–solid chemical interactions are still not completely understood. A host of variables affect the reaction and the products. Some of the more



agent. Most organic chemical manufacturers, however, use different reducing agents or, if they use iron, are more concerned with the organic compound than with the iron oxides produced. Consequently, most iron oxide sludges from the reduction of organic compounds are, generally, an impure waste product.

If nitrobenzene is reduced to aniline in the presence of various chemicals, it will produce specific colors of iron oxides (Love 1946). AlCl_3 (aluminum chloride) can be used to produce yellow oxides but is omitted when blacks are desired. Reds can be produced by calcining either yellows or blacks. In each, the choice of iron source is carefully controlled and usually consists of iron filing or iron powder. This route is known as the Laux process.

Miscellaneous Manufacturing Processes. Another related product line consists of tan pigments. The tan pigments are zinc or magnesium ferrites (Downs and Martin 1950, 1959). These are formed by interaction of iron oxides with metallic oxides to form the ferrites. The reactions are as follows:



A final example of a product that is between a synthetic and a natural, with respect to its variable nature and very high impurity level, is the by-product oxide from the basic oxygen furnace (BOF) steel production. The by-product oxide is collected from gases evolved during the lancing process.

Products and Properties

The synthetic manufacturing approach opens up an almost infinite number of distinct product possibilities. An iron oxide producer wishing to cover all major synthetic marketing applications may have more than 100 iron oxide products available for sale. The product shape often becomes critical to optimum pigment performance.

The typical shape of a calcined copperas red (Figure 5) can be compared to a precipitated red oxide (Figure 6).

Figure 7 shows a yellow iron oxide before (left) and after (right) being subjected to a high temperature of 1,038°C.

Figure 8 shows a synthetic, precipitated black iron oxide.

Specifications

Specifications vary widely based on the end-use application. A paint manufacturer will be most concerned with color and top size, whereas a manufacturer of ferrites requires chemical purity (see Table 5).

Natural pigments will have much wider tolerances and, in some cases, are usually not as tightly controlled for color and tinting strength.

Applications

As previously noted, there is an overlap between natural and synthetic oxides. Some applications, either by custom or necessity, use only synthetics.

Paint. Synthetic oxides have higher chroma or color purity and greater tinting strength than natural oxides. The color purity variation from lot to lot can be closely controlled, which is not always true of a natural. They have excellent dispersion properties. Consequently, they are ideally suited for universal tinting systems, powder coatings, automotive finishes, appliance enamels, and interior and exterior paints (Parker 1965; Patterson 1967; Anon. 1968; Parfitt 1969). They are nontoxic and meet existing federal regulations.

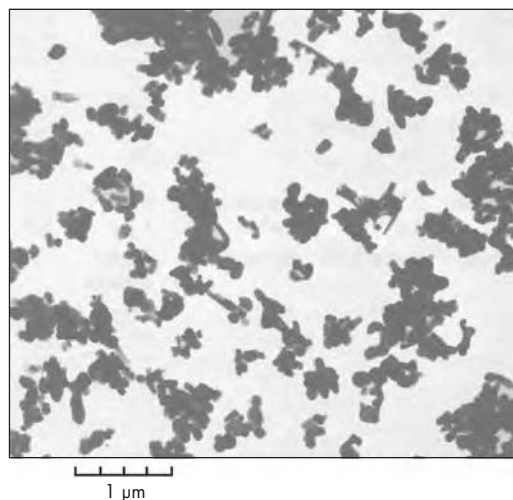


Figure 5. Light synthetic red iron oxide, copperas red type

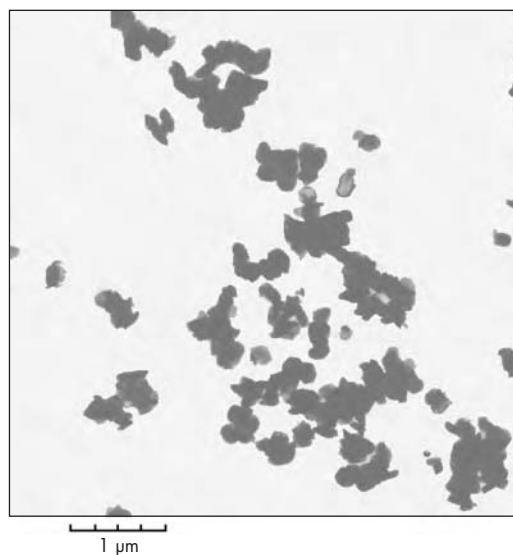


Figure 6. Light synthetic red iron oxide, precipitated type

A group of ultrafine iron oxide pigments are known as transparent or low-opacity products. These pigments have found application in the automotive industry in the manufacture of metallized finishes in the copper and orange color range. These iron oxide pigments are used with other metal pigments (e.g., aluminum) to produce striking automobile finishes.

Electronic Applications (Ferrites). The conventional synthetic reds had the major share of the ferrite raw material market until about 1975. Today, steel mill oxides derived from ferrous chloride (regenerated, or "regen," oxides) have become dominant in this market. The soft ferrite market remains a more limited consumer of synthetic reds. Copperas reds and calcined yellows are sometimes preferred because of chemical purity, high density, and minimum volatiles (Stephens 1959). The 1990 western world production of permanent magnetism was estimated to be about \$2 billion; the iron oxide portion of the total ferrite dollar sales was less than 5% (Kline 1981).

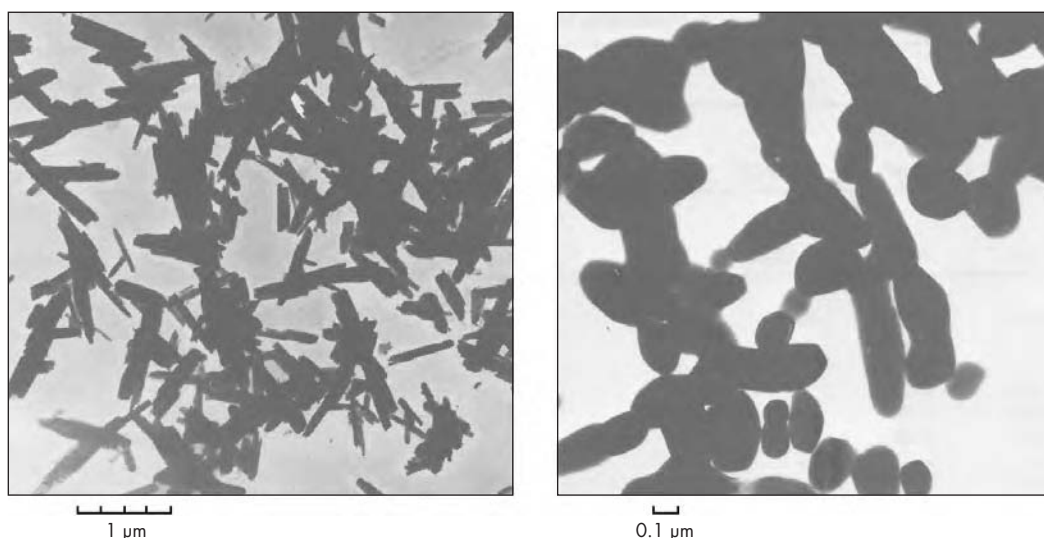


Figure 7. Change in morphology in synthetic yellow iron oxide (FeOOH) by heat treatment to red oxide (Fe_2O_3)

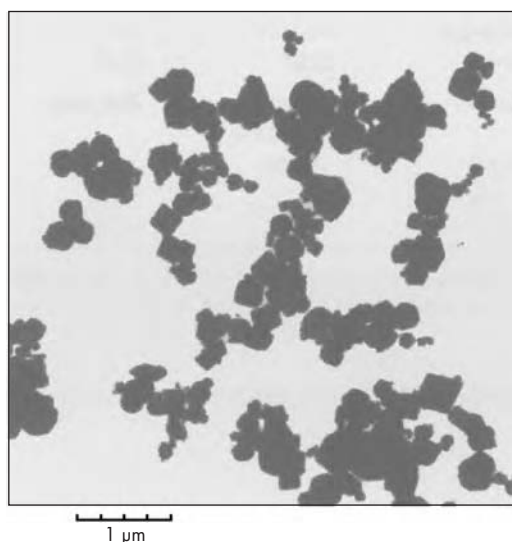


Figure 8. Synthetic black iron oxide (precipitated magnetite)

Magnetic Recording. Magnetic tape recording and magnetic ink oxides represented a U.S. market of greater than 14 ktpy in 1990 for all applications, but this market continues to decline drastically. Most magnetic recording tape applications that use gamma ferric oxide or cobalt-treated gamma ferric oxide products are being replaced by optical recording discs (CDs and DVDs).

The requirements for audio, video, and data recording vary, and special oxides are produced for these applications. Slow recording speeds and high fidelity require ultrafine oxides. Cobalt modification is required to elevate the intrinsic coercivity of gamma ferric oxide to the higher levels required by video and the higher density applications.

Magnetic inks for check processing (magnetic image character recognition, or MICR), credit cards, and railway tickets use synthetic magnetite or other ferrites, which provide high pigment concentrations in the binder system.

Table 5. Typical color pigment specifications

Mass color	1.5 DE CIE-Lab, 3.0 FMC-II units (maximum)*
Tint tone	1.5 DE CIE-Lab, 3.0 FMC-II units (maximum)*
Tint strength	±5% of standard (maximum)
Fe_2O_3 (copperas red type)	Minimum 99.0%
Fe_2O_3 (precipitated red type)	Minimum 96.0%
+325 mesh sieve retention	0.10% maximum
Moisture at 110°C	0.30% maximum
H_2O soluble salts	0.20% maximum
Dispersion for specialty milled reds	6.0 minimum Hegman fineness (ASTM D1210)
Oil absorption	±10% of standard (maximum)

* International Commission on Illumination (CIE) $L^*a^*b^*$ color system; CIE-Lab color difference method as described by Nassau (1998). FMC-II described by Chickering (1971).

Concrete Products and Building Materials. Synthetics have the advantage of greater tinting strength and uniformity and have replaced naturals in most applications. This is a growing market, consuming approximately 50 % of the 1.5 Mt global total (Will 2004). Construction grades are produced in three forms: fine powder, liquid, and granular. Popularity of the granular form continues to grow. Granulation processes include compaction, spray drying, and extrusion.

Plastics, Floor Tile, Linoleum, and Rubber. High chemical purity, high chroma masstones, and strong tints result in a low cost per color unit, accounting for high usage of synthetics. Many plastics require stabilization, which is more easily accomplished with the consistent chemical purity of the synthetic iron oxide.

Chemical and Miscellaneous. Synthetic iron oxides are used singly or in combination with other elements as catalysts in various conversions for ammonia, styrene, butadiene, hydrogen, desulfurization, and formaldehyde (Mills 1964). Aerospace and airbag propellants also use iron oxides, although the azide technology requiring iron oxide oxidants has been essentially replaced by

alternate technologies using organic fuels and other oxidants. A critical rocket application is the Space Shuttle booster rockets. A copperas red-type iron oxide is used as a burn rate control agent in this application. Here, the iron oxide serves as a catalyst to promote the activity of the ammonium perchlorate oxidizer.

Iron oxide is added to animal feeds, primarily for color coding, and also as a coloring agent for pet foods.

Iron oxides are considered to have a "generally recognized as safe" (GRAS) rating by the Food and Drug Administration (FDA). Certain grades that meet the maximum of 3 ppm arsenic, 10 ppm lead, and 3 ppm mercury are approved for drug and cosmetic use. Iron oxides for pet foods must not exceed 5 ppm arsenic, 20 ppm lead, and 3 ppm mercury. The European Union has also adopted E-172 regulations. These require conformance for 9 trace metals: maxima in ppm are 5 arsenic; 50 barium; 5 cadmium; 100 chromium; 50 copper; 20 lead; 1 mercury; 200 nickel; and 100 zinc; also, 1.0% maximum water soluble salts. Even lower nickel levels are becoming the standard in Europe.

Synthetic oxides are used for ophthalmic polishing and as the iron source for coloring glass and providing ultraviolet (UV) absorptive properties.

An interesting application is in medicine. Magnetic oxides have the ability to absorb myxoviruses, which can then be magnetically separated from the system (Warren 1969). Another medical application for magnetic iron oxides is in analyzing red blood cell population and targeting cancer sites with magnetically modified medicines (N. Shaffer, personal communication).

Marketing

The demand for iron oxides is closely related to domestic and worldwide requirements of the construction, coatings, automotive, plastics, electronics, and chemicals industries.

Iron oxide prices were very stable from 1960 through 1970. The inflationary costs of labor and supplies plus high energy and environmental regulation costs necessitated significant price increases from 1970 to 1990. Today, with continued increases in energy costs and dramatic increases in scrap prices, price adjustments are required. The 11-year price trend of a selected range of natural and synthetic iron oxides is found in Table 6; they continue to be the most cost-effective color pigment. Pricing for special grades, including high-purity iron oxides and electronic grades, is not shown in the table.

Iron Oxide Statistics—United States

Table 7 shows U.S. sales, including import and export data, for natural and synthetic iron oxides for 1998–2002. The value has continued to decrease because of a steady price erosion. Table 8 shows U.S. sales data available to the U.S. Geological Survey (USGS) by iron oxide type.

Environmental Considerations

One of the major factors affecting iron oxide manufacturing today has been federal and state regulations regarding the environment. Whereas the major steel and titanium processors were disposing of their iron salts by dumping, they are now required to recover and process these salts before disposal. This has resulted in large quantities of cheap by-product iron oxides. The iron oxide manufacturers have also been required to recover and process any soluble iron salts that were previously discharged, resulting in increased manufacturing costs.

Table 9 shows the heavy metal content in several iron oxide products, both natural and synthetic. The synthetic iron oxides are generally low in these elements, as can be expected by the chemical

Table 6. Typical iron oxide prices, 1980–1991

Iron Oxide Type	1980, ¢/kg	1991, ¢/kg
Black		
Synthetic	0.95–1.08	1.80–2.09
Micaceous	1.21	1.96
Brown		
Ground iron ore	0.22–0.29	0.33
Metallic	0.40–0.44	0.44–0.81
Pure synthetic	1.03–1.21	1.85–1.98
Burnt sienna (Italy)	1.54	1.32–1.91
Burnt umber (Turkey)	0.68–0.79	1.14–1.56
Red		
Domestic primers	0.48–0.64	na*
Pure synthetic	0.99–1.14	1.94–2.27
Spanish	0.62–0.70	na
Yellow		
Synthetic	1.14	1.65–2.13
Ochre (French)	0.51	na
Ochre (domestic)	0.29	0.73–1.25

* na = not available.

Table 7. Salient U.S. iron oxide pigments statistics*

Pigment Quantity and Value	1998	1999	2000	2001	2002
Crude pigments sold or used, t†	46,100	44,100	57,100	61,500	W‡
Value, thousand \$	7,290	7,740	4,470	3,460	1,070
Finished pigments sold, t§	180,000	183,000	154,000	135,000	115,000
Value, thousand \$	193,000	187,000	142,000	130,000	117,000
Exports, t	14,600	13,800	9,640	9,100	6,270
Value, thousand \$	18,200	15,200	17,200	16,800	12,100
Imports for consumption, tons	63,800	80,800	91,300	89,900	132,000
Value, thousand \$	62,900	71,400	76,700	76,900	96,300

Courtesy of USGS.

* Data are rounded to no more than three significant digits.

† Mined.

‡ W = Withheld to avoid disclosing company proprietary data.

§ Natural (mined) and synthetic.

control provided in their manufacture. Certain grades of copperas reds show particularly low values of arsenic, lead, and mercury. Precipitated reds, synthetic yellows, and synthetic blacks are somewhat higher in the heavy metals but are low compared with the naturals. Table 9 shows this natural red to be particularly high in arsenic, lead, and barium. Natural iron oxides can show considerable variation in heavy metal content in different areas of the world and sometimes in the same ore deposit.

Trends and Opportunities for Iron Oxides

Two major markets for iron oxides are coatings and concrete products. Today, key new sources for iron oxides include China and India. It is estimated that in 2000, China produced 26% of the global total of 1.5 Mt; Western Europe, 25%; India (largest natural iron oxide producer), 22%; Japan, 15%; and the United States, 11% (Will 2004). The growth of China as the leading synthetic iron oxide producer is likely to continue.

New iron oxide developments during the past 20 years have included granular forms of iron oxides and new versions of nano-sized (less than 0.1 µm) materials. It is expected that future developments will focus on using iron oxides in nano composites and

Table 8. Finished iron oxide pigments sold by processors in the United States, by type*

Pigment Type	2001		2002	
	Quantity, t	Value, thousand \$	Quantity, t	Value, thousand \$
Natural				
Black: Magnetite	16,000	2,630	W†	W
Umbers				
Burnt	2,010	3,180	1,680	2,260
Raw	W	W	W	W
Red: Iron oxide‡	38,900	8,020	W	W
Undistributed and other§	13,000	8,680	58,200	17,800
Total	69,900	22,500	60,000	20,600
Synthetic				
Black: Iron oxide	W	W	W	W
Brown: Iron oxide	W	W	W	W
Red: Iron oxide	W	W	W	W
Yellow: Iron oxide	19,600	33,600	19,700	34,900
Mixtures of natural and synthetic iron oxides	W	W	W	W
Total	64,700	107,000	54,600	96,000
Grand total	135,000	130,000	115,000	117,000

Courtesy of USGS.

* Data are rounded to no more than three significant digits; may not add to totals shown.

† W = Withheld to avoid disclosing company proprietary data; included with undistributed and other, and in total.

‡ Includes pyrite cinder.

§ Includes raw umber, burnt sienna, ocher, and raw sienna, and data indicated by W.

Table 9. Concentrations of heavy metals in light or medium shade iron oxides, ppm

Element	Copperas Reds	Precipitated Reds	Precipitated Yellow	Synthetic Black	Natural Red	Raw Sienna	Burnt UMBER
Arsenic	<3*	20–60	5–40	3–15	50–100	70–120	100–200
Antimony	5–15	5–20	5–20	10	40–80	Potassium spectral interference	Potassium spectral interference
Cadmium	<10	<20	<20	<20	<50	<50	<50
Selenium	<20	<20	<20	<20	<100	<100	<100
Mercury	<5	<5	<5	<5	<5	<5	<5
Lead	1–15	10–140	10–50	50–100	6,000+	100–500	100–300
Barium (acid soluble)	<10	30–120	100–1,000	100–1,000	100–2,000	na†	400–1,100

* Symbol "<" indicates that if the element is present at all, it is below the detection limit of analytical method used. Mercury is determined by flameless atomic absorption; arsenic is determined by USP colorimetry method. Remaining elements are determined by x-ray fluorescence.

† na = not available.

new chemical applications, with the paint/coatings and construction industries continuing to dominate, as in the past.

TITANIUM DIOXIDE

White pigments have been known and used since antiquity. Metal oxides such as antimony oxide and lead oxide were in general use for centuries. Zinc sulfide, barium sulfate, and blends of these materials with each other and with other materials have been used since at least the late 1800s and are still used in some applications today. The advent of the 20th century saw the large-scale commercial introduction of titanium-based white pigments possessing many advantages over those used historically. High brightness, high opacifying power, lack of toxicity, and long-term stability allowed titania-based pigments to rapidly overtake other materials used in these applications (Wicks, Jones, and Pappas 1992). Engineering of new surface architectures was developed in the 1950s. The continued refinement of this aspect of manufacture has led to a tremendous increase in the

ability to tailor these ultimately composite materials into ever-broader end-use arenas (Braun, Baidins, and Marganski 1992).

Pigmentary materials based on the chemistry and physics of rutile and anatase titanium dioxide are the predominant items of commerce used to generate white, opaque articles and to tint materials. These pigmentary materials are almost never simply titanium dioxide. An intermediate titanium dioxide is generated from a titanium-bearing ore such as ilmenite or from a titanium slag. The surface architectures of these materials are then modified by both inorganic and organic chemistry to produce a variety of preferred performances based on intended market end use (Furlong 1994). In addition, the particle-size distribution and the solid-state phase chemistry have marked effects on the manner in which these materials interact with actinic radiation (van de Hulst 1981). Despite these facts, it is not uncommon for users to describe titanium dioxide pigments simply as *Pigment White 6*. This oversimplification can lead to erroneous grade selections and subsequent failure in use

of end products made with improperly selected pigments. Given the ubiquity of titania pigments in the commercial world, it is of value to understand those factors differentiating performance in various end uses and to understand their origins. This, in large part, forms the basis of this section on titanium dioxide.

Terms and Definitions

The pigmentary materials discussed here are referred to as *titania pigments* for sake of conciseness. Certain specific terms are often used in discussions of these materials and this short list covers those considered most important.

- **Anatase:** Anatase is a polymorph of TiO_2 with a refractive index of 2.5. Tetragonal, space group $I4_1/amd$ (141) (Wells 1975)
- **Brookite:** Brookite is a polymorph of TiO_2 . Not of commercial utility in pigmentary applications. Orthorhombic, space group P/cab (61) (Wells 1975)
- **Durability:** Although TiO_2 readily absorbs UV light in the solar spectrum, it also acts as a photocatalyst as a result of the formation of electron-hole pairs from its wide band gap and resulting semiconductor behavior. To prevent the UV-induced catalytic destruction of paints, polymer films, and other matrices in which it may be used as an opacifier and/or a UV screener, the surfaces of the particles are modified to prevent photochemical reactions (Rabek 1990; Diebold 2005).
- **Dispersability:** For a titania pigment to provide optimal performance, it must be uniformly dispersed and distributed in the carrier matrix of the finished good in which it is used. As TiO_2 itself has a relatively high surface-free energy, surface modifications are made to lower the surface-free energy and thus improve the compatibility of the pigment with the medium in to which it is being dispersed. This reduces the amount of energy required to carry out the initial dispersion, thus lowering costs for the end user. For fluid systems, surface modifications are also used to stabilize the dispersions once they have been formed. The intention is to both prevent flocculation and to reduce settling over time (Wicks, Jones, and Pappas 1994).
- **Particle-size distribution:** To maximize the scattering of visible light, the median particle size of pigmentary titanias is typically controlled to approximately $0.25 \mu\text{m}$, or roughly half the wavelength of blue light in the visible spectrum. Distributions are typically log-normal. Particles larger than $\sim 0.5 \mu\text{m}$ are avoided because of the adverse impact these have on certain appearance properties in film applications (particularly gloss) (Allen 1990).
- **Refractive index:** The refractive index is the ratio of the velocity of an electromagnetic wave (e.g., visible light) in a vacuum to the velocity of an electromagnetic wave in the medium of interest. Differences in refractive indices between carrier matrices, such as paint or polymer films, and a filler, such as a titania pigment dispersed in them, largely dictates opacity (Wicks, Jones, and Pappas 1992).
- **Rutile:** This is a polymorph of TiO_2 with the highest refractive index available (2.73). Tetragonal, space group $P4_2/mnm$ (Wells 1975)
- **Surface treatment:** This is an inorganic or organic modification to the surface of an intermediate TiO_2 particle. Surface treatments are used to induce specific surface architectures that dictate the end-use behavior of the material. Inorganic treatments are typically comprised of a hydrous, often multiphase coating of silica and alumina, often deposited step-

wise. The alumina coating may be further modified by the addition of other species. Other oxides, particularly zirconium oxide, may also be included. Organic treatments are typically added as the last tier of the surface architecture. These may include polyols, alkanolamines, siloxanes, silanes, fatty acids, and a number of other materials.

Production

Titania pigments are produced by two large-scale processes: the sulfate and the chloride routes. At present, roughly 75% of the titania pigments produced worldwide are manufactured using the chloride process, and the balance is produced by the sulfate process. Plants are currently in operation in North and South America, Europe, Asia, Africa, and Australia. Ores used as feedstocks for these processes are obtained from a wide variety of sources.

Infrastructure

The infrastructure supporting the titania pigments industry includes the mining industry (titaniferous feedstocks), the steel industry (slag ores), and the chemical industry (sulfuric acid, chlorine, and related raw material feedstocks).

Titanium is generally considered to be the 9th most abundant terrestrial element. Titanium-containing ores are mined on every continent except Antarctica. Both rock ores and sand ores (usually found in alluvial deposits) are mined commercially. Because of the high relative density of titanium-bearing ores, it is possible to find relatively uniform deposits of very high heavy-mineral content in a large number of locations. Slags containing high concentrations of titanium are generated in certain steelmaking processes. These materials may be ground to a useful size and consumed in both the chloride and the sulfate production processes. Higher concentrations of titanium in feedstocks obviously result in lower volumes of nontitanium side streams that must be managed as a part of the overall manufacturing process. As such, higher-grade feedstocks generally command considerably higher prices than low-grade materials.

Chlorine for the chloride process is generally obtained from chlor-alkali plants. Although the majority of the chlorine used is recycled in the process, some so-called make-up chlorine is required to maintain production. With the decrease in chlorine use in the bleaching of paper, the relative consumption of chlorine by the TiO_2 pigments industry has increased, most markedly in the United States. Sulfuric acid and oleum used in the sulfate process are generally produced by the oxidation of elemental sulfur and by the conversion of off-gases containing the oxides of sulfur. These are also largely recycled in the process, although dilution occurring during processing results in the requirement of concentration of dilute waste acid before reintroduction to the process.

Raw and Intermediate Materials

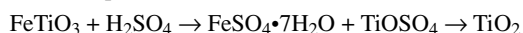
The critical raw materials for the sulfate process are titanium-bearing ores, strong sulfuric acid, and surface treatment chemicals. The chloride process requires titanium-bearing ores, chlorine, oxygen, and surface treatment chemicals. Single ores or their blends can be used in either process. The ore requirements for the two processes are not identical. Certain ores are not amenable to dissolution in strong sulfuric acid, and as such cannot be used as feedstocks for the sulfate process. Ores of extremely fine particle size cannot readily be used in either process because of material handling and related processing concerns. The nontitanium elemental composition of the ores is also quite important, because these materials report to a secondary stream from the primary pigment process. The difficulty in handling these streams is generally taken to be directly proportional to the nontitanium content of the feedstock.

Technology

The two major technologies in use today for the manufacture of titania pigments are based on the sulfate process, commercialized early in the 20th century, and the chloride process, commercialized in the 1950s.

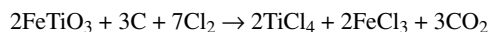
Sulfate Process

In the sulfate process, titanium-containing ores are dried, crushed, and reacted with sulfuric acid to form a mixture of titanium sulfate and other sulfates, predominantly iron, in a batch process. Scrap iron is added to facilitate the precipitation of iron as copperas (iron sulfate heptahydrate). The remaining titanium-bearing solution is then purified. The precipitation of titanium dioxide from the solution is then induced, and the material formed serves as the intermediate from which the finished titania pigments are produced. The intrinsic polymorph obtained from the sulfate process is anatase. Calcination is required for conversion to rutile (Anon. 1991b).



Chloride Process

In the chloride process, a mixture of titanium-bearing ores, a carbon source, and chlorine gas are allowed to react at high temperature in a continuous process. The resulting mixture of chlorides is then separated and the resulting titanium tetrachloride is further purified. This material is then reacted with oxygen at high temperature to form an intermediate from which the finished titania pigments are produced (Braun, Baidins, and Marganski 1992).



Economic Production Factors

The production of titania pigments is quite capital intensive at any commercially reasonable scale. Although many extremely small (<10,000 tpy) sulfate-technology facilities exist around the world, more than 80% of the material produced globally is generated by facilities with individual capacities ranging from approximately 50,000 tpy to more than 350,000 tpy. It is also a concentrated industry in terms of the producers involved, with about 80% of world capacity operated by the top 5 producers.

The largest factor operative in the costs associated with the manufacture of titania pigments is feedstock costs—most specifically, the cost of titanium-containing raw materials. Although a large variety of ores are used in the industry, they can generally be separated into four classes: ilmenites, beneficiated ilmenites, slags, and natural rutiles. The cost spectrum spanned by these materials is quite large, often a factor of four to five, depending on requirements. Because everything in the ore except the titanium must be removed, higher-grade ores are intrinsically advantageous—but also, therefore, command higher prices. In addition, some titanium-bearing ores occur in association with naturally occurring radioactive materials, specifically minerals containing either thorium or uranium. These are generally not of great value to the industry because of government regulations in some countries and concerns about the formation of low-level radioactive materials that result from concentration effects in certain manufacturing processes.

Contaminants such as alkaline earth elements can also reduce the utility of some ores. In addition, some elements cannot be readily removed in the sulfate process, leading to the formation of unacceptable color centers in the final product. Most transition metals (particularly iron, chromium, vanadium, and nickel) can degrade the color performance of titania pigments to an extent that is commercially unacceptable at levels of less than 25 ppm. The oxidation state of the

contaminant can also have a substantial impact on the degree of color degradation. Transition metal contaminants must therefore be reduced to extremely low levels to avoid adverse color effects in finished pigments.

Consumption

Global consumption of titania pigments is about 6 Mtpy. Because of the ubiquity of titania pigments, consumption typically tracks gross domestic product (GDP) and has been noted to be a leading indicator of economic performance.

The materials are consumed in a very broad manifold of end uses. These can be broken out into the following categories: Coatings (paints), polymers, paper, and specialties. Coatings is the largest segment globally, followed in order by polymers, paper, and (distantly) by other specialty end uses. More than half of the titania pigments produced are consumed in the manufacture of coatings.

Specifications

Specifications for titania pigments differ for each end use. One measure, *hiding power*, applies across all end-use segments. It is a measure of the opacifying capability of a given pigment in a given application on a weight basis. Titania pigments are primarily sold as opacifying agents, and as such, their performance in this regard is most critical and applies across all end-use segments (Balfour 1990).

Coatings Applications

The most common applications in coatings follow.

- **Color:** This refers to what some call “dry color.” It is measured on a dry pigment sample and is typically reported in terms of the International Commission on Illumination (CIE) $L^*a^*b^*$ color system. Several other color systems are also used by various industries (Berns 2000). For titania pigments it is a direct measurement of transition metal (nontitanium) impurities remaining after the manufacturing process.
- **Dispersability:** A measure of the difficulty with which the pigment is incorporated into a matrix. Both distributive and dispersive mixing play a role in this behavior. Performance can be evaluated by standard methods including the preparation of a millbase or a finished paint, and subsequent evaluation using a Hegman gage or related device to determine the number of oversized particles present. Resistance to flocculation is also an important aspect for paint systems, as the end user does not wish the particles to form agglomerates once the dispersion has been prepared.
- **Durability:** Long-term durability performance is initially evaluated during product development using an actual exterior panel exposed for 24 to 48 months in a variety of locations around the world to obtain a broad representation of natural conditions. From these, derived accelerated tests have been generated. For surface-modified pigments using dielectric encapsulation as a means of inducing durability (a widely practiced route), it is possible to measure the amount of “exposed”—and, therefore, photoactive—titania by means of an acid solubility test. This test correlates very well with long-term durability testing and is sufficiently rapid to allow its use as a product release test (Holtzen, Diebold, and Niedenzu 2002).
- **Gloss:** This is an appearance characteristic related to the degree to which the pigment decreases the level of luster or brightness inherent in an unpigmented film because of changes in the relative ratios of specular and diffuse reflectance. It is typically evaluated in an actual paint system and is

carried out using standard gloss meter measurement technology. The particle-size distribution, which is related to this appearance characteristic, is also often measured (Wicks, Jones, and Pappas 1994).

- **Grit:** This is typically measured by screening an aqueous dispersion of the pigment through a 325 -mesh screen to determine the amount of large agglomerates in the pigment. High grit content adversely impacts appearance of finished paint films and also results in reduced throughput in the paint manufacturing process.
- **Oil absorption:** This property reflects both the surface area and the surface pore structure of the pigment. It is typically measured by determining the amount of an organic fluid (linseed oil, for example) that can be absorbed by a measured amount of the pigment. The formulation of a paint can be greatly affected by changes in oil absorption.
- **pH:** Reciprocal of hydrogen ion content, measured for an aqueous dispersion of the pigment. The chemistry of some paints can be very sensitive to pH and must be monitored closely (Hunter 1996).
- **Resistance:** This is electrical resistance, as measured on an aqueous dispersion of the material. It is a measure of the ionic content of the pigment. Excessive ionic content can adversely affect paint chemistry.
- **Tinting strength:** This is a means of determining the unit opacifying power of a pigment, usually carried out in a paint system and measured by standard optical techniques.

Polymers

The information on polymers is taken primarily from Saechtling (1992).

- **Dispersion:** For polymer applications, different types of dispersion measurements are used depending on the end use. For vinyl systems, it is common to use a rolled soft vinyl sheet to determine dispersion performance. It is also possible to use polyolefin dispersion measurements. The two most common tests are screen-pack dispersion and the so-called filter test. In both, the pigment sample is combined with a polymer (typically a polyethylene) at 50% to 70% pigment loading by weight. This is then extruded through a screen. The material on the screen may be analyzed for oversize particle content (screen pack value) or the increase in pressure in the system as a function of time may be measured (the filter value). In both cases, a 500-mesh screen is typically used, although extremely high-performance applications such as fibers may utilize 1,400-mesh screens (Shenoy 1999; Holtzen, Reid, and Sedar 2003).
- **Color, pH, and resistance:** See Coatings Applications section in this chapter.
- **Other optical characteristics:** These are also measured in multiple ways, although a common approach is to prepare a vinyl masterbatch and to determine the performance of the material in this exhibit. Other matrices are also used. The values are reported differently by the various producers (Harper and Modern Plastics 1999).

Paper

The information on paper is taken from Hagemeyer (1997).

- **Abrasion:** A measure of the degree to which a filler leads to the dulling of slitter knives and other equipment used in paper processing. Abrasion is generally measured by determining

the amount of metal removed from a screen that is placed into an aqueous dispersion of the filler and rotated several hundred thousand times to simulate blade movement. Another measurement used by some producers is a needle penetration test, wherein lab-generated paper samples are stacked and a needle is moved in and out of the stack several hundred thousand times. The mass loss of the needle is used as a gauge of abrasiveness of the filler employed.

- **Color, pH, and resistance:** See Coatings Applications section in this chapter.
- **Lightfastness:** The degree to which photobleaching occurs in a paper laminate. In such a system, there is neither oxygen nor water available to allow the occurrence of TiO₂-mediated photochemistry. As such, free radical degradation does not play a major role in these applications. The photoreduction of Ti(IV) to Ti(III) can occur, however, leading to a phenomenon called *graying*. The resistance of a specially treated titania pigment to this phenomenon is called *lightfastness* and is measured in an authentic laminate exhibit exposed to intense UV light for a prescribed period. The color change after bombardment is used as the determinant of lightfastness.

Finishing Processes

The front end of the two major commercial processes was previously described. The so-called finishing steps include unit operations that allow the construction of the surface architecture of the finished pigment particles commensurate with the intended end uses of the materials.

In the finishing process, the surface of the titanium dioxide pigment particle is modified via inorganic and/or organic surface treatments to induce requisite behaviors in end-use applications. Inorganic surface treatments are generally applied by deposition in an aqueous environment, usually in a stepwise manner. Photochemical stability is generally induced by coherent encapsulation of the pigment particles with hydrous silica. Because the resulting silica surface does not exhibit good dispersion performance or flocculation resistance, the silica jacket is typically covered by a layer of hydrous alumina. Some processes include a slurry milling step prior to surface treatment to ensure that the feedstock is fully deagglomerated and will therefore provide a more uniform core particle dispersion for the subsequent deposition reactions.

The deposition reactions lead to the formation of ionic species that must be removed from the pigments to ensure proper performance of the final product. As such, the materials are filtered to remove the ionic materials, dried, and then ground to remove any agglomerates formed during the drying step. The processing of the material as a dry pigment is complete at this stage. For purposes of use in waterborne applications (e.g., latex paints or paper coatings), the dry product may be slurried in water and stabilized with dispersants to yield a product that can be pumped directly into downstream equipment for use as a raw material.

End Uses, Applications, and Markets

The three major market segments for titania pigments are coatings, polymers, and paper. The important subsegments for these are as follows:

- Coatings—automotive, industrial, powder, architectural, special purpose
- Polymers—polyolefins, polyvinyl chloride, engineering resins
- Paper—wet-end applications, paper and paperboard coatings, laminates

The specialty segment includes everything from welding rods and shoe polish to toothpaste and solid rocket fuels. This is considerably smaller in volume than the three major segments. A specialty segment of particular importance is the use of titania pigments to deluster polymer fibers, particularly polyamides and polyesters. A segment related to coatings but generally discussed separately is the use of titania pigments in ink applications.

Generally speaking, the largest applications for titania pigments in all three segments include opacity and the protection of finished goods from UV radiation.

Using titania pigments in coatings allows high opacity to be obtained at nominal cost. In addition, exterior coatings (those exposed to the natural elements for the life of the article) are protected from the UV component of solar radiation by the pigment. Differing levels of durability (discussed earlier) can be used as a function of the expected service use and lifetime of the article being painted. For example, an interior flat paint will not typically be exposed to a substantial amount of UV radiation. As such, there is no reason to use a titania pigment that has been surface-modified to induce long-term stability to UV. Conversely, a material used in formulating an automotive topcoat high-gloss paint will need to have the best possible long-term performance in the face of the full brunt of nature. In this case, special surface modifications are made to the titania pigments used in the applications to ensure extended performance in this aggressive end use (Christensen et al. 1999).

Titania pigment use in polymers can be quite diverse—from the coloration of the ubiquitous white plastic shopping bag to the protection of vinyl siding and window profiles in home construction (Holtzen and Reid 2004). White roofing materials also contain titania pigments, as do many types of packaging materials and agricultural products. Applications in polyolefins are by far the largest-volume use in the polymer segment, with applications in vinyl second, and uses in so-called engineering resins (a term used to include a vast number of polymers, including essentially anything that is not either a polyolefin or a vinyl resin) applications third (Abel 1999; Cho and Choi 2001).

Titania pigment use in paper and paper laminates differ greatly in their performance requirements. They have been supplanted in many so-called wet-end applications, in which the pigment is added directly into a sheet of paper to provide opacity and brightness, by calcium carbonate. Much higher loadings of the latter are required because of a much lower refractive index (~1.63) versus rutile (~2.73) or anatase (~2.5).

In paperboard coatings, such as those used for cereal and beverage packaging, coatings similar in some ways to interior flat house paints are used to provide an opaque surface with very high brightness and excellent printability and print contrast. This is applied directly to the board in a high-speed continuous process.

Paper laminates require lightfastness. Color stability of the final laminate article is not possible without good performance in this regard. Many paper laminate formulas contain between 30% and 40% by weight titania pigment, and as such the performance of the laminate is strongly affected by the performance of the pigment used.

Competitive Alternatives

Because of the almost unique combination of properties of titania pigments—high refractive index, lack of toxicity, geological stability, high brightness—a direct not-in-kind replacement is not feasible in many end-use applications. For certain applications, it has been possible to supplant the use of titania pigments either with greatly increased loadings of a material with a much lower refractive index (e.g., calcium carbonate in wet-end paper applications)

or by substituting the hiding power of air voids (e.g., certain BOPP [biaxially oriented polypropylene] film applications).

Much effort has been expended over the last 50 years in attempting to develop and commercialize substitutes for titania pigments. Thus far, these efforts have been thwarted by higher costs, toxicity concerns, or difficulties in controlling the chemistries involved.

Environmental Considerations

Converting titanium-bearing ores into titania pigments requires removing all elements except titanium from the feedstocks during processing. The remaining materials will obviously be produced to a greater or lesser extent as a function of the titanium content of the ores. Managing the resulting material stream is handled in a number of ways as a function of the manufacturing process used and of the available end uses for the materials produced.

The largest component of this material stream is iron, particularly so when ilmenite is used as the feedstock or as a substantial portion of the feedstock. Some sulfate-process operators convert the iron to iron sulfate. This material can then be used as a soil adjuvant; as an additive to fertilizers, concrete, and other building products; as a flocculant for water purification; and as a source of iron for other manufacturing processes. Chloride process streams are typically smaller because of the use of higher-grade feedstocks, but substantial amounts of secondary materials (iron again being predominant) are generated nonetheless. Some of these materials are used in the manufacture of iron oxide pigments, whereas ferric chloride is also used as a flocculant for water purification.

The various producers exercise a variety of options for handling the portion of the secondary stream for which markets are not available. Chloride and sulfate producers can neutralize the acidic streams and landfill the resulting solids. The solids can also be roasted to produce iron oxides that can be stored or consumed by the steel industry. Deep-well injection of the secondary stream can also be practiced. Developing new means of addressing secondary component streams is an ongoing concern for all producers.

Trends and Opportunities for Titanium Dioxide

Growth in consumption of titania pigments continues to track or exceed GDP growth rates and is expected to do so for the foreseeable future. As such, increased consumption rates are noted in developing economies, particularly in Asia, Central and South America, and Eastern Europe. No substantive not-in-kind replacements with acceptable economics have been identified for pigmentary titanias, although this is always a possibility.

Major producers continue to develop new surface architectures for high-performance titania pigments. Synergic opportunities exist as new polymers, polymer blends, and alloys are introduced, which is also true for new coatings resins and paper chemistries.

One of the more fascinating aspects of the future of titania pigments actually lies in the nonpigmentary arena—namely, in nanotechnology. Many small companies and major multinational chemical companies are performing research in this field. Although it is unlikely that the volumes associated with these materials will ever challenge the enormous base applications of titania pigments, the value in use of the materials will be quite high on a unit basis. Some of the more interesting fields in which work is ongoing are covered in work by Kellar, Herpfer, and Moudgil (2003).

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Refractories

Charles E. Semler

INTRODUCTION

The word “refractory” means obstinate, stubborn, or resistant to heat. According to the American Society for Testing and Materials (ASTM), refractories are nonmetallic materials with chemical and physical properties that make them applicable for structures, or as components of systems that are exposed to environments $>538^{\circ}\text{C}$ ($>1,000^{\circ}\text{F}$). In addition, refractories are used in applications $<538^{\circ}\text{C}$ ($<1,000^{\circ}\text{F}$), such as acid treatment (pickling) tanks; high-pressure hydrometallurgical autoclaves; chutes and ducts for transferring abrasive, granular materials; some cyclones and drying ovens; and more.

Refractories are the “backbone of industry” because they are essential for *all* production of important commodities worldwide such as iron, steel, cement, glass, aluminum, copper, nickel, brass, chemicals, ceramics, and petrochemicals. For this reason, the products, technology, and services of the refractories industry are a major source of support for the world’s economy. But despite their great importance, refractories are largely unknown to most people, which means that the refractories industry works anonymously as a silent partner that enables most traditional manufacturing industries to operate efficiently and profitably. This point is emphasized by the title of a book published about the history of the U.S. refractories industry, *Refractories: The Hidden Industry* (Krause 1987).

Importance of Raw Materials to Refractories

Raw materials have been, and continue to be, critically important to the refractories industry. These materials play a key role in the commercial and technical aspects of the business, such as storage, batching/mixing, product quality, properties, innovation and advancement, and profitability. Consequently, refractory companies continually search the world to locate, maintain, and enhance their raw materials supplies. Historically, refractories were first manufactured only from mined earth materials, such as clays, fireclay, sand, quartzite, schist, and others. As the knowledge and technology advanced, the usage of many other natural raw materials, such as bauxite, kyanite/sillimanite/andalusite, chrome ore, magnesite, dolomite, limestone, novaculite (silica), and zircon has increased. But over time, because of the need for higher purity and better refractoriness (i.e., improved high-temperature properties), there has been increased usage of beneficiated, processed, and synthetic raw materials, such as tabular alumina, seawater and fused magnesia, sintered and fused alumina, sintered and fused spinel, sintered

and fused magnesia-chrome, fused alumina-chrome, and sintered and fused zirconia, among others.

Classification of Refractories

Refractories are classified on the basis of the raw materials (natural, beneficiated, and synthetic) that are used. The main categories are fireclay, alumina, silica, basic (magnesia [MgO] and calcia [CaO]), insulating, and carbon, along with others such as zirconia, alumina-chrome, spinel (a complex oxide of magnesia and alumina [$\text{MgO}\cdot\text{Al}_2\text{O}_3$]), and nonoxides (e.g., silicon carbide [SiC], boron nitride [BN], aluminum oxynitride [AlON]). Specific classifications of refractory products can be found in the ASTM standards (ASTM 2005). Further description of the refractory categories was previously presented by Trostel (1994).

The relevant ASTM standard classifications are

- C27-98(2002): Standard Classification of Fireclay and High-Alumina Refractory Brick
- C155-97(2002): Standard Classification of Insulating Firebrick
- C401-91(2000): Standard Classification of Alumina and Alumina-Silicate Castable Refractories
- C416-97(2002): Standard Classification of Silica Refractory Brick
- C455-97(1999): Standard Classification of Chrome Brick, Chrome-Magnesia Brick, Magnesia-Chrome Brick, and Magnesia Brick
- C467-97(2002): Standard Classification of Mullite Refractories
- C545-97(2002): Standard Classification of Zircon Refractories
- C673-97(2003): Standard Classification of Fireclay and High-Alumina Plastic Refractories and Ramming Mixes

Several other refractory classifications should be mentioned. For more than 60 years, the U.S. Department of Commerce has classified refractories as clay and nonclay types in its annual statistical reports of refractory production and value. These categories are a historic relic of the past when “clay-based” refractories were the most important products in terms of both tonnage and value; today, however, they are less significant. Refractories technology has seen major advances over the decades, so today the clay and nonclay categories would be better termed “traditional-type” and “value-added-type” refractories, respectively.

Other refractory classifications that were widely used in the past were acid, basic, neutral, and special (Coxey 1950). Acid

refractories were those composed of silica, alumina, and aluminasilica. Basic refractories were composed of alkaline earth oxides, such as dolomite, magnesite, and lime. Neutral refractories were those that did not readily react with acidic or basic materials, such as chrome, SiC, carbon, and so forth. Special refractories were those that did not fit into the other categories (e.g., titania, zircon, zirconia, and nitrides). Over time, with the increased development of various mixed types of refractories, these chemical distinctions have become less clear and harder to apply, so the usage has declined. The basic category, however, is still accepted and widely used in reference to refractories based on magnesium (Mg), lime (Ca), and magnesium and lime (Mg-Ca).

Physical Form of Refractories

Because of the thousands of different applications and the requirements for refractories in many industries, a wide variety of physical forms are manufactured, as follows

- Brick and special shapes (shaped refractories)—fired, unfired, fusion cast, insulating
- Monolithic products (unshaped refractories)—castables, gunning mixes (dry and wet), ramming mixes, dry vibratable mixes, plastics, mortars
- Fibrous refractories—blanket, modules, board, paper, rope, vacuum-formed
- Miscellaneous products—e.g., crucibles, kiln setters, electrodes, brake pads

Manufacturing of Refractories

The main steps involved in the manufacture of bricks and monolithic (e.g., castable) refractories—the two main product types—are as follows

Brick Refractory	Monolithic Refractory
Obtain raw materials	Obtain raw materials
Prepare/treat materials	Prepare/treat materials
Store materials	Store materials
Weigh/batch	Weigh/batch
Mix	Mix
Press and inspect	Package and quality control
Dry	Store/ship
Fire	
Inspect and quality control	
Store/ship	

The refractory manufacturing process involves many variables (workers, equipment, raw materials, and procedures) that must be understood and controlled to ensure that the products will be uniform and consistent and fully meet the user's needs and guidelines. As a result, all the refractory companies of the world devote significant time and effort to the monitoring and control of product quality to try to avoid shipping of f-quality products to customers. Statistical process control, ISO-9000, Six Sigma, or other manufacturing quality control practices are commonly used.

There is a basic difference between the brick and monolithic manufacturing procedures that should be noted—brick manufacture involves the additional steps of pressing, drying, and firing. The manufacture of bricks, then, involves more capital expense and quality control concerns than monolithic refractories, and as the refractory industry evolves to meet practical and economic needs, these issues will help promote increased manufacture and use of monolithic refractories at the expense of bricks. The trend toward

increased use of monolithic refractories is already in progress as described in the Refractory Production and Usage Trends section of this chapter.

Testing of Refractories

Because of the many variables involved in the manufacture of refractories (such as multicomponent raw materials, coarse through ultrafine particle sizing, contamination possibilities, mixing efficiency, firing time and temperature, and many more), testing is necessary to ensure uniform, consistent production. In addition, tests are needed to compare “equivalent” products from different manufacturers, to determine the effects of service, and for R&D, among other purposes. Most countries have organizations that develop standard refractory tests. In the United States, ASTM develops and issues the standard refractory tests. Internationally accepted test methods are available from the International Organization for Standardization (ISO).

The evaluation of refractory properties is very important, especially with the increase in global sourcing of refractories from the worldwide marketplace. A product data sheet, which shows the general properties obtained by standardized tests, is available for every commercial refractory product. Although these property data sheets allow a general comparison of refractories from different manufacturers and are widely used, it is not appropriate to use them for purchase specification purposes. For detailed product comparisons, and the establishment of purchasing specifications, it is important to obtain the most current data and statistical ranges from the refractory manufacturer(s).

The general categories of refractory tests, which are used individually or in combination for a wide variety of purposes, are as follows

- Chemical analysis—bulk and/or localized, specific analyses
- Chemical resistance—slag, molten metal, acid, alkalis, gas species
- Physical properties—porosity, density, specific gravity, permeability
- Mechanical properties—strength (room temperature and hot), fracture energy, abrasion resistance, modulus of elasticity, crack propagation rate
- Thermal properties—expansion/shrinkage, creep, conductivity, refractoriness, resistance to rapid temperature change (thermal shock)
- Technical modeling—image analysis, finite element analysis, fractal analysis

It is significant to note that any given refractory type (e.g., 90% alumina brick, mullite brick, low cement alumina castable, MgO–13% C brick, and graphite plastic) from different manufacturers will not be identical in composition or properties, as opposed to other industrial commodities (e.g., 310 stainless steel) that are virtually identical from any manufacturer. Consideration of the variation in refractories (between manufacturers and lot-to-lot), must be included in lining design, product comparison, purchase specifications, bid/quote evaluation, and acceptance criteria, although the need is frequently not known or overlooked. The characterization testing of refractories, including quality control, is extremely important for the optimization of refractory performance.

REFRACTORY STATISTICS

The steel industry is by far the major consumer of refractories, as indicated by Table 1.

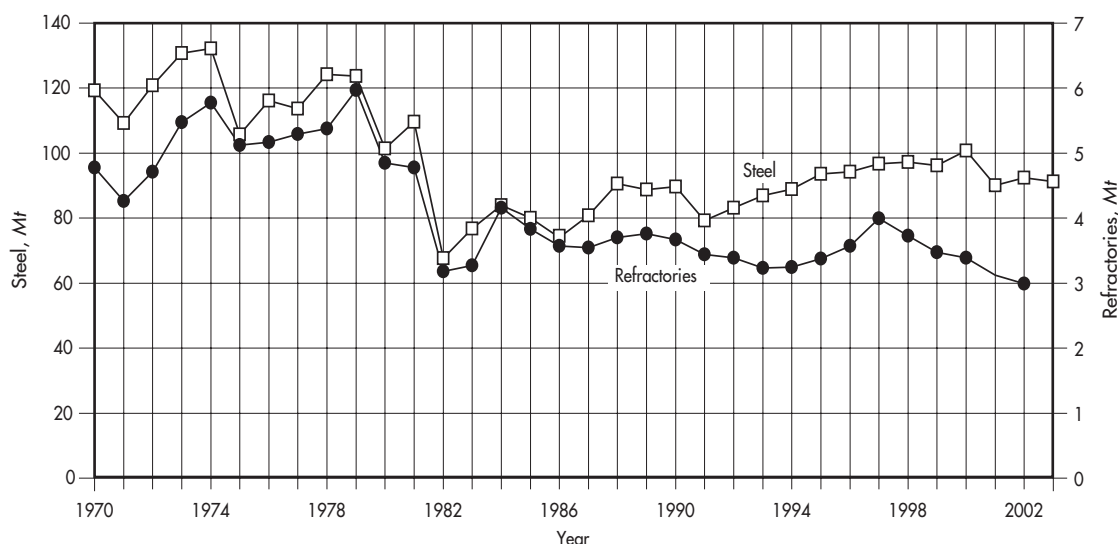


Figure 1. U.S. annual production of steel and refractories

Table 1. Two breakdowns of the global refractories market

Industry	Mosser and Karhut 1999, %	Meier 2004, %
Steel	70	63
Cement and lime	6	14
Chemicals	6	NR*
Ceramics	5	NR
Glass	4	9
Nonferrous metals	3	9
Other	6	5

* NR = not reported.

Historically, there has been a relationship between the annual production of steel and refractories. Figure 1 shows the annual production of steel and refractories in the United States since 1970 (International Iron & Steel Institute 2001–2003; U.S. Department of Commerce 1970–2002). In 1979, the maximum refractory production in the United States was about 6 Mt, and annual production has now decreased by roughly 50%. Generally, in the past, when steel production increased, refractory production increased. But since about 1991, that direct relationship has changed, as there have been years when refractory production decreased despite an increase in steel production. Various factors are involved in this change, such as (1) more refractories are being imported; (2) refractories are continually being improved and last longer in service; and (3) since 1970, the rate of consumption of refractories by the steel industry in the United States and Japan has declined from 25 to 30 kg of refractory per ton of steel to about 8 kg/t (see Figure 2). It is expected that the refractory consumption rate by the steel industry will continue to decrease, albeit at a very slow rate. The data for Brazil and China indicate that their refractory consumption rates are decreasing and eventually will be very similar to those of the United States and Japan. And like the steel industry, the decrease in refractory consumption is occurring in other industries, such as cement, glass, and copper (Semler 2004), so this ongoing decrease in the refractory consumption rate must be included in the consideration of future refractory production requirements.

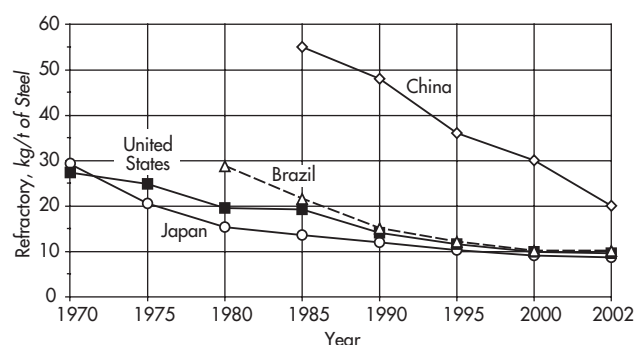


Figure 2. Refractory consumption trend: Steel industry

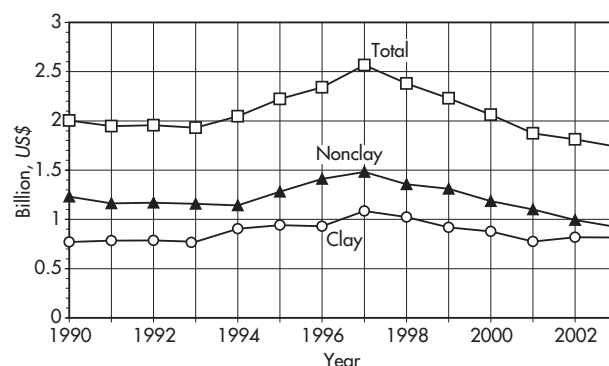


Figure 3. Annual value of clay and nonclay refractories in the United States

Figure 3 shows the annual value of the U.S. refractories market since 1990 (U.S. Department of Commerce 1970–2002). The total market value peaked in 1997 at \$2.57 billion and has declined each year since then, reaching \$1.74 billion in 2003. Figure 3 also displays a breakdown of the market value according to the two

Table 2. Price changes for selected refractory product types (1993–2003)

Refractory Product	1993, \$/t	2003, \$/t
Fireclay bricks	440	489
Insulating firebricks	914	1,300
High-alumina bricks	600	763
High-alumina castables	540	623
High-alumina plastic/ram	460	635
>88% alumina bricks/shapes	3,770	3,820
>88% alumina plastic/ram	1,140	1,220
MgO-C bricks	1,120	610
Zircon/zirconia bricks	6,400	6,830

refractory categories used by the U.S. Department of Commerce (i.e., clay and nonclay products, which were discussed previously). In recent years, nonclay refractories have accounted for a higher percentage (58%) of the annual market value than clay refractories. This trend correlates with the continuing advancement of refractories technology, including the usage of more synthetic, higher purity raw materials.

REFRACTORY PRICING

The overall average price per ton for refractories in the United States peaked at \$659 in 1995, but since then the price has decreased, reaching \$578 in 2002. These price-per-ton figures are derived from the U.S. Department of Commerce (1970–2002) figures for annual tonnage of production and the associated total market value.

Representative examples of the price change (US\$) for several refractory product types in the United States between 1993 and 2003 are given in Table 2.

REFRACTORY PRODUCTION AND USAGE TRENDS

Based on the ever-changing operations/requirements of the refractory users, including the constant demand for cheaper refractories, there are changing trends in refractory usage.

Figure 4 (U.S. Department of Commerce 1970–2002) shows the change in fireclay, high alumina, and magnesia-carbon refractory production in the United States since 1988. The data show that in the early 1990s the annual production of these products was stable or slightly increasing, but in the last 5 years, production has decreased. Figure 5 (U.S. Department of Commerce 1970–2002) shows the change in silica and magnesia-chrome refractory production in the United States since 1990. Except for an increase in production of these two refractory products in the mid-1990s, their output has decreased significantly since 1990.

Since the mid-1980s, there have been major advances in the properties and types of monolithic refractories, especially castables, and the installation technology has been improved (e.g., shotcasting/wet gunning). Based on improvements that have allowed the cement addition to be reduced, there are now multiple classes of castables:

- Conventional—15 to 30 wt % cement
- Low cement (LCC)—1 to 5 wt % cement
- Ultralow cement (ULC)—0.2 to 1 wt % cement
- No cement (NCC)

As a result, a wide variety of material options and installation methods are available for consideration. Because the performance and cost-effectiveness of castables can now be equivalent to or better than that of pressed/fired bricks and shapes, the production/use of castable refractories has continuously increased, as shown in

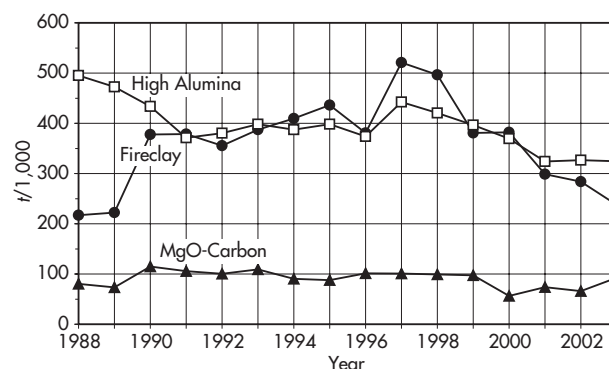
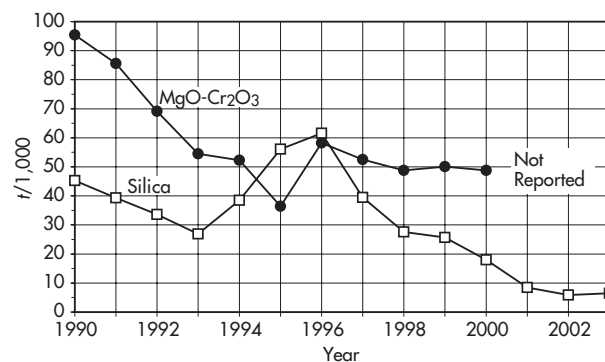
**Figure 4. U.S. refractory brick trends (alumina, fireclay, magnesia-carbon)****Figure 5. U.S. refractory brick trends (magnesia-chrome, silica)**

Figure 6. In Japan and the United States, the production of monolithic refractories has exceeded brick production since 1992 and 2000, respectively. This trend can be expected to continue because the ongoing R&D will further improve and advance the properties and practical utility of monolithic refractories.

ECONOMIC STATUS OF REFRACTORIES

The annual value of the world refractory market is estimated to be \$16 to \$18 billion, for a demand of 25 Mt or more. China is the major contributor to the world market with roughly \$5.5 billion in value and about 18.7 Mt of production in 2004 (Liu and Zhou 2004), which is about 6 times more than the United States production. The role of China as a manufacturer, exporter, and user of raw materials and refractories will continue to dominate the world scene. The world's main refractory companies in terms of annual sales are outside China—RHI Refractories, Cookson Group, and Saint-Gobain each have sales that exceed \$1 billion.

According to Barr et al. (1973), by any meaningful criteria, the refractories industry is fundamental to the functioning of the total economy and makes a highly significant contribution to both the total industrial activity and the generation of gross national product. So the refractories industry occupies a fundamental and strategic position in the structure of the U.S. (and global) economy, and any reduction in the output will tend to cause an equal proportionate reduction in the output and income of every other industry.

In summary, the economic impact of refractories worldwide is enormous. Without refractories, business and life as we know it today would simply not be possible (McCracken 2004). But the

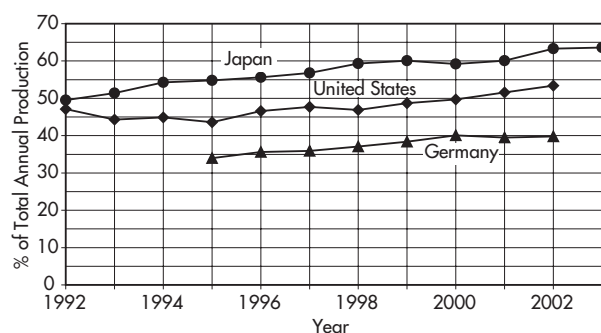


Figure 6. Monolithic refractory market share (Japan, United States, and Germany)

overall economic impact of refractories on the national or global economy is not routinely monitored and tracked to provide a clear indication of their critical importance in industrial manufacturing. In the absence of such an indicator, they are relegated to a role of silent anonymity in the global marketplace, not unlike farmers who play the critical supply role in the food chain (the staples of human life), but are not fairly compensated for their products, in comparison with the value received by others later in the chain. Likewise, it could probably be documented that the refractory industry is not fairly compensated for the R&D, technical service, and the improved, more durable products that they continually provide to the users. The users, however, realize major benefits, including the opportunity to maintain and increase their output, enhance efficiency, and increase income and profitability. A win-win relationship would seem fair, in which the refractories industry is appropriately rewarded, rather than penalized, for continually providing improved products that result in reduced demand (sales) for refractories while allowing customers to realize significant practical and economic benefits.

The refractories industry has a long history of direct communications and interaction with customers, which in many cases involves daily, on-site collaborative work and the development of close personal relationships. To promote and develop an increased understanding of the value of refractories, the industry should better utilize its long and successful history of involvement with customers. In addition, the industry needs to fully explore the unlimited opportunities worldwide that are afforded by cyber-business, partnering, joint ventures, technical service needs, and currency fluctuations, among others. There might also be aspects of the Japanese system of "sister companies" and keeping the business in the family that could be developed to advantage elsewhere in the world.

Despite the ongoing decline in refractory production and market value, new players can still find many opportunities to participate and succeed in business by focusing on the requirements for new technology/processes, offering creative solutions to customer's problems and needs, recognizing niche market opportunities, developing novel/improved products, and many other options.

REFRACTORIES ADVANCEMENT AND OUTLOOK

The refractories industry has changed significantly in recent years because of domestic and global factors such as the decreasing consumption of refractories, consolidation and downsizing, reduction of manufacturing capacity, globalization of the marketplace, legal and financial liabilities, and the decline of refractories education. It

is not expected that the activity level or business will ever return to the levels of earlier years. Instead, the refractories industry will continue to evolve, to maintain and enhance the business success in conjunction with the challenges and competitive pressures of the new global marketplace, becoming leaner, more efficient, and more cost-effective. It is known that the need for refractories will continue for many decades, because they are essential for all traditional, and other, manufacturing industries. It is clear that many more improvements and innovations will emerge in the coming years, based on the past history of ongoing refractory advances, and even more attention will be directed to environmental, recycling, and safety and health issues.

Examples of some refractory R&D topics that can be expected to yield advances in the coming years are

- Raw materials, additives, particle sizing
- Engineered microstructures
- Castables (carbon-containing, rheology, dryout, additives, etc.)
- Monolithic refractory installation
- Spinel (primary, in-situ, and prescription types)
- Non-oxide and composite materials
- Modeling and sophisticated engineering analysis

As stated by T. Vert of Dofasco Steel, Hamilton, Ontario, Canada (personal communication), "Refractories are moving from a commodity bought by the pound, to an engineered material that must be designed differently for every customer." Experience has shown that focused R&D can result in significant improvements, specific to a process or application, but there must be an economic reason to undertake such projects because they commonly involve smaller markets with smaller monetary returns. Refractory users need to understand that many more refractory advances are possible, and for specific, niche-type applications, if they are willing to pay in accordance with the benefits that will result from prescription-designed refractories.

As W.H. McCracken has commented, "Refractories companies are not going out of business. Someone will always be around to produce them, somewhere, and someone will always be using them. A past president of Harbison-Walker Refractories Co. always said that refractories are not going to become obsolete and disappear, EVER" (O'Driscoll 2004).

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Soil Amendments

Gretchen K. Hoffman and George S. Austin

INTRODUCTION

Soil amendments are defined as any natural or synthetic soil-conditioning materials that are worked into the soil or applied on the surface to enhance plant growth. This term commonly refers to added materials other than those used primarily as fertilizers (SSSA 2004), which are discussed in the Fertilizers chapter. Soil amendments mainly modify physical characteristics and microbial action, or change the pH of a soil, or both, rather than directly supplying nutrients to plants. They give soil the needed physical properties to allow plant growth, fight erosion, or retain water. Although some soil amendments do provide nutrients in addition to altering the physical, biological, or chemical characteristics of soil, this is not their primary purpose.

Both inorganic and organic materials are used as soil amendments. Several inorganic soil amendments have been used since the early twentieth century: limestone, lime, and similar calcium-rich carbonates and oxides for acid soils, and calcium sulfate (gypsum) and native or uncombined sulfur for alkaline soils. The use of these amendments (limestone, lime, gypsum, and sulfur) or their equivalents has been studied and documented in many basic soils studies (see, for example, McCaslin and Boyle 1980). Only the most commonly used and those that appear to have potential to become commonly used are discussed in this chapter. In some cases—such as perlite and vermiculite—the soil amendment application covered in this chapter is only a minor end use of a particular mineral or rock, and other chapters in this book offer detailed discussions of these minerals and rocks.

Peat is the principal natural organic soil amendment, but manure, both as a fertilizer and soil conditioner, is used in every part of the world. In less-developed countries, manure is the primary soil fertilizer/conditioner. An organic-rich material designated as *humate* or *leonardite* has been marketed as a soil amendment for many years and is addressed in this chapter.

Other materials (such as synthetic products) are not discussed here but can be found in the Soil Science Society of America's (SSSA) special publication 7, *Soil Conditioners* (Stewart 1975). These products include bitumen emulsion, polyacrylamide, polyvinyl acetate, polyvinyl alcohol, bentonite, nonionic surfactants, and natural mulches. Zeolites can be added to the list of miscellaneous soil amendments (McCaslin and Boyle 1980), as can calcium chloride (Pressler and Pelham 1985), sulfuric acid, ferric and ferrous sulfate, aluminum sulfate, ammonium polysulfide, calcium polysulfide,

and ammonium bisulfite (Stromberg and Tisdale 1979). Sludge is not considered a soil amendment because it has properties more consistent with fertilizers. All these other materials, which account for a very small part of the volume and value of soil amendments used, are discussed only briefly.

Soil Types

Soils amenable to treatment with amendments are separated into five general categories: acid, saline, alkaline (pH >7.0), saline-alkali, and calcareous (soil containing sufficient free calcite [CaCO_3] and other carbonates to effervesce visibly or audibly when treated with cold 0.1 M hydrochloric acid [HCl]; SSSA 2004). Optimum plant growth occurs for a great majority of crops and plants at a soil pH of 6 to 7 (neutral). Acid soils (pH 3.5 to 6.0) are created when calcium is leached by relatively high rainfall, which lowers the soil pH, producing acid. Aluminum also comes into play to the extent that highly acidic soils can result from aluminum saturation. Soils become acidic because the cations of soil colloids, primarily calcium, are replaced by hydrogen ions. This involves ion exchange and other adsorption reactions that are associated with the colloids. The total soil acidity is made up of two components—active and exchangeable (reserve) acidity. Active acidity, which is the H^+ ion concentration in the solution phase, is measured by pH. Exchangeable acidity is the hydrogen (H^+) and aluminum (Al^{3+}) ions that are chemically bound to cation-exchange sites on clays and organic matter. Exchangeable acidity makes up the greatest portion of total acidity (SSSA 2004; Beegle and Lingenfeller 1995). Soil exchangeable acidity determines the amount of aluminum and hydrogen that can be replaced by an unbuffered salt solution such as potassium chloride (KCl) or sodium chloride (NaCl; SSSA 2004). Because clay minerals and organic particles have large surface areas, they usually have much higher total acidity than sandy soils, and it takes a larger volume of neutralizing soil amendment to raise the pH of these soils.

A saline soil is one having an electrical conductivity of the saturated extract (EC_e) of more than 4 millisiemens* per centimeter (mS/cm) at 25°C and an exchangeable sodium percentage (ESP)[†] of less than 15 (Stromberg and Tisdale 1979). Ordinarily, the pH of

* A millisiemens is equivalent to a millimho.

† The total amount of exchangeable cations a soil can retain is called the cation-exchange capacity (CEC) and is usually expressed in milliequivalents per 100 g of soil. The ESP is the ratio of the exchangeable sodium to the CEC.

Table 1. Soil amendments statistics (2003)

Soil Amendment	Producing States (2003)	U.S. Consumption, t	Average Price, \$/t	Exports to the United States
Agricultural limestone and dolomite (Tepordei 2003)	34 states (top producers are Alabama, Kentucky, Missouri, Nevada, Ohio, Pennsylvania, and Texas)	Limestone, 10×10^9 ; Dolomite, 1.38×10^9	Limestone, 5.84; Dolomite, 11.16	Canada, Mexico
Gypsum (Olson 2004)	17 states (top producers are Oklahoma, Texas, Nevada, Iowa, California, Indiana, and Michigan); 25 companies	33×10^9 uncalcined gypsum; 1.0×10^9 for agricultural purposes	6.90	Canada, Mexico
Perlite (Bolen 2004)	7 states (Arizona, California, Idaho, Nevada, New Mexico, Oregon, Utah); 8 companies	0.712×10^9 ; 13% of total end use	37.36	Greece
Vermiculite (Potter 2004)	2 states (South Carolina and Virginia); 2 companies	0.110×10^9 exfoliated; agricultural, insulation, and other, 73% of end use	143 (concentrate)	South Africa, China
Peat (Jasinski 2003, 2004)	16 states (top producers are Florida, Michigan, and Minnesota)	1.39 million, 5% of total domestic production for horticultural use	Sphagnum moss, 63.20	Canada (sphagnum)
Humate	3 states (North Dakota, Utah, New Mexico)	$\sim 80,000$ t	90–450*	Canada

* Range is for wholesale price.

these soils is less than 8.2. A saline soil can be recognized by the accumulation of white salts on the surface. The chief cations are sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}), and the chief anions are chloride (Cl^-) and sulfate (SO_4^{2-}), with lesser amounts of nitrate (NO_3^-) and carbonate (HCO_3^-). Soluble carbonate is rarely present in saline soils.

An alkali or sodic soil has an ESP of greater than 15 and an EC_e of less than 4 mS/cm. The soil pH is usually greater than 8.5 and may reach 10 or more. The high ESP of alkali soils causes them to lose their structure. Because of the destruction of soil aggregates, which is responsible for the presence of large pores, the soils become almost impervious to water and air. Root penetration is impeded, clods are hard, and seedbeds are difficult to prepare. Saline-alkaline soils are both saline and alkaline (i.e., they have an EC_e of greater than 4 and an ESP greater than 15). Their physical properties are similar to saline soils as long as excess salts are present. As soon as they are irrigated and the soluble salt content of the surface horizon is reduced to a low level, they act as alkaline soils. Calcareous soils contain free calcium carbonate throughout the profile. They are nonsaline and have a pH ranging from about 7.5 to a maximum of 8.2. The EC_e is below 4 mS/cm and the ESP is usually less than 10.

Many crops exhibit symptoms of nutritional deficiencies on some alkaline and calcareous soils. This is often attributed to the failure of the plant to assimilate some of the nutrient elements, such as phosphorus, iron, copper, manganese, and zinc—all of which are micronutrients except phosphorus. Deficiencies of these elements are sometimes exhibited by a yellowing of the leaves, often termed *lime-induced chlorosis*. This is an oversimplification of a more complex problem. It must be recognized that crops grown on many calcareous soils with a pH of 8.0 do not show these symptoms. The solubility, however, increases by a hundred- to a thousandfold from a pH of 8.0 to 7.0. Micro nutrient deficiencies may also exist in acidic soils. In such cases, they may be true deficiencies and not a case of the plants being unable to absorb the nutrients because of a high soil pH (Stromberg and Tisdale 1979).

STATISTICS

Many of the soil amendments are sold by the companies that mine, process, and market the product for many end uses including soil amendments. For several of the soil amendments such as limestone, perlite, vermiculite, and peat, the producers are members of trade associations that promote the product and supply information to

both the supplier and buyer. Table 1 outlines production, consumption, price, and major exporting countries for the principal soil amendments.

A general barrier to entry for any soil amendment is distance to market. If the deposit is not close to a market area, it will not be able to compete. Exceptions exist, however, such as with peat imported from Canada to the United States.

CLASSIFICATION

Soil amendments can be divided into categories—those that are primarily used to change the soil's pH and those that are added to change the soil's physical characteristics. Some soil amendments are also used as carriers for fertilizer or insecticides. Table 2 lists the significant chemical and physical properties of the inorganic and organic soil amendments discussed.

Inorganic Soil Amendments

Limestone and Dolomite

Limestone and dolomite, often referred to as agricultural lime or aglime, are the most common carbonate rocks used as soil amendments to neutralize the acidity of soil and promote plant growth. In the Fertilizers chapter, limestone and dolomite are discussed as sources of calcium and dolomite as a source of magnesium for plant growth. Four factors are important in aglime quality: chemical purity, speed of reaction, magnesium content, and moisture (Beegle and Lingenfeller 1995). Chemical purity determines the amount of soil acidity the material can neutralize, expressed in terms of calcium carbonate equivalents (CCE). Pure calcite is assigned a CCE of 100, although pure dolomite [$\text{CaMg}(\text{CO}_3)_2$] has a theoretical value of 108.6. Dolomite is 8.6% more effective than calcite as a neutralizer because the molecular weight of magnesium (MgCO_3) is 84.32 as compared to CaCO_3 , which has a molecular weight of 100.9. Because of the difference in solubility of dolomite in contrast to limestone, however, it takes longer to neutralize with pure dolomite than with pure limestone. The composition of limestone and dolomite varies greatly because of impurities such as clay minerals, quartz, and organic matter. It is also very important to establish the exact chemical composition of the soil before making a decision about the liming material. Liming materials of less than 50% CCE would require too much material to reduce the acidity of the soil.

Although most agricultural liming today is achieved with pulverized limestone, many farmers still use ground quicklime (CaO) and hydrated lime [$\text{Ca}(\text{OH})_2$], particularly in the U.S. mid-Atlantic

Table 2. Major soil amendment properties

Soil Amendment	Main Use	Chemical Attributes	Physical Attributes
Limestone – Dolomite (Beegle and Lingenfeller 1995; USDA 1999a)	Agriculture, to treat acidic soils	Neutralize by base exchange Ca and Mg cations	Increases soil tilth; improves microbial activity
Gypsum (Olson 2004; Harben 2002)	Agriculture, to treat alkaline, saline, and alkaline-saline or calcareous soils	Calcium replaces sodium ions in clay soil. Source of calcium and sulfur	Improves permeability, drainage, aeration
Vermiculite (Harben 2002)	Horticulture	High CEC. As material breaks down, it is a source of potassium and magnesium	Improves workability, aerates soil, acts as a carrier for fertilizers and pesticides
Perlite (Harben 2002)	Horticulture	Chemically inert, low CEC	Retains two to four times its dry weight in water, aerates soil, resists compaction
Zeolites (Hall 1998; Harben 2002)	Agriculture, horticulture	High CEC, low sodium, low clay content	Open structure; retains moisture and nutrients
Fly Ash (EPRI 2002; Mittra et al. 2003)	Agriculture	High calcium; neutralizes acidic soils	Improves soil texture. Sandy soils: improves water retention; clayey soils: increases porosity
Humates (Hoffman, Barker, and Austin 1995; Wallace 1998)	Agriculture, horticulture	High CEC	Helps retain nutrients and moisture
Peat (Wallace 1998)	Agriculture, horticulture	Decomposed organic material, high CEC; provides acidity	Acts as anticompaction agent, helps retain water and aerate soil

states. Lime costs more than limestone on an equivalent calcium oxide basis, but it reacts faster, neutralizing soil acidity rapidly so that crop yields do not suffer. In some sandy soils, dolomitic lime is used because of persistent magnesium deficiencies. Because agricultural lime serves as a source of calcium and magnesium, the magnesium content can vary depending on the source. A magnesium analysis is necessary to determine the percentage of magnesium content. The moisture content of agricultural lime is important because the product is sold by weight. Other products that are used as aglime include lime (burnt or lump) and quicklime as a form of calcium oxide; hydrated, slaked, or builder's lime as calcium hydroxide; marl or shells as calcium carbonate; and slag (CaSiO_3).

Speed of reaction to neutralize the acidity is determined by the material's fineness. The finer the limestone is ground, the greater the increase in solubility and the faster it will react with the soil. Agricultural lime particles larger than 20 mesh react slowly in soil, showing little neutralizing effect within 2 to 3 years (Beegle and Lingenfeller 1995). Material of 100 mesh reacts within a practical time (<1 year), but the cost of grinding must be considered. A material with 95% passing through 20-mesh, 60% through 60-mesh, and 50% percent through 100-mesh screens is considered adequate (Beegle and Lingenfeller 1995). Aglime contains both fine and coarse material, and the percentage can vary from producer to producer. Many states require that 75% to 100% of the material passes an 8- to 10-mesh screen and that 25% passes a 60-mesh screen. In some southern states, lime laws require that no more than 10% remain on a 10-mesh screen and no more than 40% can remain on the 60-mesh screen. At least 50% must pass through the 60-mesh screen (USDA 1999a). The CaCO_3 and MgCO_3 equivalent or content is of major significance for agricultural use.

Agricultural lime is one of the many products marketed by crushed-stone operators. At a typical quarry in relatively flat-lying strata, the limestone or dolomite bed near the surface is stripped of overburden and quarried in a conventional manner, then crushed and screened to a appropriate sizes at a nearby plant. Specifications for agricultural liming materials are outlined in American Society for Testing and Materials C602. The fineness of aglime is classified



Courtesy of Martin Limestone, Inc.

Figure 1. Spreading crushed limestone on a field before spring planting

by the minimum percentage passing and remaining on the 8-mesh (2.36-mm) and 60-mesh (250- μm) screens. The 8-mesh is used to control the upper limit on the amount of coarse particles in the product. Specifications for CCE are set for burnt lime (not <140 CCE), hydrated lime (not <110 CCE), and limestone (not <80 CCE). The maximum size as regulated by the state varies but is generally between 8 and 20 mesh. The smallest size fraction is <120 mesh and the optimum size fraction is 60% to 40% <60 mesh (B. W. Remick, personal communication).

Agricultural limestone is dispersed onto the surface to raise the pH in pasture soil (Figure 1). For deep-root plants, it is disked into the soil to a maximum depth of about 15 cm. From 1.1 to 1.5 t/ha (0.11 to 0.15 kg/m^2) is considered the maximum amount of agricultural lime that should be applied to soil during a year (B.W. Remick, personal communication). For the most part, agricultural lime is

marketed to large operations in bulk form; however, packaged lime can be found at nurseries for home gardening. Lime is also marketed in a pelletized form. The fine lime particles are bonded together with lignosulfonates. The use of pelletized lime in agricultural applications is limited by the extra cost.

Several industrial by-products can be used as substitutes for aglime. Air-cooled blast furnace slag or granulated blast furnace slag, which are products of iron and steelmaking processes, have significant amounts of calcium and are potential substitutes for traditional sources of agricultural lime. Cement kiln dust has been used successfully as a liming agent for acidic soils. In some Canadian provinces, cement kiln dust is used to maintain soil fertility by restoring soil pH acidified by fertilizers while supplying potassium and sulfur (Risdale 1994).

Gypsum

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is the most common of the naturally occurring sulfate minerals. Crude gypsum is marketed for use in cement, agriculture, and fillers. Since the eighteenth century, gypsum has been used as a soil conditioner in Western Europe and is used today in many parts of the eastern United States. It is a source of calcium and sulfur in the form of sulfate and can reclaim alkaline (high-sodium) soils by replacing sodium with calcium (see discussion in Fertilizers chapter). As a soil amendment, gypsum neutralizes sodic soils by replacing the sodium with calcium. The displaced sodium must then be leached from the soil by watering to a depth greater than the root zone. The addition of gypsum also improves the permeability of argillaceous materials, and improves aeration, drainage, and penetration of water (Harben 1995). Gypsum also provides sulfur and catalytic support for maximum fertilizer utilization and leguminous productivity (Pressler 1985). Unlike lime, gypsum is effective in the amelioration of subsoil acidity (Levy and Sumner 1998). Lime does not move readily into the subsoil and is costly to incorporate. Gypsum has greater solubility than lime and can migrate into the subsoil and increase the calcium in the subsoil. Because gypsum has little or no effect on the soil pH, it is the preferred calcium source to remediate high-sodium soils (Zublena, Rubin, and Crouse 1995). The calcium in gypsum also promotes clay flocculation, which can reduce the tendency of soils to form seals, surface crusts, and subsoil hardpans (Levy and Sumner 1998).

Agricultural gypsum requires little processing and is sometimes referred to as "land plaster." Gypsum is extracted from surface pits and underground mines, then milled to different sizes, depending on the end use. It is typically used in large agricultural operations and delivered in bulk by truck to the farmer. Gypsum is also pelletized to decrease the amount of dust generated during application to croplands or turf and is available in bags or in bulk.

Uncalcined gypsum can vary in purity, but 70+% CaSO_4 (calcium sulfate) is required for application as a soil conditioner. For agricultural use, grinding to a fineness of 80% to 90% through 100 mesh is preferred (Harben 2002). Some low-grade ore is upgraded by log washing, sink flotation, or selective crushing and screening, both wet and dry. These methods produce a commercial gypsum product of 80% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or higher (Pressler 1985). The requirements for agricultural gypsum are not very rigid, but the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ content or equivalent is of major significance. To reclaim alkaline soils, gypsum should be incorporated into the soil at a rate of 4.48 to 6.75 t/ha (0.45 to 0.67 kg/m²). If the goal is water penetration, gypsum can be added using the broadcast method (2.24 to 4.48 t/ha). Application rates to promote the movement of calcium into the subsoil in low-calcium, acidic soils can be on the order of 6.7 to 8.06 t/ha. Solution-grade gypsum can also be added to the irrigation water to add gypsum to cultivated acreage.

Flue gas desulfurization (FGD) products (discussed in detail in the chapter on Flue Gas Desulfurization) and ground scrap wallboard material can be used as a substitute for gypsum in agricultural applications. Ground wallboard will still have paper in the product, but this can be broken down by soil organisms. The phosphate fertilizer industry also produces large quantities of a high-purity, fine-grained gypsum by-product termed "phosphogypsum." This material is not usable for agriculture because its uranium content makes it slightly radioactive.

Sulfur

A small amount of elemental sulfur is used as a soil amendment and as a nutrient. At times it is difficult to distinguish between sulfur as a nutrient and sulfur as a soil conditioner. As a conditioner, sulfur is used by itself or in combination with various nitrogen compounds to lower the pH in alkali soils, to improve water filtration, or both. This action, however, also improves the uptake of sulfur and the availability of certain micronutrients to the soil (Miyamoto 1998).

In agriculture, refined sulfur with a purity of 99.5% is ground and applied directly to the soil. Crude sulfur, formed into granules or pellets before grinding, or as fines separated from bulk sulfur, may also be used. In a few cases, sulfur in the form of sulfuric acid or as gypsum is used as a soil amendment.

Vermiculite

Finer-size grades of vermiculite are used as a plant-growth medium, chemical fertilizer, extender, anticaking agent, and carrier for pesticides and herbicides (Meisinger 1985). The high CEC, a result of vermiculites' platy structure, facilitates many of these applications (Strand and Stewart 1983). Vermiculite also has a high water-holding capacity because of its high surface-area-to-volume ratio, low bulk density, and almost neutral pH. As vermiculite breaks down, available potassium (5% to 8%), magnesium (9% to 12%), and calcium (<1%) are gradually released to the plants.

Vermiculite is similar to perlite in that it is shipped from the mine site in raw form and exfoliated at plants near market areas. Processing of vermiculite includes heating the raw material to 900°C to convert the water trapped between the structural layers to steam, which expands or exfoliates the material. The volume of exfoliated vermiculite is 15 to 20 times greater than that of the raw product. Vermiculite is produced in different grades for different applications. The grades are differentiated by bulk density and average particle size. The finer particle sizes (grades 3 to 5) have more surface area and are used for soil amendment applications. Expanded vermiculite is generally sold in bags and used in horticultural applications at nurseries and for home gardening. Vermiculite is often mixed with peat and other material and sold in bags as potting soil mix. A mixture of one third vermiculite and two thirds soil is recommended for heavy soils. Alternatives to vermiculite include peat and perlite, as well as sawdust, bark, and other plant materials (Potter 2004).

Perlite

The important properties of expanded perlite for use as a soil amendment are (1) chemical inertness, which results in the product remaining in the soil for a long time; (2) low CEC; and (3) a closed cell composition (bubbles) that resists compaction and enhances drainage. Perlite can retain two to four times its dry weight in water, giving it greater total inner porosity than sand. In addition, perlite aerates the soil, which allows air and moisture to get to the plant roots and is essential for optimum plant development. The uniform spherical size of expanded perlite resists compaction and increases

permeability and drainage of the soil. Perlite has many applications in hydroponics and soil-less growing media with peat. The Horticultural Committee of the Perlite Institute specifications for aggregate and horticulture are considered coarse grades that have 70% minimum +16 mesh or 1 mm. Fine and medium grades, however, are recommended for some horticultural applications.

Perlite deposits occur in remote areas, particularly in the western United States. This can be a barrier because of transportation costs and low value. Raw perlite is shipped by rail from the mine site in an unexpanded form to expansion plants located near market areas. Expanded perlite is 10 to 20 times the original volume of perlite. When flash-heated to 870°–1,000°C, the perlite softens and the water within the structure vaporizes, causing the material to pop (Harben 2002). Expanded perlite is then bagged for further shipping, often by truck, to nearby markets. Perlite is used in horticultural applications such as hydroponics, landscaping, and home gardening. It also helps to deter compaction in heavy-traffic areas such as golf greens and stadium turf and to maintain porosity so water will soak into the soil. Perlite is marketed for its neutral pH, its durability, and its ability to improve water retention.

Zeolites

Zeolites are hydrated aluminosilicates of volcanic origin that have an open structure, which gives them a high CEC. Zeolites can absorb and release nutrients or moisture without changing the characteristics of the minerals. Fertilizers and moisture stay accessible to the plant roots longer when they are within the zeolitic structure. They are useful in reducing the leaching of nutrients from sandy soils. Zeolites are widely used as soil amendments in Eastern Europe and Japan, but have a limited market in the United States (Hall 1998).

Diatomite

Diatomite is composed of fossilized skeletal remains of microscopic single-celled aquatic plants called diatoms, which consist of amorphous hydrous silica. Diatomite has several uses including filter aids, absorbents, and fillers. The porous skeletal structure of the diatoms have a high surface area and low bulking value, allowing them to absorb up to three times their weight while remaining free-flowing (P. Harben, personal communication). As a soil amendment these properties are exploited for water absorption and retention in turf farm and golf course applications. Zeolites are often used instead of diatomite because their superior CEC helps retain nutrients, maximizing fertilizer productivity and minimizing nutrient run-off (P. Harben, personal communication).

Silica Sand

Sand is used primarily to improve the physical properties of the soil. Although silica sand may be added to soil to improve drainage, it may have the opposite effect in heavy clay soils. The clay will tend to fill the spaces between the sand particles, acting like a cement. Coarse sand improves the drainage properties of container mixes that do not include clay soil.

Fly Ash

Fly ash is a by-product of the coal combustion process. It is the noncombustible material in the pulverized coal that is kept in suspension in the flue gas and captured by either electrostatic precipitators or mechanical means. Fly ash that is not suitable for its major use in concrete and cement has the potential for use as a soil additive. About 60% of fly ash tends to be spherical because the molten material is suspended in the flue gas (Figure 2). As a soil amendment, Class C fly ash, which contains increased amounts of

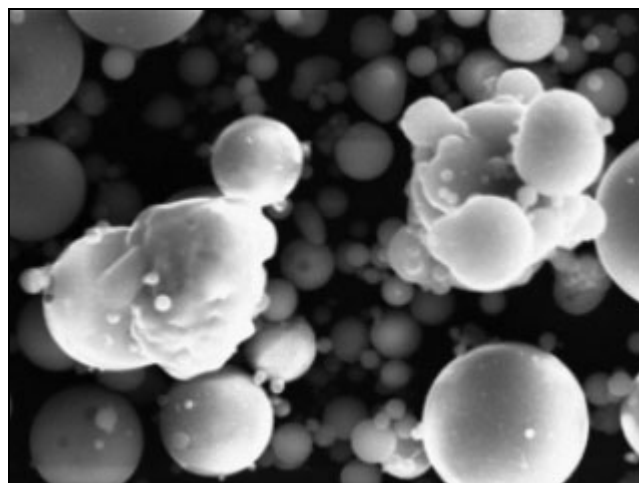


Figure 2. Secondary electron image of fly ash glass spheres and masses (field of view = 42 μ m)

calcium, can neutralize acidic soils and increase availability of nutrients (see Construction Uses: Pozzolans and Other Supplementary Cementitious Materials chapter for classification). High-calcium Class C fly ash can also control the swell potential of expansive soils and stabilize coarse-grained soils. Class F fly ash, (70% silica [SiO_2] + aluminum oxide [Al_2O_3] + iron oxide [Fe_2O_3]) aids in the compaction and soil density of poorly graded sandy soils. Water retention is increased in sandy soils by adding the small fly ash particles that fill the voids between the sand-sized grains. With silty soils, lime is required to create pozzolanic (cementitious) reactions between the clay and fly ash before adding Class F fly ash to reduce soil plasticity and improve workability. In clayey soil or a sandy soil, fly ash increases microporosity and water retention (Mitra et al. 2003). Class F fly ash can also improve soil texture because of its fineness and spherical nature. Fly ash mixed with bottom ash and blended with biosolids may be substituted for peat as a soil amendment (EPRI 2002). Fly ash does not currently have a developed market in soil amendments.

Organic Soil Amendments

Organic soil amendments are widely thought to contain humic acids that are beneficial to plants. Humic material is not a pure substance, and much confusion exists in the scientific and business communities about its terminology. *Humic acids* are defined as base-soluble humic, fulvic, and ulvic acids and their salts, formed during partial or complete decay of organic matter. This decay releases a high-molecular-weight material that is darkly colored, partly colloidal, and weakly acidic (Roybal and Barker 1986). Humic acids are organic colloids similar in behavior to clays (Siemers and Wadell 1977), increasing the water retention and CEC of the soil (Gosz, Barton, and Potter 1978). Humic acids raise the acidity of alkali soil, thus increasing the availability of several elements to plants (Siemers 1975). They also stimulate the growth of microorganisms that process plant nutrients.

Humate

Humate, when used as a lithologic term, includes oxidized coals and lignites, organic-rich mudstones and claystones, and the concentrations of humic substances often found in sandstones. Three different categories of humic materials are used to denote the different origins. Humate is commonly associated with both coal and lignite.



Figure 3. Plant facilities at the Mesa Verde Resources humate operation, San Ysidro, New Mexico (supersacks shown in foreground; milling plant behind)

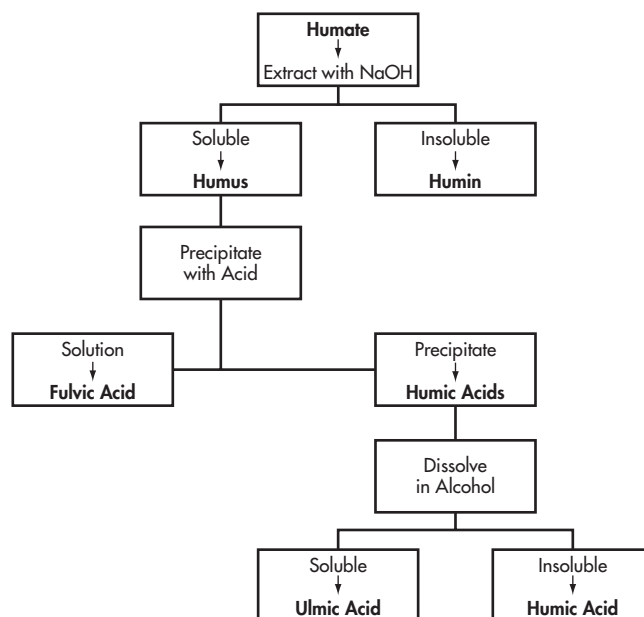
Humic material associated with oxidized lignite in the Williston Basin in North Dakota and in the Canadian provinces of Saskatchewan and Alberta has been called Leonardite, after A.G. Leonard of the North Dakota Geological Survey (Kohanowski 1970). The humic acid content of lignite decreases rapidly as coal rank increases and oxidation decreases (Abbott 1963). The third category of humates is organic-rich mudstones that are within the coal-bearing sequences. These mudstones generally have a lower humic acid content than either the oxidized lignites or coals.

Humate generally is mined by front-end loaders and stockpiled to dry before processing at the mill, where the humate is crushed and screened (Figure 3). For some uses, the material is custom blended to obtain a specific humic acid content. After the material is crushed, it is shipped in bulk, bagged, or run through an extraction process to produce a liquid. Most humate is sold to commercial farms in bulk bags or supersacks, but some of the bagged or liquid form is sold at nurseries for home gardening.

Humates are tested for the humic acid content that in part determines the product's end use. Most testing procedures include extraction of humic acid using varying concentrations of sodium hydroxide (NaOH) and different leach times in nitrogen or air atmosphere (Figure 4). Studies by Verploegh and Brandvold (1990) showed that leach solutions of 0.1 M NaOH and leach times of 1 hour are sufficient to determine the humic acid content. Reporting on humic and fulvic acids on an ash-free basis eliminates metals inherent in the humate structure (Stevenson 1985) and contaminants such as Na^+ and Cl^- . This is especially true for fulvic acids. The addition of an ashing step to the procedure and reporting on an ash-free basis would make the analyses of humate consistent by eliminating differences in results caused by varying leach times, NaOH concentrations, or both (Verploegh and Brandvold 1990).

Humate is applied to fields in the dry form at a rate of 448 to 672 kg/ha, depending on the pH of the alkali soil (Shomaker and Hiss 1974). Liquid humate may be used alone or added to other nutrients and sprayed on the soil (J.T. Spence, personal communication).

Transportation of humate in the United States is predominantly by truck, although rail is used for some shipments. Overseas shipments are generally of the liquid or bagged product. Markets



Courtesy of the New Mexico Geological Society.

Figure 4. General analytical flowchart for determining the various components of humate

for humate from New Mexico sold as a soil additive include all the contiguous states and Hawaii, plus Central America, the Caribbean, and Taiwan (T. Taylor and B. Reid, personal communication).

The beneficial use of humate as a soil amendment has often been discounted. Several studies have not shown significant improvement in yield with humate application (e.g., McFarland, Stichler, and Lemar 2002). Humates are not beneficial for every type of soil, particularly soils already rich in clay material. The humic and fulvic acids in humates are organic colloids, similar in behavior to clay minerals that increase the water retention and CEC of the soil. Humate lowers the pH of alkaline soil, thus increasing plant nutrient availability and stimulating growth of microorganisms (Hoffman, Barker, and Austin 1995).

A perusal of Web sites and literature shows the variety of opinions on whether humate increases crop yield and whether the benefits of humate have been overstated (Hall 1998). This confusion and controversy has had a negative effect on the acceptance of humate in this market. Better evaluation of the raw products and standardized tests and specifications are needed to clear up the controversy.

Peat

Peat is also a source of partially decomposed plant material (humus). Peat, particularly sphagnum peat, helps retain water and aerate the soil. Sphagnum peat also tends to be acidic and can lower the pH of alkaline soil. Peat consists of decomposed to partially decomposed heterogeneous plant material that has accumulated in a water-saturated environment and in the absence of oxygen. Different types of peat are derived from different plant materials. Sphagnum peat moss has at least 90% organic matter on a dry-weight basis and contains a minimum of 75% sphagnum moss fiber. There are more than 355 species of sphagnum moss throughout the world; they grow in northern cool regions and are found in bogs in the northern United States and Canada (Kasica 1997). Hypnum peat moss is also found in the northern United States; it tends to break

down more quickly than sphagnum. Hypnum peat moss must contain 90% organic matter by dry weight and contain a minimum of 50% hypnum moss. Reed and sedge peat is made up of marsh plants, including reed grasses, rushes, and sedges. This material decomposes quickly, is characterized by fine particles and low fiber content, and is less acidic than sphagnum. Sedge peat contains more plant nutrients and has a higher CEC than sphagnum (Kasica 1997). Peat humus is composed of reed sedge or hypnum material but is extensively decomposed and has less than 33% peat fiber.

Peat is harvested from bogs during the warmer months of the year. The bog is drained using closely spaced ditches, and large plant debris such as trunks and limbs are cleared before peat harvesting can begin. The uppermost layer of the bog is harrowed to break capillary action and promote the drying process. After 1 to 3 days, the peat layer is collected using large vacuum harvesters (Figure 5). The peat is transported to the processing plant for drying, shredding, screening, grinding, and packaging. The drying process is by natural and/or artificial means. After drying, the peat is shredded and screened. The larger-size material is ground or put through a hammer mill and screened again. Some material is left in bulk form and blended for large applications, such as golf courses. The processed peat is blended with vermiculite, perlite, or sand for potting soil. Large bales (1.1 m^3 or 1.7 m^3) of peat are compressed to a 2:1 ratio.

ASTM has established requirements for different types of peat. The accepted value for air-dried peat is 55% moisture and <25% ash on a dry-weight basis. The minimum particle size is 0.15 mm and the maximum is 12.5 mm. The ASTM D1997 testing method for peat is based on the genetic origin and fiber content on an oven-dried basis. The resulting categories are moss peat, which includes sphagnum, hypnum, and other mosses; reed-sedge peat, the main organic constituents of which are derived from reeds or sedges or other swamp material; and humus, which is made up of decomposed material of indeterminate biological origin. Because sphagnum peats are light and fibrous and low in moisture content, they can be compressed into bales and sold by volume. Other peats tend to have a greater degree of decomposition, are higher in moisture content, and are sold by weight (Davis 1985).

The U.S. Department of Agriculture (USDA 1999b) developed another classification of peat based on the level of decomposition and resulting fiber content. Fibric peat has undergone little decomposition and contains three fourths or more (by volume) plant fibers. Hemic peat shows moderate decomposition and contains one third to two thirds (by volume) plant fibers. Sapric peat has undergone extensive decomposition and contains less than one sixth (by volume) fibers.

Another method of classifying peat used in Canada is the von Post system, which assigns grades according to the degree of decomposition or the level of humification (Troyer 1985). There are ten grades in this system, from H1 through H10. Horticultural peat, which has little or no decomposition of plant material, is in the range from H1 to H4 on the von Post scale. With greater degrees of decomposition or humification, peat loses its absorptive properties and has increased density. This peat has a higher von Post grade (H5 to H10) and is used for fuel.

Peat is tilled into clay soils to loosen the soil and added to sandy soils to retain moisture. The organic matter in peat helps to enrich depleted soils. Peat is mixed with fertilizers, vermiculite, and perlite to form a substrate. It is also mixed with limestone, soil, and fertilizers for potting soil (Prud'homme 1989). Principal commercial uses of peat are as a base for building lawns and gardens, for turf maintenance of golf courses, and for potting soil (Jasinski 2003). Peat is also used in mushroom beds and as an earthworm-culture medium.



Figure 5. Peat harvester vacuuming peat at an operation in Nova Scotia, Canada

Common uses are as a seed carrier and in the production of peat pots for sprouting plants (Prud'homme 1989).

Most peat produced in the United States is sold within a 240-km radius of the source because of the high moisture content and the resulting density (approximately 370 kg/m^3), which make it economically prohibitive to transport great distances. Because of its lower density (171 kg/m^3), sphagnum moss is baled and shipped greater distances, typically by truck (Cantrell 1991; R. Cantrell, personal communication). Generally, long distances to market are a barrier for low-cost soil amendments; however, Canadian peat is an exception. Peat imports from Canada are shipped almost anywhere in the United States because of the wide acceptance and popularity of peat as a soil amendment.

Canadian peat producers have formed a national peat association to increase sales in the United States (Prud'homme 1989), and several European countries have peat associations as well. The International Peat Society promotes scientific and technical knowledge of peat production and usage. Belarus, Russia, Ukraine, and other countries of the Commonwealth of Independent States control a large portion of the European peat market because of their large reserves and production. In many parts of the world, the major market for peat is as an energy source with secondary use as a soil amendment (Table 3). The majority of Ireland's and Finland's peat production is for fuel usage. Germany and Canada are major producers of horticultural peat.

GOVERNMENT, ENVIRONMENTAL, AND HEALTH CONSIDERATIONS

Other than simple dust problems, no environmental or health considerations are currently recognized for lime stone, dolostone, gypsum, perlite, sulfur, or humate. In the case of vermiculite, there is a question of possible association with common amphibole asbestos minerals as was the case in the deposit at Libby, Montana. This deposit, however, is no longer being mined. Vermiculite sold in the United States, produced domestically in Virginia and South Carolina or imported from South Africa, is not associated with asbestos-like minerals.

Some trace elements are concentrated in fly ash during the combustion process. There is some concern that trace elements could be leached from fly ash and could contaminate the groundwater; however, many of these elements have very low solubility in the ash (glass) matrix (D. Pflughoeft-Hassett, personal communication). The

Table 3. Peat production by country in 2003, kt

Country	Fuel Use	Horticulture Use	Total
Belarus	2,000	100	2,100
Canada	0	1,341	1,341
Denmark	0	295	295
Estonia	na*	na	1,500
Finland	7,000	800	7,800
France†	0	200	200
Germany†	0	2,500	2,500
Hungary	0	45	45
Ireland†	2,739	375	3,114
Latvia	na	na	560
Lithuania	na	na	500
Moldova†	475	0	475
Norway†	0	30	30
Poland	0	320	320
Russia	na	na	2,100
Sweden†	750	450	1,250
Ukraine†	na	na	1,000
United Kingdom†	na	na	500
United States	0	634	634
Total	16,064	6,770	26,064

Source: Jasinski 2004.

* na = not available (the breakdown between fuel use and horticulture use is unknown).

† Estimated.

permitting of new bogs for peat harvesting is a growing problem because they overlap with wetland areas. The cost of compliance and permitting new peat bogs is eliminating small operators. The Canadian Sphagnum Peat Moss Association is working with the North American Wetlands Conservation Council on conservation and restoration projects (Daigle and Gautreau-Daigle 2001).

TRENDS AND OPPORTUNITIES

The trend toward sustainable development is increasing the need to use by-products instead of nonrenewable materials. As an example, the increased use of synthetic gypsum from FGD could result in less use of natural gypsum. In addition, recycled gypsum or ground scrap wallboard can be used for agricultural uses. Slag from iron and steel processes could capture some of the agricultural additive markets, particularly in the eastern United States. The horticultural market in Canada is growing, as is the export market for U.S. perlite, as imports of perlite from Greece are taking over part of the market along the east coast of the United States.

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Well Drilling Materials

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INTRODUCTION

Drilling fluids—or *muds* as they are commonly called—play a crucial role in the drilling of oil and gas wells. These fluids are formulated to perform a variety of functions under a wide range of downhole temperatures, pressures, and lithologies. The drilling fluid is pumped down the hollow drill string through nozzles in the drill bit at the bottom of the well, then up through the annulus (which is formed by the drill string and the wellbore), removing formation material dislodged by the drill bit. The drill bit is turned by rotating the entire drill string or by using a downhole motor to rotate the drill bit. After reaching the surface, drilling fluid passes through a series of vibrating screens, settling tanks/pits, and hydrocyclones to remove suspended formation material. The drilling fluid is then treated to maintain the desired physical and chemical properties. Once treated, the drilling fluid is pumped back into the well and the process is repeated.

Drilling fluids comprise liquids (water, petroleum oils, and other organic liquids), dissolved inorganic and organic additives, and properly sized suspended solids of various types. The chemistry of the liquid phase dictates the type and amount of materials needed to maintain the required density, viscosity, and other rheological properties. The drilling fluids must have sufficient density to offset formation pressures, prevent blowouts, and maintain a stable wellbore. They must be formulated to prevent damage to permeable formations by controlling excessive fluid loss. Other functions of drilling fluids include lubrication of the drill bit and drill string, prevention of corrosion, and collection of subsurface information through well logging.

A number of industrial minerals, chemicals, and other materials are used as additives in the drilling fluid to accomplish the aforementioned functions. Industrial minerals such as barite and bentonite make up the largest percentage of the additives in a drilling fluid. Other minerals such as gypsum, limestone, and attapulgite make up a small percentage of total demand.

INDUSTRIAL USES OF MATERIALS

Industrial minerals in drilling fluids have seven basic uses: weighting agents, bridging agents, viscosifiers, thinners, lost-circulation materials, stabilizers, lubricants, and proppants and plugs.

Weighting Agents

Barite, hematite, and galena are weighting agents with high specific gravities; they help offset pressure, control liquid flow into

the wellbore from the formation, and keep the hole open. Galena is used only in preparing extremely heavy muds that are sometimes needed to control abnormally high pressures; it is not a common component of weighted muds. A supply of galena is maintained in the U.S. Gulf Coast area for emergency use. Barite is the most common weighting material for heavy muds, followed by hematite. Siderite and limestone (calcium carbonate) are often used for low-density muds and for workover/completion fluids because they are acid soluble.

Bridging Agents

Sized calcium carbonate and sized salt are commonly used as bridging agents in drill-in fluids. The drill-in fluids enable horizontal wells to be completed without formation damage caused by conventional drilling fluids. Drill-in fluids are classified as either solids free or minimal solids systems. The solids content is limited to bridging agents, which plug the pore spaces at the wellbore face, thereby restricting the invasion of solids and fluids into the formation. The bridging agents are sized to formation properties (i.e., pore geometry) and comprise either calcium carbonate or salt crystals.

Viscosifiers

Sodium bentonite and peptized calcium bentonite are the most common viscosifiers for freshwater muds, whereas attapulgite and sepiolite are the most common for saltwater muds. The organophilic clays are used as viscosifiers in oil muds. A viscosifier carries the cuttings to the surface, builds a cake against permeable formations, and lubricates the drill string.

Thinners

Thinners are added to mud to obtain better flow properties. Materials commonly used as thinners can be broadly classified as (1) plant tannins, (2) polyphosphates, (3) leonardite, (4) specialty products derived from leonardite, and (5) lignosulfonates. Thinners are often referred to as *mud-conditioning agents*.

Lost-Circulation Materials

Gilsonite, mica, diatomaceous earth, and expanded perlite and vermiculite are used to plug or seal pores and cracks in the formation being drilled. Mica is the most common industrial mineral used to reduce lost circulation. The bentonites and organophilic clays also help with lost-circulation problems.

Stabilizers

Gilsonite and salt stabilize a wellbore when drilling through shale or salt formations. Gypsum is used as a stabilizer when drilling anhydrite or gypsum. Adding salt or gypsum prevents the drilling fluid from dissolving the salt, gypsum, or anhydrite in the formation being drilled; Gilsonite coats shales, which prevents them from absorbing water, expanding, and subsequently caving into the wellbore.

Lubricants

Graphite and bentonite lubricate the drill bit and drill pipe during a drilling operation. They also help prevent the pipe joints from sticking.

Proppants

Sized silica sand is used as a propping agent for fracturing, a process that holds the fractures open and enables the oil to flow out of the formation into the well. Sized silica sand is also used in gravel packing of poorly consolidated sands.

Plugs

Aggregate and granular-size bentonite is currently used for plugging shallow seismic holes. The completed holes are filled with this material to prevent inflow of water. Highly compressed sodium bentonite is also used for well abandonment.

Specialty Products

Attapulgit, sodium bentonite, and calcium bentonite are used to make organophilic clays. Organophilic clays are used in oil-based muds as viscosifiers and filtrate reducers. A series of specialty products are generated from leonardite through caustic treatment, sulfonation, sulfomethylation, or chelation with zinc. Attapulgit, sodium bentonite, calcium bentonite, and leonardite make up more than 50% of specialty products. The products are proprietary. Other industrial minerals are used in these specialty products in very small amounts as fillers.

INDUSTRIAL MINERALS

Table 1 lists the industrial minerals commonly used in drilling fluids, and their forms, specifications, and uses. In this section each mineral is discussed as to its mineralogy, physical and chemical properties, and the location of major deposits. More detailed information may also be found in individual chapters in this volume covering each of these mineral commodities.

Asbestos

Although no longer used in drilling fluids, at one time asbestos was commonly added to water-based muds as a highly effective viscosifier.

Asbestos is the generic name for a group of naturally occurring fibrous silicate minerals. The principal component of commercial asbestos is chrysotile (hydrated magnesium silicate). Chrysotile has a specific gravity of 2.55 and a Mohs hardness of 2.5. It consists of tubular, parallel fibers that are closely packed. The fibrous nature of chrysotile leads to the development of a brush-heap structure when it is dispersed in either salt water or freshwater. The major asbestos deposits are located in the province of Quebec, Canada, and near Coalinga, California.

Attapulgit (Palygorskite)

Attapulgit is a crystalline hydrated magnesium silicate, with partial replacement of magnesium by aluminum, iron, and other elements. Attapulgit particles are needlelike in shape. When placed in

water, attapulgit does not swell like bentonite but must be dispersed by vigorous stirring to break up the bundles of lath-like crystals. Attapulgit is used in drilling fluids solely for its suspending properties, which are not affected by dissolved salts. In fact, attapulgit generates a higher viscosity in saturated sodium chloride solution than in freshwater. Attapulgit has a specific gravity of 2.5 and a Mohs hardness of 1 to 1.5. Attapulgit, often referred to as *fuller's earth*, is also used to produce organophilic clay.

The major producing areas in the United States are in southern Georgia and north western Florida. It is also mined in Australia, India, Senegal, South Africa, and Spain.

Barite

Pure barite (BaSO_4) has a specific gravity of 4.5 and a Mohs hardness of 2.5 to 3.5. Commercial barite often exhibits a lower specific gravity because of impurities such as quartz, chert, gypsum, anhydrite, celestite, and various iron minerals. The presence of iron minerals may, however, increase the specific gravity of commercial barite. Barite is used primarily as a weighting agent in drilling fluids.

Pure barite does not react with other components of drilling fluids and is virtually insoluble in water, but impurities in barite can influence drilling-fluid properties. For example, calcium sulfate minerals (i.e., gypsum and anhydrite) may thicken drilling mud. Likewise, properties of drilling mud may be adversely affected by the presence of sulfide minerals (i.e., pyrite and sphalerite), which can undergo oxidation, forming soluble salts.

The United States is a major producer and by far the leading consumer of barite. The oil industry uses 90% of domestic production and almost all the imported barite. Major producing states are Georgia and Nevada. The principal sources of imported barite are China, India, and Morocco.

Bentonite

Bentonite is primarily composed of the clay mineral montmorillonite, a magnesium–aluminum silicate. Bentonite hydrates in freshwater and disperses to varying degrees, depending on the nature of the cations that are loosely held and exchangeable (high cation exchange capacity). The presence of exchangeable sodium ions enhances hydration and dispersion. Divalent cations such as calcium reduce the degree to which the individual platelets disperse. Bentonite is added to freshwater muds for one or more of the following purposes: (1) to increase the borehole cleaning capability; (2) to reduce filtration into the permeable formations; (3) to form a thin, low permeability filter cake; (4) to promote borehole stability in poorly consolidated formations; and (5) to control loss of circulation. Bentonite has a specific gravity of 2.5 and a Mohs hardness of 1 to 1.5. It ranks second in quantity only to barite as a drilling-fluid additive. Bentonite is also used to produce organophilic clays. Calcium bentonite is often treated with sodium carbonate and polyacrylates to meet American Petroleum Institute (API) specifications.

Bentonite, in which sodium naturally predominates as the exchangeable cation, is mined primarily in Montana, South Dakota, and Wyoming. Arizona, California, Nevada, Oregon, and Utah also supply sodium bentonite. Production of calcium bentonite occurs in Alabama, Arizona, California, Colorado, Mississippi, Nevada, Oregon, and Texas. Major deposits outside the United States are in Argentina, Brazil, Cyprus, Germany, Greece, India, Italy, Mexico, and Turkey.

Diatomite (Diatomaceous Earth)

Diatomite, or diatomaceous earth, is composed primarily of diatom skeletons (hydrous silica). It has a limited use in drilling fluid as a fluid-loss control agent. Diatomite is primarily used as a filter

Table 1. Industrial minerals used in well drilling

Additives	Form	Specifications	Use
Asbestos	Fibrous	None	No longer used either as a viscosifier or lost-circulation material because it is classified as a carcinogen
Attapulgitite*	Powder—75 µm	30-min reading on a motor-driven, direct indicating viscometer at 600 rpm with a mixture of 20.0 g material in 350 cm ³ saturated salt solution; residue >75 µm: 8% max.; moisture: 16% max.	Viscosifier in saltwater
Barite*	Powder—75 µm	Density: 4.20 g/cm ³ min.; water-soluble alkaline earth metals as calcium: 250 mg/kg max.; residue >75 µm: 3% max.; particles <6 µm: 30% max.	Weighting agent
Bentonite (sodium)*	Powder—75 µm	30-min reading on a motor-driven, direct indicating viscometer at 600 rpm with a mixture of 22.5 g material in 350 cm ³ distilled water; yield point/plastic viscosity ratio: 3 max.; filtrate: 15 cm ³ max; residue >75 µm: 4% max.; moisture: 10% max.	Viscosifier in freshwater
Nontreated bentonite*	Powder—75 µm	30-min reading on a motor-driven, direct indicating viscometer at 600 rpm with a mixture of 25.0 g material in 350 cm ³ distilled water; yield point/plastic viscosity ratio: 1.5 max.; dispersed plastic; viscosity: 10 Cp min.; filtrate: 12.5 cm ³ max.	Viscosifier in freshwater
OCMA-grade bentonite (calcium)†	Powder—75 µm	30-min reading on a motor-driven, direct indicating viscometer at 600 rpm with a mixture of 22.5 g material in 350 cm ³ distilled water; yield point/plastic viscosity ratio: 6 max.; filtrate: 16 cm ³ max.; residue >75 µm: 2.5% max.; moisture: 13% max.	Viscosifier in freshwater
Diatomaceous earth	Powder	None	Lost-circulation material
Galena	Powder	None	Weighting agent
Gilsonite	Powder	None	Stabilizer
Graphite	Powder	None	Lubricant
Gypsum	Powder	None	Stabilizer
Hematite*	Powder—75 µm	Density: 5.05 g/cm ³ min. water-soluble alkaline earths metal as calcium: 100 mg/kg max.; residue >75 µm: 1.5% max.; residue >45 µm: 15% max.; particles <6 µm: 15% max.	Weighting agent
Ilmenite	Powder	None	Weighting agent
Itabirite	Powder	None	Weighting agent
Leonardite	Powder	None	Thinner
Limestone	Powder	None	Low-density weighting agent
Mica	Flake	None	Lost-circulation material
Perlite	Powder	None	Lost-circulation material
Quartz sand	Sand	Various mesh sizes	Propping agent; gravel-packing sand
Salt	Granular	None	Stabilizer; weighting/bridging agent
Sepiolite*	Powder—75 µm	30-min reading on a motor-driven, direct indicating viscometer at 600 rpm reading 20 g material in 350 cm ³ saturated salt solution; residue >75 µm: 8% max.; moisture: 16% max.	Viscosifier in saltwater
Siderite	Powder	None	Low-density weighting agent
Soda ash	Powder	None	Remove calcium salts
Ulexite	Powder	None	Cross-linking agent
Vermiculite	Flake	None	Lost-circulation material

Source: Adapted from Davis and Lefond 1983.

* American Petroleum Institute (API) specifications (Spec. 13A; API 1993).

† OCMA = Oil Companies Materials Association.

medium for completion brines. It has a specific gravity of 1.95 and a Mohs hardness of 4 to 4.5. The major deposits in the United States are in California and Nevada. Other notable producers are China, France, Italy, Japan, and Mexico.

Galena

Galena (PbS), with a specific gravity of 7.4 to 7.7 and a Mohs hardness of 2.5, is used only in preparing extremely heavy muds,

which often are required to control abnormally high pressures. Since galena is expensive, it is not a normal component of weighted muds. It is used only in emergency situations requiring weights up to 32 lb/gal. The largest galena deposits in the United States are located in Missouri, with minor production from Alaska, Idaho, and Montana. Outside the United States, the major deposits are in Australia, Canada, China, Kazakhstan, Mexico, and Peru.

Gilsonite

Gilsonite is a naturally occurring, solid carbonaceous material that is classified as an asphaltite. It is a pure hydrocarbon without any significant amounts of mineral impurities. Gilsonite has a low specific gravity and a softening point of approximately 370°F (188°C). It is used to control fluid loss, stabilize sloughing shales, and reduce borehole erosion. Major deposits of Gilsonite are found in northeastern Utah.

Graphite

Graphite is a naturally occurring carbon. It has a specific gravity of 2.3 and a Mohs hardness of 1 to 2. It is occasionally used in drilling fluids as a lubricant. Graphite is not currently mined in the United States. The major deposits are in Brazil, China, the Czech Republic, India, Madagascar, Mexico, and Sri Lanka.

Gypsum

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has a specific gravity of 2.32 and a Mohs hardness of 2. It is a primary source of calcium ions in "gyp" muds. The gyp muds are used for drilling sloughing shales and anhydrite formations. Nondrilling uses, however, account for most gypsum consumption. Major producing states are California, Indiana, Iowa, Michigan, Nevada, Oklahoma, and Texas. The largest producers of gypsum outside the United States are Canada, China, Iran, Japan, Mexico, Spain, and Thailand.

Halite

Halite (NaCl), or rock salt, has a specific gravity of 2.16 and a Mohs hardness of 2.5. Halite is used in formulating salt-saturated muds that are used for drilling in salt sequences, and for shale inhibition. Sized salt is often used as a water-soluble bridging agent for sealing porous formations. Recently, the use of sized salt has increased as a main component of salt-based drill-in fluid for horizontal wells.

Major salt deposits in the United States are in Louisiana, Michigan, New York, Ohio, and Utah. Outside the United States, other major deposits are found in Canada, China, and Germany.

Hematite

Hematite (Fe_2O_3) has a specific gravity of 5 to 5.26 and a Mohs hardness of 5.5 to 6. In the early 1980s, an anticipated worldwide barite shortage led to the use of hematite as a weighting agent in drilling fluids. Then it was discovered that hematite tended to increase filtrate loss and filter cake thickness. This problem, coupled with complaints from rig personnel of serious skin and clothing discoloration, caused a decline in the use of hematite as a weighting agent. In addition, hematite is more abrasive to drill bits, drill strings, and pump parts than is barite.

Hematite is mined in the Lake Superior and Appalachian Mountain regions of the United States. Outside the United States, major producing countries are Australia, Brazil, and China.

Ilmenite

Ilmenite (FeTiO_3) has a specific gravity 4.5 to 5.1 and a Mohs hardness of 5 to 6. The heavy metal content of ilmenite is lower than barite. In addition, the bioavailability of the heavy metals is lower. Environmentally, it is more desirable to use ilmenite than barite as a weighting agent in drilling fluids. Recently, a field trial was conducted using ilmenite as a weighting agent in the mud system on the Norne Field in Norway. It clearly demonstrated that the performance of ilmenite was comparable to barite. Supplies of ilmenite are abundant.

Itabirite

Itabirite is a micaceous hematite. It is called micaceous because it splits easily into thin, flat flakes, making it easily friable. It has a specific gravity of 5.1 and a Mohs hardness of 5 to 6. Abrasion is minimized if a maximum particle size of 45 μm is specified. This limiting of particle size has an additional advantage in that 120- or 150-mesh screens can be used on the shakers without excessive loss of itabirite. It can be used as weighting agent in both oil-based and water-based muds. Itabirite has successfully been used in Latin America. Brazil is a major source of itabirite.

Leonardite (Lignite)

Leonardite is naturally oxidized lignite, resulting from prolonged weathering. Leonardite is used in drilling fluids as a thinner and a filtration control agent. The name *leonardite* applies to the lignite oxidation product containing a high humic acid content. It has greater temperature stability than other thinning agents. Leonardite is a versatile material for emulsion stabilization. A derivatized version of leonardite is used in oil-based muds to reduce filtration loss and to improve the stability of water-in-oil emulsions.

North Dakota is the principal source of leonardite for drilling use. Minor deposits are located in South Dakota, Montana, New Mexico, and Texas.

Limestone (Calcium Carbonate)

Limestone, or calcium carbonate (CaCO_3), has a specific gravity of 2.7 and a Mohs hardness of 3. Calcium carbonate is often used as a weighting material because the resulting filter cake can be removed easily by treatment with hydrochloric acid. Calcium carbonate disperses more readily in oil muds than does barite. The low specific gravity of limestone limits the maximum density of the mud to about 12 lb/gal. Calcium carbonate is readily available as ground marble or oyster shells. Calcium carbonate is available in fine, medium, and coarse grades. It is used primarily as a bridging agent in both oil- and water-based drill-in fluids. Limestone deposits are ubiquitous and are mined throughout the United States and the rest of the world.

Magnetite

Magnetite (Fe_3O_4) has a specific gravity of 5.0 to 5.2 and a Mohs hardness of 5.5 to 6.5. Magnetite is no longer used as a weighting material in drilling fluids because of its relatively higher abrasiveness to drill-bit, drill-string, and pump parts. Because it is magnetic, it also causes interference with electrical logging and causes flow lines to clog.

Mica

Muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$) is the preferred mica mineral in drilling fluids. It has a specific gravity of 2.76 to 3.1 and a Mohs hardness of 2 to 2.5. Muscovite is flexible and insoluble in acids. It is primarily used to control loss circulation. The major deposits in the United States are in Georgia, New Mexico, North and South Carolina, and South Dakota. Outside the United States, the major deposits are in Brazil, Canada, France, and India.

Perlite

Perlite is a hydrated volcanic glass that expands greatly when heated. Expanded perlite is used for controlling loss of circulation. The largest deposits in the United States are in northern New Mexico. Outside the United States, Greece has major deposits.

Pyrite

Although pyrite (FeS_2) is not used in drilling mud, an iron-oxide weighting material is made from the residue of the pyrite roasting

process. The residue is quenched, neutralized, leached, washed, and dried. The product is milled to desired particle-size distribution. Desirable characteristics claimed for the product are high specific gravity of 4.7; low abrasion and low magnetic susceptibility; 85% solubility in hydrochloric acid; and reaction with H_2S to form polysulfides. Supplies of pyrite are abundant.

Quartz Sand

Quartz sand (SiO_2) has a specific gravity of 2.7 and a Mohs hardness of 7. Only high-quality, clean, properly sized sand is used as a proppant in fracturing of oil and gas for permeability enhancement. It is also used in gravel packing of poorly consolidated sands. The largest production of quartz sand in the United States is in Illinois, followed by Michigan, California, North Carolina, Texas, Wisconsin, New Jersey, and Oklahoma. Large deposits of high-silica industrial sand are widespread throughout the world.

Sepiolite (Meerschaum)

Sepiolite, or meerschaum, is a hydrated magnesium silicate that contains less substituted aluminum than does attapulgite, which it closely resembles. The crystal structure of sepiolite also is similar to that of attapulgite; the unit cell of sepiolite, however, is somewhat larger. Sepiolite occurs in fibrous, elongated lath-like particles. It has a specific gravity of 1 to 2 and a Mohs hardness of 2 to 2.5. It is used as a viscosifier for saltwater muds. The reported stability of sepiolite at elevated temperatures led to its application in geothermal drilling. Among the cited applications are (1) as a replacement for attapulgite in saltwater muds, (2) as a replacement for asbestos in "sweep" slugs for hole cleaning, and (3) as a packer mud. Although some sepiolite is produced in southern Nevada, Spain is the largest producer. Major deposits of sepiolite also occur in Somalia and Turkey.

Siderite

Siderite is a ferrous carbonate ($FeCO_3$). It has a specific gravity of 3.7 to 3.9 and a Mohs hardness of 3.5 to 4. It is highly soluble in acids. Siderite can be used as a weighting agent in both oil- and water-based muds. Its higher density enables the formulation of muds weighted up to 19 lb/gal. In laboratory core tests, muds containing siderite did not cause permanent damage by particulate invasion. Present domestic production of siderite is from east Texas.

Soda Ash

Soda ash is a sodium carbonate (Na_2CO_3). It has a specific gravity of 3.23 and a Mohs hardness of 3. Soda ash is used primarily to remove calcium salts from make-up waters and muds. It is also used in clay beneficiation. It is produced from either brines or trona deposits. The largest production is from trona deposits in southwestern Wyoming with additional production in California and Colorado. Botswana, Kenya, Mexico, and Turkey are the major producers outside the United States.

Ulexite

Ulexite is a hydrous sodium calcium borate ($NaCaB_5O_9 \cdot 8H_2O$). It has a specific gravity of 1.6 to 1.9 and a Mohs hardness of 2.5. It is used primarily as a source of borate for cross-linking hydrated guar gum. Cross-linked guar is used as a fracturing fluid. The largest deposits of ulexite are in Boron, California.

Vermiculite

Vermiculite is a micaceous mineral that expands when heated. The expanded form of vermiculite is used for controlling loss of circulation. The principal sources of vermiculite in the United States are

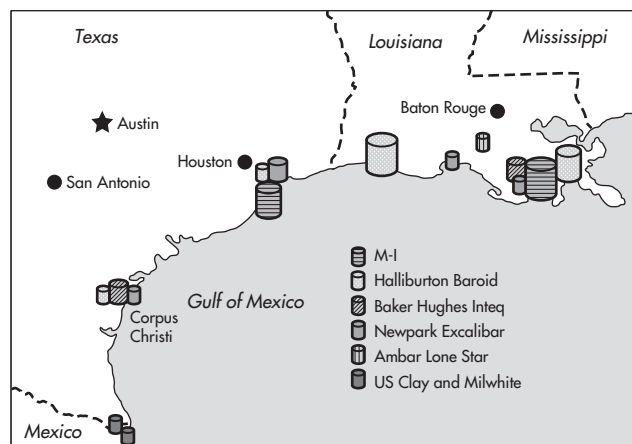


Figure 1. Plants that grind barite for drilling fluids located along the Louisiana-Texas Gulf Coast

South Carolina and Virginia. Elsewhere, the largest deposits are in South Africa.

SUPPLIERS

The industrial minerals used in drilling fluids in major amounts are barite, sodium bentonite, hematite, attapulgite, leonardite, and mica. Except for silica sand, which is used as a propping agent, the other industrial minerals are used in only minor amounts.

Drilling-fluid companies generally move the materials used in drilling fluids directly to the well site. These companies maintain warehouses and stockpoints in the major drilling areas throughout the world. If requested, they also supply drilling-fluid technologists (mud engineers), who supervise the mixing and use of the drilling mud.

There are three major worldwide drilling-fluids companies: M-I SWACO, a Smith/Schlumberger company; Baroid Drilling Fluids, a Halliburton company; and Baker Hughes Drilling Fluids, a Baker Hughes company. Additionally, there are numerous smaller, regional companies throughout the United States and worldwide. Drilling-fluid companies mine and grind the major products, or purchase them from other producers.

In the United States today, 13 plants along the Louisiana-Texas Gulf Coast (Figure 1) grind barite for drilling fluids. In addition, two other grinding plants in the same region custom grind barite for drilling-fluid companies or provide their own ground barite.

Three major mud companies own 8 of the 15 plants. The plants along the Gulf Coast supply 85% of the drilling mud barite in the United States.

In the West, three plants operate near Battle Mountain, Nevada, the largest barite mining area in the United States, and one operates near Salt Lake City. The ground product from these areas supplies the western United States and Alaska. Additionally, two other plants, one in Oklahoma and another in West Texas, grind barite for the drilling-mud market.

Other plants throughout the United States grind barite for the drilling-mud market, but their primary business is other minerals or the filler-grade barite market. In addition to the operating plants, several plants have been mothballed since the downturn in the market in 1982.

Sodium bentonite is the second largest industrial mineral used in drilling fluids based on tonnage. Five companies with 12 operating

plants produce drilling-grade products: American Colloid; Bentonite Corporation (formerly part of Baroid); Black Hills Bentonite; M-I SWACO; and WYO-BEN Corporation. Eleven of the plants are in Wyoming: five are in the Big Horn Basin in northwestern Wyoming, two are in the Casper area, and four are in the northeastern part of the state. The twelfth plant is in the northwestern corner of South Dakota. The plants produce ground and granular bentonite for domestic and foreign markets, and crushed and dried bentonite for export to grinding plants in other major drilling-mud markets in the world.

M-I SWACO and Densimix import specularite hematite from Brazil for the drilling-fluid market. Two plants on the Gulf Coast screen, dry, and, if necessary, grind the filter cake. These companies supply the other drilling-fluid companies with most of the product that they require.

Four companies produce attapulgite in the Georgia-Florida area as a ground product for the drilling-mud market and other uses. The four companies are Engelhard Mineral and Chemical Company; Floridin Company; Oil-Dri Corporation of America; and the Milwhite Company. The products are packaged in bags bearing the names of the drilling-fluid companies. Attapulgite-sepiolite is also ground and packed in Spain and Senegal.

Leonardite is produced in southwestern North Dakota and near Glenrock, Wyoming, for the drilling-fluids market. The three major suppliers are Black Hills Bentonite in Wyoming and American Colloid and Geo Resources in North Dakota. The material is supplied in powder form and packed and labeled in multiwalled paper bags from either the producer or the customer. The producers also sell leonardite in crushed and dried lumps for further processing.

Mica is supplied to the drilling-mud industry in ground form. The two major producers for the drilling-mud market are KMG Minerals in North Carolina and Mineral Mining Corporation in South Carolina. Most of the material is a flotation product or from scrap. The producers package the ground or screened product in paper bags with the customer's trade name. Canada and India supply mica to the drilling-mud industry in some international markets.

Other minerals used in minor amounts in drilling are obtained from suppliers either in generic bags or with the customer's name. These minerals are only a very small portion of the producers' total output.

TECHNOLOGY

Processing barite involves a rotary breaker that uses water at high pressure to separate the softer barite from the harder gangue, which is discarded. The barite and the remaining gangue move on to log washers, where any clay is separated. A trammel screen is used to discard oversize gravel material. The remaining material containing barite then moves on to jigs for the final gravity separation of barite from the remaining fine gravel gangue. The barite is then dried, ground, and packed in multiwalled paper bags.

For attapulgite, bentonite, sepiolite, and leonardite, all the raw materials used to produce the finished products are crushed, dried, ground, and packed in multiwalled paper bags. Before this processing, the clays and leonardite are dried either at the mine or on the stockpiles at the plant. This decreases the amount of water that must be removed in drying and makes the material easier to crush. Rotary dryers dry the clays at relatively low temperatures. If too-high temperatures are used, molecular and spatial water is driven off, and the swelling capability of the clays is decreased.

Table 1 lists specifications for the three grades of drilling-fluid bentonite recognized by API. The higher performance grades are produced mainly in Montana, South Dakota, and Wyoming. This bentonite contains montmorillonite clay in both sodium and cal-

cium forms; the sodium form, however, predominates. Most of these bentonites are processed using a small amount of a peptizing polymer to enhance the viscosity-building properties of the clay. This peptized bentonite is referred to as the standard API bentonite. The high-quality bentonite that is not treated in any way to enhance its viscosity-building characteristics is designated and sold as API nontreated bentonite.

Large deposits of calcium bentonite found in the coastal plains of the Gulf of Mexico and many other areas around the world are low-yielding bentonites. These can be used in drilling muds if upgraded with sodium carbonates and peptizing polymers such as polyacrylates. The name API OCMA bentonite identifies such bentonites for drilling use. "OCMA" refers to the defunct organization Oil Companies Materials Association, which set specifications until the early 1980s for drilling-fluid materials used outside the United States. The API, which has adopted and upgraded many of the old OCMA specifications, is the organization that today determines and sets such specifications.

Fast-yielding bentonites, when treated with high-molecular-weight polyacrylamide and polyacrylates, produce roughly the same viscosity as twice the amount of untreated bentonite. These polymers are referred to as bentonite extenders. Another bentonite extender is a mixed metal (magnesium and aluminum) layered hydroxide, or MMH. A MMH is most frequently used to increase viscosity sufficiently so that metal cuttings can be removed from the well during the milling operation. MMH-treated muds also are finding applications in horizontal wells. Unfortunately, when bentonites are treated in this manner, it can decrease the shelf life of the product and may increase fluid loss beyond specifications. This is especially true for calcium bentonites.

It is not uncommon to treat attapulgite with magnesium oxide and magnesium hydroxide to increase its mud-thickening ability. The effect can be heightened by including mannogalactan from guar.

Organophilic clay supplies viscosity and suspending qualities in oil-based muds. It is prepared from bentonite or attapulgite and aliphatic amine salts. The organophilic clays obtained from amines having 12 or more straight-chain carbon atoms that swell and form gels in oils. The amino groups replace the sodium and calcium originally present on the clay surface. Organophilic clays can suspend solids in oil without requiring additional emulsifying surfactants.

Processing leonardite involves moving the soft, moist deposit to stockpiles, where some drying and possibly some oxidation occur. This material is then passed through a low-temperature dryer to reduce the moisture content to 15%–20%. The dried product is then crushed and bagged. The performance of leonardite can be greatly improved by solubilizing processes such as caustic treatment, sulfonation, sulfomethylation, or chelation with heavy metals.

Specular hematite is mined and partially processed in Brazil before shipment as filter cake to the United States, where the final processing steps are performed. A small amount of agglomerated material may have formed, and some tramp material may have been picked up during transportation and storage. Because of these possibilities and the 8% to 10% moisture content, the material is dried either in a rotary dryer or a flash dryer (on the mill) and screened before packing. A hammer mill or a ring-roller mill breaks up the agglomerates.

Mica for drilling-mud products is dry-ground flake mica. It is ground further and screened to the sizes required for drilling mud use.

All these products are packaged in multiwalled paper bags and/or plastic 1-t supersacks. Barite and hematite are also delivered in bulk.

Specifications

Table 1 gives specifications for industrial minerals used in well drilling. API publishes specifications for barite, bentonite (sodium), hematite, nontreated bentonite (sodium), OCMA bentonite (calcium), attapulgite, and sepiolite (API 1993). These specifications are revised periodically. A few users set additional specifications for some products. For barite, the amount of caustic soluble material is usually limited to 3,000 mg/L for carbonates and 50 mg/L for sulfides. The amount an API bentonite can be extended with polyacrylates and still have an acceptable yield point is limited to 1.81 kg/t of polyacrylate and a minimum yield point of 60. Drilling-fluid companies usually set the specifications for the other minerals. Additionally, U.S. Environmental Protection Agency (EPA) and also some state agencies in the United States have set limits for heavy metal content (i.e., their use and disposal) in barite, muds, and cuttings.

Testing

The API has set standard test procedures along with specifications for the industrial minerals used in drilling fluids. In addition, API also has a recommended practice for chemical analysis of barite (API 1996). The EPA has standard test procedures for measuring mercury and cadmium. Most drilling-fluid companies have their own test methods for materials other than those specified by API. Some states require certification of processing facilities by NSF International for products used in water-well drilling.

ECONOMIC FACTORS

Costs

The largest industrial use of barite and bentonite is in well drilling. The other industrial minerals used in well drilling comprise only a small portion of the total tonnages produced each year. The major cost items to produce barite, bentonite, and most other industrial minerals are mining, grinding, and packaging. Mining must be economical; therefore, surface mining is usually practiced. Generally, it is prohibitive to concentrate barite for the drilling-mud market by any means other than screening, washing, or jigging. Dry grinding with ring-roller mills is more economical than grinding with ball mills.

Packaging is becoming more automated with palletizers to reduce labor costs. Other costs that continue to increase are those related to quality control, environmental considerations, and reclamation.

Markets

Most of the well-drilling outlay in the United States and worldwide is for oil and gas. The API sets the specifications for the major additives used in the drilling industry. If a company wishes to use the API logo on its products, it must have an API-approved Q-I program (quality control).

The largest single market area for drilling muds in the United States is the Louisiana–Texas Gulf Coast. Fifteen barite grinding plants on the Gulf Coast supply this market. The other major market areas for drilling muds are California and Alaska, the Rocky Mountains, and the midcontinent region (Kansas, New Mexico, Oklahoma, and Texas). Drilling-fluid companies maintain warehouses to supply their customers in these areas.

Transportation

Most of the industrial minerals used in well drilling have unique physical properties and are found in only a few areas. Materials of restricted occurrence that are shipped long distances, such as sodium bentonite, leonardite, and attapulgite, usually are shipped by rail in carload lots.

Lump barite and specularite hematite are mostly imported. The volume of sea freight of barite from the foreign producing countries in bulk quantities is less than the volume of rail freight from Nevada to the U.S. Gulf Coast, the largest consuming area.

GOVERNMENTAL CONSIDERATIONS

Taxes and Depletion

Most states have severance or ad valorem taxes on the industrial minerals used in well drilling. The trend is for increases in the taxes. Depletion allowances apply to all the industrial minerals used in well drilling. Import taxes are collected on most of the industrial minerals used in well drilling. The rates are different and depend on the source country, and whether it has Normal Trade Relations status; for a developing country, the imports are duty free.

Land Use

All mining operations in the United States must now reclaim mined areas whether on private or public lands. Usually an equivalent area must be reclaimed for the area mined each year. Each state has slightly different regulations.

Environmental Regulations

In 1988, EPA proposed a limit of 1 mg/kg mercury and 1 mg/kg cadmium in barite. The industry argued that the availability of barite at the proposed concentrations was limited and that the limit would increase the cost of barite by 65%. Industry-supplied data indicated that adequate supplies of barite containing <3 mg/kg mercury and 5 mg/kg cadmium were available. In 1993, EPA proposed a new regulation based on barite containing a maximum of 3 mg/kg mercury and 5 mg/kg cadmium. The use of barite would not be regulated, but the discharge of the mud and the cuttings would be monitored and regulated. Louisiana has some limits on heavy metals contained in the mud stored in mud pits. Current EPA permits for discharge require limits of 1 mg/kg mercury and 3 mg/kg cadmium.

In the United States there are regulations on rainwater runoff from mines and processing plants, acid mine drainage, and dust emissions.

Safety Regulations

Mines, concentrating plants, and grinding plants in the United States are regulated under the Mine Safety and Health Act of 1977.

PROBLEMS AND FUTURE TRENDS

The trend in the United States is to import oil rather than produce it because of the economics of drilling in the United States versus drilling elsewhere. This trend will reduce the amount of industrial minerals used in domestic well drilling. Increased governmental regulations on the environment, land use and land withdrawals, and increases in severance and ad valorem taxes all increase the cost of production, thus reducing the competitiveness of the United States. China has become the largest supplier of barite and is increasingly producing large quantities of other oilfield minerals and chemicals.

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Appendixes

Resource and Reserve Classification

Unless stated otherwise, reference to *reserves* and *resources* in this volume follows the terminology promulgated by SME's *Guide for Reporting Exploration Information, Mineral Resources, and Mineral Reserves*, a report submitted by the Resources and Reserves Committee to the Board of Directors of the Society for Mining, Metallurgy, and Exploration, Inc., dated March 1, 1999. The terminology is shown in Figure 1 and described as follows.

Public reports of *exploration information* relating to mineralization (but not classified as a mineral resource or mineral reserve) must contain sufficient information to allow a considered and balanced judgment of the significance of the results. This must include relevant information such as the geological setting, sampling intervals and methods, sample locations, assay data, laboratory analyses, data aggregation methods, plus other information that is material to an assessment. The reporting of exploration sampling or geophysical results must not be presented so as to unreasonably imply that a potentially economic deposit has been discovered.

A *mineral resource* is a concentration or occurrence of material of intrinsic economic interest in or on the earth's crust (a *deposit*) in such form and quantity that there are reasonable prospects for eventual economic extraction. The location, quantity, grade, geological characteristics, and continuity of a mineral resource are known, estimated, or interpreted from specific geological evidence and knowledge. Mineral resources are sub-divided, in order of increasing geological confidence, into inferred, indicated, and measured categories. Portions of a deposit that do not have reasonable prospects for eventual economic extraction must not be included in the mineral resource category.

An *inferred mineral resource* is that part of a mineral resource for which tonnage, grade, and mineral content can be estimated with a low level of confidence. It is inferred from geological evidence and assumed but not verified geological and/or grade continuity. It is based on information gathered through appropriate techniques from locations such as outcrops, trenches, pits, workings, and drill holes that is limited or of uncertain quality and/or reliability. An inferred mineral resource has a lower level of confidence than that applying to an indicated mineral resource.

An *indicated mineral resource* is that part of a mineral resource for which tonnage, densities, shape, physical characteristics, grade, and mineral content can be estimated with a reasonable level of confidence. It is based on exploration, sampling, and testing information gathered through appropriate techniques from locations such as outcrops, trenches, pits, workings, and drill holes. The

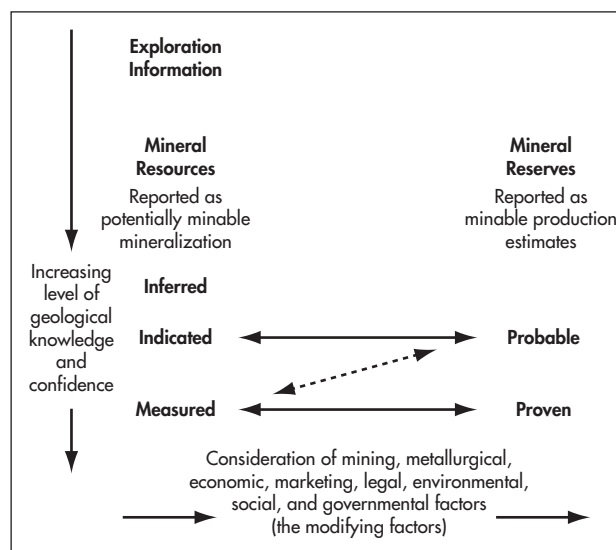


Figure 1. General relationship among exploration information, mineral resources, and mineral reserves

locations are too widely or inappropriately spaced to confirm geological continuity and/or grade continuity but are spaced closely enough for continuity to be assumed. An indicated mineral resource has a lower level of confidence than that applying to a measured mineral resource, but has a higher level of confidence than that applying to an inferred mineral resource.

A *measured mineral resource* is that part of a mineral resource for which tonnage, densities, shape, physical characteristics, grade, and mineral content can be estimated with a high level of confidence. It is based on detailed and reliable exploration, sampling, and testing information gathered through appropriate techniques from locations such as outcrops, trenches, pits, workings, and drill holes. The locations are spaced closely enough to confirm geological and/or grade continuity.

A *mineral reserve* is the economically minable part of a measured or indicated mineral resource. It includes diluting materials and allowances for losses that may occur when the material is mined. Appropriate assessments, which may include feasibility

studies, have been carried out and include consideration of, and modification by, realistically assumed mining, metallurgical, economic, marketing, legal, environmental, social, and governmental factors. These assessments demonstrate, at the time of reporting, that extraction is reasonably justified. Mineral reserves are subdivided in order of increasing confidence into probable mineral reserves and proved mineral reserves.

A *probable mineral reserve* is the economically minable part of an indicated and, in some circumstances, measured mineral resource. It includes diluting materials and allowances for losses that may occur when the material is mined. Appropriate assessments, which may include feasibility studies, have been carried out and include consideration of, and modification by, realistically assumed mining, metallurgical, economic, marketing, legal, environmental, social, and governmental factors. These assessments demonstrate, at the time of reporting, that extraction is reasonably justified. A probable mineral reserve has a lower level of confidence than a proved mineral reserve.

A *proved mineral reserve* is the economically minable part of a measured mineral resource. It includes diluting materials and

allowances for losses that may occur when the material is mined. Appropriate assessments, which may include feasibility studies, have been carried out and include consideration of, and modification by, realistically assumed mining, metallurgical, economic, marketing, legal, environmental, social, and governmental factors. These assessments demonstrate, at the time of reporting, that extraction is reasonably justified.

The U.S. Securities and Exchange Commission (SEC) regulates the reporting of exploration information, resources, and reserves by entities subject to the filing and reporting requirements of the SEC. Decisions as to when and what information should be publicly reported are the sole responsibility of the entity owning the information and are subject to SEC rules and regulations. These rules and regulations vary from time to time and, at any given time, may not be consistent with Figure 1 nor the descriptions of exploration information, resources, and reserves presented here. The advice of securities counsel should be sought in preparing filings for the SEC or other securities regulatory authorities, and in preparing other public disclosures.

APPENDIX B

Sieve Chart

Table B1. Sieve Chart

International ISO 566 (Table 2): 1983 Nominal Opening mm, μ m	American ASTM E 11-87 Alternate U.S. Standard in., sieve	Tyler Standard Screen 1910 Equivalent in., mesh	British BS 410: 1986 Aperture BS mesh	German DIN 4188: 1977	
				mm, μ m	DIN No.
26.50 mm	1.06 in.	1.05 in.		4.00 mm	2E
25.00	1.00			2.00	3E
22.40	7/8	0.883		1.50	4
19.00	3/4	0.742		1.20	5
16.00	5/8	0.624		1.00	6
13.20	0.530	0.525		750 μ m	8
12.50	1/2			600	10
11.20	7/16	0.441		500	12
9.50	3/8	0.371		430	14
8.00	5/16	2.5 mesh		400	16
6.70	0.265	3		340	18E
				300	20
5.60	3.5 sieve	3.5	3	250	24
4.75	4	4	3.5	200	30
4.00	5	5	4	170	35E
3.35	6	6	5	150	40
2.80	7	7	6	120	50
2.36	8	8	7	100	60
				90	70
2.00	10	9	8	75	80
1.70	12	10	10	67	90E
1.40	14	12	12	60	100
1.18	16	14	14	56	110
1.00	18	16	16	50	120
				36	130
				25	200
850 μ m	20	20	18	French	
710	25	24	22	AFNOR NFX11-501: 1970	
600	30	28	25	mm/ μ m	TAMIS No.
500	35	32	30	5.00 mm	38
425	40	35	36	4.00	37
355	45	42	44	3.15	36
				2.50	35
300	50	48	52	2.00	34
250	60	60	60	1.60	33
212	70	65	72	1.25	32
180	80	80	85	1.00	31
				800 μ m	30
150	100	100	100	630	29
125	120	115	120	500	28
106	140	150	150	400	27
90	170	170	170	315	26
75	200	200	200	250	25
63	230	250	240	200	24
53	270	270	300	160	23
45	325	325	350	125	22
				100	21
38	400	400	400	80	20
32	450		440	63	19
25	500			50	18
20	635			40	17

APPENDIX C

Conversion Chart

Table C1. Conversion of English to SI Units, listed alphabetically (symbols of SI units given in parentheses)

To convert from	to	Multiply by	
abampere	ampere (A)	1.000 000*	E+01
abcoulomb	coulomb (C)	1.000 000*	E+01
abfarad	farad (F)	1.000 000*	E+09
abhenry	henry (H)	1.000 000*	E-09
abmho	siemens (S)	1.000 000*	E+09
abohm	ohm (Ω)	1.000 000*	E-09
abvolt	volt (V)	1.000 000*	E-08
acre foot (US survey) [†]	cubic meter (m ³)	1.233 489	E+03
acre (US survey) [†]	square meter (m ²)	4.046 873	E+03
acre	hectare (ha)	4.046 873	E-01
ampere hour	coulomb (C)	3.600 000*	E+03
are	square meter (m ²)	1.000 000	E+02
angstrom	meter (m)	1.000 000*	E-10
astronomical unit	meter (m)	1.495 979	E+11
atmosphere (standard)	pascal (Pa)	1.013 250*	E+05
atmosphere (technical = 1 kgf/cm ²)	pascal (Pa)	9.806 650*	E+04
bar	pascal (Pa)	1.000 000*	E+05
barn	square meter (m ²)	1.000 000*	E-28
barrel (for petroleum, 42 gal)	cubic meter (m ³)	1.589 873	E-01
board foot	cubic meter (m ³)	2.359 737	E-03
British thermal unit (International Table)	joule (J)	1.055 056	E+03
Btu (International Table) •ft/hr•ft ² •°F (k, thermal conductivity)	watt per meter kelvin (W/m•K)	1.730 735	E+00
Btu (International Table) in./hr•ft ² •°F (k, thermal conductivity)	watt per meter kelvin (W/m•K)	1.442 279	E-01
Btu (International Table) in./sec•ft ² •°F (k, thermal conductivity)	watt per meter kelvin (W/m•K)	5.192 204	E+02
Btu (International Table)/hr	watt (W)	2.930 711	E-01
Btu (International Table)/ft ²	joule per square meter (J/m ²)	1.135 653	E+04
Btu (International Table)/hr•ft ² •°F (C, thermal conductance)	watt per square meter kelvin (W/m ² •K)	5.678 263	E+00
Btu (International Table)/sec•ft ² •°F	watt per square meter kelvin (W/m ² •K)	2.044 175	E+04
Btu (International Table)/lb	joule per kilogram (J/kg)	2.326 000*	E+03
Btu (International Table)/lb•°F (c, heat capacity)	joule per kilogram kelvin (J/kg•K)	4.186 800*	E+03
bushel (US)	cubic meter (m ³)	3.523 907	E-02
caliber (inch)	meter (m)	2.540 000*	E-02
calorie (International Table)	joule (J)	4.186 800*	E+00
calorie (kilogram, International Table)	joule (J)	4.186 800*	E+03
cal (International Table)/g	joule per kilogram (J/kg)	4.186 800*	E+03
cal (International Table)/g•°C	joule per kilogram kelvin (J/kg•K)	4.186 800*	E+03
cal (thermochemical)/min	watt (W)	6.973 333	E-02
cal (thermochemical)/cm ² •min	watt per square meter (W/m ²)	6.973 333	E+02
carat (metric)	kilogram (kg)	2.000 000*	E-04
centimeter of mercury (0°C)	pascal (Pa)	1.333 22	E+03
centimeter of water (4°C)	pascal (Pa)	9.806 38	E+01
centipoise	pascal second (Pa•sec)	1.000 000*	E-03
centistokes	square meter per second (m ² /sec)	1.000 000*	E-06
circular mil	square meter (m ²)	5.067 075	E-10
clo	kelvin square meter per watt (K•m ² /W)	2.003 712	E-01

(Table continued next page)

Table C1. Conversion of English to SI Units, listed alphabetically (symbols of SI units given in parentheses) (continued)

To convert from	to	Multiply by	
cup	cubic meter (m ³)	2.365 882	E-04
curie	becquerel (Bq)	3.700 000*	E+10
day (mean solar)	second (sec)	8.640 000	E+04
day (sidereal)	second (sec)	8.616 409	E+04
degree (angle)	radian (rad)	1.745 329	E-02
degree Celsius	kelvin (K)	$t_K = t_C + 273.15$	
degree Fahrenheit	degree Celsius	$t_C = (t_F - 32)/1.8$	
degree Fahrenheit	kelvin (K)	$t_K = (t_F + 459.67)/1.8$	
degree Rankine	kelvin (K)	$t_K = t_R/1.8$	
°F hr•ft ² /Btu (International Table) (R, thermal resistance)	kelvin square meter per watt (K•m ² /W)	1.761 102	E-01
denier	kilogram per meter (kg/m)	1.111 111	E-07
dyne	newton (N)	1.000 000*	E-05
dyne-cm	newton meter (N•m)	1.000 000*	E-07
dyne•cm ²	pascal (Pa)	1.000 000*	E-01
electronvolt	joule (J)	1.602 19	E-19
EMU of capacitance	farad (F)	1.000 000*	E+09
EMU of current	ampere (A)	1.000 000*	E+01
EMU of electric potential	volt (V)	1.000 000*	E-08
EMU of inductance	henry (H)	1.000 000*	E-09
EMU of resistance	ohm (Ω)	1.000 000*	E-09
ESU of capacitance	farad (F)	1.112 650	E-12
ESU of current	ampere (A)	3.335 6	E-10
ESU of electric potential	volt (V)	2.997 9	E+02
ESU of inductance	henry (H)	8.987 554	E+11
ESU of resistance	ohm (Ω)	8.987 554	E+11
erg	joule (J)	1.000 000*	E-07
erg/cm ² •sec	watt per square meter (W/m ²)	1.000 000*	E-03
erg/sec	watt (W)	1.000 000*	E-07
faraday (chemical)	coulomb (C)	9.649 57	E+04
faraday (physical)	coulomb (C)	9.652 19	E+04
fathom	meter (m)	1.828 8	E+00
fermi (femtometer)	meter (m)	1.000 000*	E-15
fluid ounce (US)	cubic meter (m ³)	2.957 353	E-05
foot	meter (m)	3.048 000*	E-01
foot (US survey)†	meter (m)	3.048 006	E-01
foot of water (39.2°F)	pascal (Pa)	2.988 98	E+03
ft ²	square meter (m ²)	9.290 304*	E-02
ft ² /hr (thermal diffusivity)	square meter per second (m ² /sec)	2.580 640*	E-05
ft ² /sec	square meter per second (m ² /sec)	9.290 304*	E-02
ft ³ (volume; section modulus)	cubic meter (m ³)	2.831 685	E-02
ft ³ /min	cubic meter per second (m ³ /sec)	4.719 474	E-04
ft ³ /sec	cubic meter per second (m ³ /sec)	2.831 685	E-02
ft ³ /ton (tonnage factor)	cubic meter per metric ton (m ³ /t)	3.121 39	E-02
ft ⁴ (moment of section)‡	meter ⁴ (m ⁴)	8.630 975	E-03
ft/hr	meter per second (m/sec)	8.466 667	E-05
ft/min	meter per second (m/sec)	5.080 000*	E-03
ft/sec	meter per second (m/sec)	3.048 000*	E-01
ft/sec ²	meter per square second (m/sec ²)	3.048 000*	E-01
ft/ton (drilling factor)	meter per metric ton (m/t)	3.359 8	E-01
footcandle	lux (lx)	1.076 391	E+01
footlambert	candela per square meter (cd/m ²)	3.426 259	E+00
ft•lbf	joule (J)	1.355 818	E+00
ft•lbf/hr	watt (W)	3.766 161	E-04
ft•lbf/min	watt (W)	2.259 697	E-02
ft•lbf/sec	watt (W)	1.355 818	E+00

(Table continued next page)

Table C1. Conversion of English to SI Units, listed alphabetically (symbols of SI units given in parentheses) (continued)

To convert from	to	Multiply by	
ft•poundal	joule (J)	4.214 011	E-02
ft•ton (moment)	meter•metric ton (m•t)	2.765 1	E-01
free fall, standard (g)	meter per square second (m/sec ²)	9.806 650*	E+00
gallon	meter per square second (m/sec ²)	1.000 000*	E-02
gallon (Canadian liquid)	cubic meter (m ³)	4.546 090	E-03
gallon (UK liquid)	cubic meter (m ³)	4.546 092	E-03
gallon (US dry)	cubic meter (m ³)	4.404 884	E-03
gallon (US liquid)	cubic meter (m ³)	3.785 412	E-03
gallon (US liquid)/day	cubic meter per second (m ³ /sec)	4.381 264	E-08
gallon (US liquid)/min	cubic meter per second (m ³ /sec)	6.309 020	E-05
gallon (US liquid)/hp•hr (SFC, specific fuel consumption)	cubic meter per joule (m ³ /J)	1.410 089	E-09
gamma	tesla (T)	1.000 000*	E-09
gauss	tesla (T)	1.000 000*	E-04
gilbert	ampere (A)	7.957 747	E-01
gill (UK)	cubic meter (m ³)	1.420 654	E-04
gill (US)	cubic meter (m ³)	1.182 941	E-04
grad	degree (angular)	9.000 000*	E-01
grad	radian (rad)	1.570 796	E-02
grain (1/7,000 lb avoirdupois)	kilogram (kg)	6.479 891*	E-05
grain (lb avoirdupois/7,000)/gal (US liquid)	kilogram per cubic meter (kg/m ³)	1.711 806	E-02
gram	kilogram (kg)	1.000 000*	E-03
g/cm ³	kilogram per cubic meter (kg/m ³)	1.000 000*	E+03
gram-force/cm ²	pascal (Pa)	9.806 650*	E+01
hectare	square meter (m ²)	1.000 000*	E+04
horsepower (550 ft•lbf/sec)	watt (W)	7.456 999	E+02
horsepower (boiler)	watt (W)	9.809 50	E+03
horsepower (electric)	watt (W)	7.460 000*	E+02
horsepower (metric)	watt (W)	7.354 99	E+02
horsepower (water)	watt (W)	7.460 43	E+02
horsepower (UK)	watt (W)	7.457 0	E+02
hour (mean solar)	second (sec)	3.600 000	E+03
hour (sidereal)	second (sec)	3.590 170	E+03
hundredweight (long)	kilogram (kg)	5.080 235	E+01
hundredweight (short)	kilogram (kg)	4.535 924	E+01
inch (in.)	meter (m)	2.540 000*	E-02
inch of mercury (32°F)	pascal (Pa)	3.386 38	E+03
inch of mercury (60°F)	pascal (Pa)	3.376 85	E+03
inch of water (39.2°F)	pascal (Pa)	2.490 82	E+02
inch of water (60°F)	pascal (Pa)	2.488 4	E+02
in. ²	square meter (m ²)	6.451 600*	E-04
in. ³ (volume; section modulus)	cubic meter (m ³)	1.638 706	E-05
in. ³ /min	cubic meter per second (m ³ /sec)	2.731 177	E-07
in. ⁴ (moment of section)†	meter ⁴ (m ⁴)	4.162 314	E-07
in./sec	meter per second (m/sec)	2.540 000*	E-02
in./sec ²	meter per square second (m/sec ²)	2.540 000*	E-02
kayser	1 per meter (1/m)	1.000 000*	E+02
kelvin	degree Celsius	t _C = t _K - 273.15	
kilocalorie (International Table)	joule (J)	4.186 800*	E+03
kilocalorie (thermochemical)/min	watt (W)	6.973 333	E+01
kilogram-force (kgf)	newton (N)	9.806 650*	E+00
kgf•m	newton meter (N•m)	9.806 650*	E+00
kgf•sec ² /m (mass)	kilogram (kg)	9.806 650*	E+00
kgf/cm ²	pascal (Pa)	9.806 650*	E+04
kgf/m ²	pascal (Pa)	9.806 650*	E+00
kgf/mm ²	pascal (Pa)	9.806 650*	E+06

(Table continued next page)

Table C1. Conversion of English to SI Units, listed alphabetically (symbols of SI units given in parentheses) (continued)

To convert from	to	Multiply by	
kilometer per hour (km/hr)	meter per second (m/sec)	2.777 778	E-01
kilopond	newton (N)	9.806 650*	E+00
kWh	joule (J)	3.600 000*	E+06
kip (1,000 lbf)	newton (N)	4.448 222	E+03
kip/in. ² (ksi)	pascal (Pa)	6.894 757	E+06
knot (international)	meter per second (m/sec)	5.144 444	E-01
lambert	candela per square meter (cd/m ²)	1/π *	E+04
lambert	candela per square meter (cd/m ²)	3.183 099	E+03
langley	joule per square meter (J/m ²)	4.184 000*	E+04
league	meter (m)	†	
light year	meter (m)	9.460 55	E+15
liter	cubic meter (m ³)	1.000 000*	E-03
maxwell	weber (Wb)	1.000 000*	E-08
mho	siemens (S)	1.000 000*	E+00
microinch	meter (m)	2.540 000*	E-08
micrometer (μm)	meter (m)	1.000 000*	E-06
mil	meter (m)	2.540 000*	E-05
mile (international)	meter (m)	1.609 344*	E+03
mile (statute)	meter (m)	1.609 3	E+03
mile (US survey)†	meter (m)	1.609 347	E+03
mile (international nautical)	meter (m)	1.852 000*	E+03
mile (US nautical)	meter (m)	1.852 000*	E+03
mile ² (international)	square meter (m ²)	2.589 988	E+06
mile ² (US survey) †	square meter (m ²)	2.589 998	E+06
mile/hr (international)	meter per second (m/sec)	4.470 400*	E-01
mile/hr (international)	kilometer per hour (km/hr)	1.609 344*	E+00
mile/min (international)	meter per second (m/sec)	2.682 240*	E+01
mile/sec (international)	meter per second (m/sec)	1.609 344*	E+03
millibar	pascal (Pa)	1.000 000*	E+02
millimeter of mercury (0°C)	pascal (Pa)	1.333 22	E+02
minute (angle)	radian (rad)	2.908 882	E-04
minute (mean solar)	second (sec)	6.000 000	E+01
minute (sidereal)	second (sec)	5.983 617	E+01
month (mean calendar)	second (sec)	2.628 000	E+06
oersted	ampere per meter (A/m)	7.957 747	E+01
ohm centimeter	ohm meter (Ω•m)	1.000 000*	E-02
ohm circular-mil per foot	ohm square millimeter per meter (Ω•mm ² /m)	1.662 426	E-03
ounce (avoirdupois)	kilogram (kg)	2.834 952	E-02
ounce (troy or apothecary)	kilogram (kg)	3.110 348	E-02
ounce (UK fluid)	cubic meter (m ³)	2.841 307	E-05
ounce (US fluid)	cubic meter (m ³)	2.957 353	E-05
ounce-force	newton (N)	2.780 139	E-01
oz-in.	newton meter (N•m)	7.061 552	E-03
oz (avoirdupois)/gal (UK liquid)	kilogram per cubic meter (kg/m ³)	6.236 021	E+00
oz (avoirdupois)/gal (US liquid)	kilogram per cubic meter (kg/m ³)	7.489 152	E+00
oz (avoirdupois)/in. ³	kilogram per cubic meter (kg/m ³)	1.729 994	E+03
oz (avoirdupois)/ft ²	kilogram per square meter (kg/m ²)	3.051 517	E-01
oz (avoirdupois)/yd ²	kilogram per square meter (kg/m ²)	3.390 575	E-02
oz/ton (ore grade)	grams per metric ton (g/t)	3.125	E+01
parsec	meter (m)	3.085 678	E+16
peck (US)	cubic meter (m ³)	8.809 768	E-03
pennyweight	kilogram (kg)	1.555 174	E-03
perm (0°C)	kilogram per pascal second square meter (kg/Pa•sec•m ²)	5.721 35	E-11
perm (23°C)	kilogram per pascal second square meter (kg/Pa•sec•m ²)	5.745 25	E-11
perm in. (0°C)	kilogram per pascal second meter (kg/Pa•sec•m)	1.453 22	E-12

(Table continued next page)

Table C1. Conversion of English to SI Units, listed alphabetically (symbols of SI units given in parentheses) (continued)

To convert from	to	Multiply by	
perm in. (23°C)	kilogram per pascal second meter (kg/Pa•sec•m)	1.459 29	E-12
phot	lumen per square meter (lm/m ²)	1.000 000 ⁺	E+04
pica (printer's)	meter (m)	4.217 518	E-03
pint (US dry)	cubic meter (m ³)	5.506 105	E-01
pint (US liquid)	cubic meter (m ³)	4.731 765	E-04
point (printer's)	meter (m)	3.514 598 ⁺	E-04
poise (absolute viscosity)	pascal second (Pa•sec)	1.000 000 ⁺	E-01
pound (lb avoirdupois)	kilogram (kg)	4.535 924	E-01
pound (troy or apothecary)	kilogram (kg)	3.732 417	E-01
lb•ft ² (moment of inertia)	kilogram square meter (kg•m ²)	4.214 011	E-02
lb•in. ² (moment of inertia)	kilogram square meter (kg•m ²)	2.926 397	E-04
lb•min ² /ft ⁴ (air friction factor, K)	kilogram per cubic meter (kg/m ³)	1.855	E+06
lb/ft•hr	pascal second (Pa•sec)	4.133 789	E-04
lb/ft•sec	pascal second (Pa•sec)	1.488 164	E+00
lb/ft (loading factor)	kilogram per meter (kg/m)	1.488 156	E+00
lb/ft ²	kilogram per square meter (kg/m ²)	0.882 428	E+00
lb/ft ³ (specific weights)	kilogram per cubic meter (kg/m ³)	1.601 846	E+01
lb/gal (UK liquid)	kilogram per cubic meter (kg/m ³)	9.977 633	E+01
lb/gal (US liquid)	kilogram per cubic meter (kg/m ³)	1.198 264	E+02
lb/hr	kilogram per second (kg/sec)	1.259 979	E-04
lb/hp•hr (SFC, specific fuel consumption)	kilogram per joule (kg/J)	1.689 659	E-07
lb/in. ³	kilogram per cubic meter (kg/m ³)	2.767 990	E+04
lb/min	kilogram per second (kg/sec)	7.559 873	E-03
lb/sec	kilogram per second (kg/sec)	4.535 924	E-01
lb/ton (powder factor)	kilogram per metric ton (kg/t)	5.000	E-01
lb/yd ³ (powder factor)	kilogram per cubic meter (kg/m ³)	5.932 764	E-01
poundal	newton (N)	1.382 550	E-01
poundal/ft ²	pascal (Pa)	1 488 164	E+00
poundal•sec/ft ²	pascal second (Pa•sec)	1.488 164	E+00
pound-force (lbf)	newton (N)	4.448 222	E+00
lbf•ft	newton meter (N•m)	1.355 818	E+00
lbf•ft/in.	newton meter per meter (N•m/m)	5.337 866	E+01
lbf•in.	newton meter (N•m)	1.129 848	E-01
lbf•in./in.	newton meter per meter (N•m/m)	4.448 222	E+00
lbf•sec/ft ²	pascal second (Pa•sec)	4.788 026	E+01
lbf/ft	newton per meter (N/m)	1.459 390	E+01
lbf/ft ²	pascal (Pa)	1.788 026	E+01
lbf/in.	newton per meter (N/m)	1.751 268	E+02
lbf/in. ² (psi)	pascal (Pa)	6.894 757	E+03
lbf/lb (thrust/weight [mass] ratio)	newton per kilogram (N/kg)	9.806 650	E+00
quart (US dry)	cubic meter (m ³)	1.101 221	E-03
quart (US liquid)	cubic meter (m ³)	9.463 529	E-04
rad (radiation dose absorbed)	gray (Gy)	1.000 000 ⁺	E-02
rhe	1 per pascal second (1/Pa•sec)	1.000 000 ⁺	E+01
rod	meter (m)	†	
roentgen	coulomb per kilogram (C/kg)	2.58	E-04
second (angle)	radian (rad)	4.818 137	E-06
second (sidereal)	second (sec)	9.972 696	E-01
section	square meter (m ²)	†	
shake	second (sec)	1.000 000 ⁺	E-08
slug	kilogram (kg)	1.459 390	E+01
slug/ft•sec	pascal second (Pa•sec)	4.788 026	E+01
slug/ft ³	kilogram per cubic meter (kg/m ³)	5.153 788	E+02
statampere	ampere (A)	3.335 640	E-10
statcoulomb	coulomb (C)	3.335 640	E-10

(Table continued next page)

Table C1. Conversion of English to SI Units, listed alphabetically (symbols of SI units given in parentheses) (continued)

To convert from	to	Multiply by	
statfarad	farad (F)	1.112 650	E-12
stathenry	henry (H)	8.987 554	E+11
statmho	siemens (S)	1.112 650	E-12
statohm	ohm (Ω)	8.987 554	E+11
statvolt	volt (V)	2.997 925	E+02
stere	cubic meter (m^3)	1.000 000*	E+00
stilb	candela per square meter (cd/m^2)	1.000 000*	E+04
stokes (kinematic viscosity)	square meter per second (m^2/sec)	1.000 000*	E-04
tablespoon	cubic meter (m^3)	1.178 676	E-05
teaspoon	cubic meter (m^3)	4.928 922	E-06
tex	kilogram per meter (kg/m)	1.000 000*	E-06
therm	joule (J)	1.055 056	E+08
ton (assay)	kilogram (kg)	2.916 667	E-02
ton (long, 2,240 lb)	kilogram (kg)	1.016 017	E+03
ton (metric)	kilogram (kg)	1.000 000*	E+03
ton (nuclear equivalent of TNT)	joule (J)	4.184	E+09
ton (refrigeration)	watt (W)	3.516 800	E+03
ton (register)	cubic meter (m^3)	2.831 685	E+00
ton (short, 2,000 lb)	kilogram (kg)	9.071 817	E+02
ton/yd ³ (specific weight)	metric ton per cubic meter (t/m^3)	1.186 66	E+00
ton (long)/yd ³ (specific weight)	kilogram per cubic meter (kg/m^3)	1.328 939	E+03
ton (short)/hr	kilogram per second (kg/sec)	2.519 958	E-01
ton-force (2,000 lbf)	newton (N)	8.896 111	E+03
ton/yd ³ (specific weight)	metric ton per cubic meter (t/m^3)	1.186 55	E+00
torr (mm Hg, 0°C)	pascal (Pa)	1.333 22	E+02
township	square meter (m^2)	†	
unit pole	weber (Wb)	1.256 637	E-07
W•hr	joule (J)	3.600 000*	E+03
W•sec	joule (J)	1.000 000*	E+00
W/cm ²	watt per square meter (W/m^2)	1.000 000*	E+04
W/in. ²	watt per square meter (W/m^2)	1.550 003	E+03
yard	meter (m)	9.144 000*	E-01
yd ²	square meter (m^2)	8.361 274	E-01
yd ³	cubic meter (m^3)	7.645 549	E-01
yd ³ /min	cubic meter per second (m^3/sec)	1.274 258	E-02
yd ³ /ton (stripping ratio)	cubic meter per metric ton (m^3/t)	8.427 8	E-01
year (calendar)	second (sec)	3.153 600	E+07
year (sidereal)	second (sec)	3.155 815	E+07

* Exact value.

† Conversion factors for land measure may be determined from the following relationships:

1 league = 3 miles (exactly)

1 rod = 16½ feet (exactly)

1 section = 1 square mile (exactly)

1 township = 36 square miles (exactly)

‡ This is sometimes called the moment of inertia of a plane section about a specified axis.

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Note: *f.* indicates figure; *t.* indicates table.

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